mould fungi; a maltose splitting enzyme is present in the intestine (Brown and Heron, Proc. Roy. Soc. 1880, 30, 393) and in numerous other animal tissues (Tebb, J. Physiol. 1894, 15, 421). Maltase is more difficult to extract than invertase; active extracts can only be obtained from yeast after the cells have been destroyed, or, better, after a preliminary drying in a thin layer at a low temperature. The enzyme is not liberated on shaking yeast with toluene water. Yeast juice made by Buchner's method of compression contains maltase. Brown and Heron found aqueous extract of pig's intestine to have no action on maltose, but after drying at 35° fine shreds of the intestine were active. Using similar methods Tebb found most maltase in the mucous membrane of the small intestine; it was also present in the spleen, lymphatic gland, liver, kidney, and in the pancreatic and salivary glands, and least of all in muscle. When the tissue is finely minced and sufficient time (several days) is allowed for adequate extraction, active maltase may be obtained from fresh tissues. Malt does not contain maltase.

Maltase is destroyed by precipitation of the aqueous extract with alcohol, so that it has not been possible to purify it.

Maltase also hydrolyses α-methylglucoside and other synthetical α-glucosides, although it is without action on the isomeric β-glucosides. Amygdalin is hydrolysed by an enzyme akin to maltase, present in some yeasts, to dextrose and amygdonitrileglucoside (Fischer, Ber. 1895, 28, 1508). This action is due, however, not to maltase, but to amygdalase (Caldwell and Courtauld, Proc. Roy. Soc. 1907, B, 79, 350). Maltase is able to cause synthetic as well as analytic changes (Croft Hill, Chem. Soc. Trans. 1898, 73, 634; 1903, 83, 578; *see* also Bayliss, The Nature of Enzyme Action, Longmans, 1911).

The optimum temperature of maltase is 35°–40° (*v.* FERMENTATION). E. F. A.

MALTHA. A variety of 'mineral tallow' or wax, sp.gr. 0·77, soluble in alcohol, naphtha, and oil of turpentine, said to be originally found on the coast of Finland. It is white, brittle, and stains paper like oil, melts at a moderate heat, and burns with a smoky flame. A similar hydrocarbon is met with in the oil-fields of California.

MALTODEXTRIN *v.* DEXTRIN.

MALTOSE *v.* CARBOHYDRATES.

MAMMIN *v.* SYNTHETIC DRUGS.

MANACCANITE. A variety of titaniferous magnetic oxide of iron found in grains and small angular fragments at Manaccan near Helstone, and other places in Cornwall, *v.* ILMENITE; TITANIUM.

MANCHESTER YELLOW. *Dinitronaphthol v.* NAPHTHALENE. Dinitronaphthol-yellow has been used to artificially colour natural saffron. To detect the adulteration, an infusion of the matter is prepared, to which some tartaric acid is added. A hank of wool is then dipped in the boiling solution. The wool thus dyed is washed in very dilute sulphuric acid, and the acid afterwards neutralised with ammonia. If saffron contained any dinitronaphthol, the wool or the solution will be coloured yellow, whereas wool dyed with a decoction of genuine saffron and treated in the same manner becomes colourless (Cazeneuve and G. Ginnossier, J. Soc. Chem. Ind. 5, 437).

MANDELIC ACID (*Phenylglycollic acid; α-phenylhydroxyacetic acid*) $C_6H_5\cdot CH(OH)CO_2H$. Discovered by Winkler in 1852 in the emulsion of bitter almonds. It may be obtained by warming ω-dibromoacetophenone with dilute alkali (Engler and Wöhrle, Ber. 1887, 2202); by oxidising ω-hydroxyacetophenone with copper sulphate (Breuer and Zincke, *ibid.* 1880, 635); by boiling phenylchloracetic acid with alkali (Spiegel, *ibid.* 1881, 239); and by warming benzoylformaldehyde with alkali (Pechmann, *ibid.* 1887, 2905; Müller and Pechmann, *ibid.* 1889, 2558). It is best prepared by shaking commercial benzaldehyde with a concentrated solution of sodium disulphite, filtering off and drying the disulphite compound. This is then made into a paste with water, and the calculated quantity of potassium cyanide solution added with stirring. The oily mandelonitrile soon separates, and is hydrolysed by boiling with three times the theoretical quantity of hydrochloric acid (Pape, Chem. Zeit. 1896, 20, 90; Chem. Fab. vor. Hofmann and Schoetensack, Eng. Pat. 14886; J. Soc. Chem. Ind. 1896, 614; *cf.* Müller, Arch. Pharm. [iii.] 2, 385, 389; Ber. 1872, 980; Wallach, Annalen, 193, 38; Luginin, *ibid.*, 139, 299; Winckler, *ibid.* 18, 310).

Forms colourless rhombic prisms; m.p. 118° (Claisen, Ber. 1877, 847); sp.gr. 1·361 at 4°/4° (Schröder, *ibid.* 1889, 1612); readily soluble in alcohol and ether. On heating the acid at 200°, benzaldehyde and an amorphous mass is obtained; benzaldehyde, water and diphenylmaleic anhydride are formed when it is heated in a current of air under reduced pressure (Bischoff and Walden, Annalen, 279, 118; Liebig, *ibid.* 18, 312). Fuming nitric acid yields *o-* and *p*-nitrophenylglycollic acids (Pratesi, Gazz. chim. ital. 21, ii. 402). Electrolysis of an aqueous solution of the potassium salt results in the production of hydrobenzoin and a small quantity of *iso*hydrobenzoin (Walker, Chem. Soc. Trans. 1896, 1279); but according to Miller and Hofer (Ber. 1894, 469) benzaldehyde, carbon dioxide, and carbon monoxide are the products. By passing carbonyl chloride into an ice-cold solution of the acid in pyridine the bimolecular anhydride, m.p. 240°, is formed (Einhorn and Pfeiffer, Ber. 1901, 2951). Hydrogen iodide and phosphorus convert mandelic acid into phenylacetic acid, and fuming hydrochloric acid at 140° yields phenylchloracetic acid. Mandelic acid condenses with phenols in the presence of 73 p.c. sulphuric acid to *o*-hydroxydiarylacetic acid lactones and *p*-dihydroxydiarylacetic acids (Bistrzycki and Flatau, Ber. 1895, 989; 1897, 124); *v.* also Simonis (Ber. 1898, 2821) for condensation with β-naphthol, resorcinol, and orcinol. The nitrile prepared as above, is a yellow oil, solidifying at −10°. The amide has m.p. 190°, the anilide 151°–152°, and the phenylhydrazide 182° (Tiemann and Friedländer, Ber. 1881, 635; Reissert and Kayser, Ber. 1890, 3701; Biedermann, *ibid.* 1891, 4083; Bischoff and Walden, Annalen, 279, 118). The methyl ester has m.p. 52° (Zincke and Brewer, Ber. 1880, 636; Ruhe, *ibid.* 1895, 259), and the ethyl ester has m.p. 34°, b.p. 253°–255° (Michael and Jeanprêtre, Ber. 1892, 1684;

Beyer, J. pr. Chem. [ii.] 31, 389); m.p. 37° (McKenzie, Chem. Soc. Trans. 1899, 755).

Mandelic acid contains an asymmetric carbon atom, and hence can be split into two optically active isomerides. Lewkowitsch (Ber. 1882, 1505; 1883, 1565, 2722) obtained *l*-mandelic acid by treating the inactive acid with *Saccharomyces ellipsoideus* (Rees) and *d*-mandelic acid by using various microzoa, such as *Pencillium glaucum*, &c. Partial resolution of the inactive acid has also been effected by means of the fractional crystallisation of salts with alkaloids, such as quinine and morphine, and with active amines such as methylhydrindamine; and by esterification with active alcohols, such as menthol and borneol (McKenzie, Chem. Soc. Trans. 1899, 968; 1904, 378; McKenzie and Thompson, *ibid.* 1905, 1004; Marckwald and Paul, Ber. 1906, 3654; Kipping, Chem. Soc. Trans. 1909, 416; Findlay and Hickman, *ibid.* 1909, 1386). Racemisation is found to take place on boiling the active acid with alkali (Holleman, Rec. trav. chim. 1898, 17, 323; McKenzie and Müller, Chem. Soc. Trans. 1907, 1814). Asymmetric syntheses have been conducted by McKenzie and Humphries (*ibid.* 1909, 1106) from *l*-menthylbenzoylformate, and by Rosenthaler (Biochem. Zeitsch. 1908, 14, 238) from *d*-benzaldehydecyanhydrin. *d*- and *l*-Mandelic acids can also be prepared by the hydrolysis of amygdalinic acid (Dakin, Chem. Soc. Trans. 1904, 1512; *cf.* Wöhler, Annalen, 66, 238; Tutin, Chem. Soc. Trans. 1909, 663; Feist, Arch. Pharm. 248, 101; Rosenthaler, *ibid.* 105). Incomplete hydrolysis of the ethyl ester by *lipase* yields the *d*-acid, whilst the ester remaining is lævorotatory (Dakin, Chem. Soc. Proc. 1903, 161; J. Physiol. 1903, 30, 253).

l-Mandelic acid has m.p. 132·8°, and $[\alpha]_D$ $-153{\cdot}1°$ in water (Walden, Zeitsch. physikal. Chem. 1895, 17, 705; *cf.* Lewkowitsch, *l.c.*; Rimbach, Zeitsch. physikal. Chem. 1899, 28, 251; Ber. 1899, 2385). *d*-Mandelic acid has m.p. 132·8°, and $[\alpha]_D+156°$ (Kipping, Chem. Soc. Trans. 1909, 416). For experiments on the *Walden Inversion* with mandelic and phenylchloracetic acids, *v.* McKenzie and Clough, Chem. Soc. Trans. 1909, 777.

MANDRAGORA ROOT. In 1889 Ahrens (Annalen, 251, 312) extracted from *Mandragora* root an alkaloid possessing similar physiological properties to atropine, and which he named *mandragorin.* Thoms and Wentzel (Ber. 1898, 31, 2031) showed that the *mandragorin* of Ahrens was a mixture of bases, the chief of which was *hyoscyamine,* and subsequently isolated another base, which they named *scopolamine* (Ber. 1901, 31, 2031). Hesse (J. pr. Chem. 1901, 64, 274) further investigated the subject and found that *madragora* root contains 0·36 p.c. *hyoscyamine,* 0·04 p.c. *hyoscine* (*scopolamine* of Thoms and Wentzel), 0·01 p.c. *ψ-hyoscyamine,* and a still smaller quantity of a new base *mandragorine.* To obtain these alkaloids, the roots are powdered, moistened with a solution of caustic soda, and extracted with ether under a reflux apparatus. The ethereal solution is repeatedly extracted with dilute sulphuric acid, the acid solution being made alkaline with sodium bicarbonate and extracted with chloroform. This operation is then repeated, whereby the hyoscyamine remains in the aqueous solution. The bases from the chloroform extract are neutralised with hydrobromic acid, and the filtered solution allowed to crystallise. The hydrobromides of the bases are then extracted with acetone, which leaves the pure hydrobromide (m.p. 194°) of hyoscine, $C_{17}H_{21}NO_4$. The free base is decomposed by baryta into tropic acid and oscine, $C_8H_{13}NO_2$. The mother liquors of the hyoscinehydrobromide yield *ψ*-hyoscyamine on addition of sodium bicarbonate and extraction with chloroform. On adding sodium carbonate to the residual solution, a new alkaloid *mandragorine,* forming a gold double salt $C_{15}H_{19}NO_2HAuCl_4$ is obtained. The free base is decomposed by baryta into atropic acid, and a base resembling tropine.

MANGANATES *v.* Manganese.

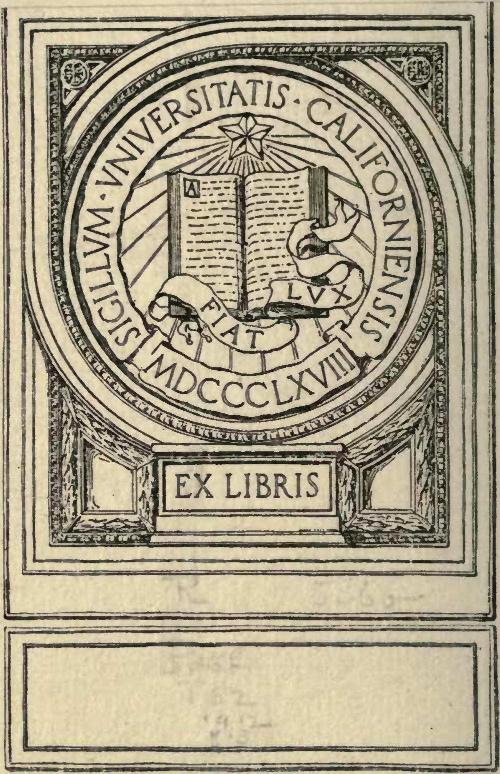
MANGANESE. Sym. Mn. At.wt. 54·93. (Fr. *Manganèse*; Ger. *Mangan.*) Manganese is not found in the metallic state. In combination, especially as oxide, it is widely distributed. The most important ores are those corresponding with the dioxide MnO_2, *pyrolusite.* It is also found as the oxides *braunite* Mn_2O_3, *hausmannite* Mn_3O_4, as hydrated oxide Mn_2O_3,H_2O in *manganite,* and associated with barium oxide in *psilomelane.* As sulphide it occurs as *alabandite* MnS and *hauerite* MnS_2; as carbonate in *rhodocrosite* or *dialogite* $MnCO_3$; as silicate in *rhodonite* $MnSiO_3$. The latter is of a beautiful red colour, found largely in the Ural Mountains, and used as an ornamental stone. It is often present to a small extent in other silicates, and confers on them its colour. The chief sources of the manganese ores are Russia, the Caucasus, Brazil, and India. Manganese is present in soils, and frequently in mineral, particularly chalybeate, waters. It occurs in many plants, especially in tea and tobacco.

Preparation.—Metallic manganese is not used in the arts except when alloyed with other metals. It may be prepared by reduction of the oxide with carbon, but the temperature necessary for the reduction is so high (1105°C., Greenwood, Chem. Soc. Trans. 1908, 1491) that it is only obtained with difficulty in ordinary furnaces. The original method of preparation described by John (Gehlen's Jour. für. Chem. Phys. 3, 452) consisted in making an intimate mixture of finely divided manganous oxide and carbon by mixing with oil and heating, and exposing it to as high a temperature as possible in a crucible lined with charcoal. The impure manganese so obtained was purified by fusing under salt and nitre.

Brunner (Annalen, 102, 330) prepared the metal by heating a mixture of sodium and manganese chloride or fluoride in a blast furnace for 15 minutes. It may also be obtained by the reduction of the chloride by magnesium.

Deville obtained the metal by the reduction of the pure red oxide Mn_3O_4 by means of sugar charcoal present in insufficient quantity to reduce the whole (Ann. Chim. Phys. 1856, 46, 182).

Valenciennes (Compt. rend. 70, 907) produced it by reduction of the pure oxide with carbon in a magnesia-lined crucible as a hard and brittle mass, quickly oxidised by exposure to air.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ABBREVIATIONS

OF THE TITLES OF JOURNALS AND BOOKS.

Amer. Chem. J.	American Chemical Journal.
Amer. J. Pharm.	American Journal of Pharmacy.
Amer. J. Sci.	American Journal of Science.
Analyst	The Analyst.
Annalen	Annalen der Chemie (Justus Liebig).
Ann. Chim. anal.	Annales de Chimie analytique appliquée à l'Industrie, à l'Agriculture, à la Pharmacie et à la Biologie.
Ann. Chim. Phys.	Annales de Chimie et de Physique.
Ann. Falsif.	Annales des Falsifications.
Ann. Inst. Pasteur.	Annales de l'Institut Pasteur.
Arch. Pharm.	Archiv der Pharmazie.
Bentl. a. Trim.	Bentley and Trimen. Medicinal Plants.
Ber.	Berichte der Deutschen chemischen Gesellschaft.
Ber. Deut. pharm. Ges.	Berichte der Deutschen pharmazeutischen Gesellschaft.
Bied. Zentr.	Biedermann's Zentralblatt für Agrikulturchemie und rationellen Landwirtschafts-Betrieb.
Bio-Chem. J.	The Bio-Chemical Journal.
Biochem. Zeitsch.	Biochemische Zeitschrift.
Brewers J.	Brewers Journal.
Bull. Imp. Inst.	Bulletin of the Imperial Institute.
Bull. Soc. chim.	Bulletin de la Société chimique de France.
Chem. Ind.	Chemische Industrie.
Chem. News	Chemical News.
Chem. Soc. Proc.	Journal of the Chemical Society of London. Proceedings.
Chem. Soc. Trans.	Journal of the Chemical Society of London. Transactions.
Chem. Zeit.	Chemiker Zeitung.
Chem. Zentr.	Chemisches Zentralblatt.
Compt. rend.	Comptes rendus hebdomadaires des Séances de l'Académie des Sciences.
Dingl. poly. J.	Dingler's polytechnisches Journal.
Färber-Zeit.	Färber-Zeitung.
Flück. a. Hanb.	Flückiger and Hanbury. Pharmacographia.
Frdl.	Friedländer's Fortschritte der Teerfarbenfabrikation.
Gazz. chim. ital.	Gazzetta chimica italiana.
Jahrb. Min.	Neues Jahrbuch für Mineralogie, Geologie und Palaeontologie.
J. Amer. Chem. Soc.	Journal of the American Chemical Society.
J. Ind. Eng. Chem.	Journal of Industrial and Engineering Chemistry.
J. Inst. Brewing	Journal of the Institute of Brewing.
J. Pharm. Chim.	Journal de Pharmacie et de Chimie.
J. Phys. Chem.	Journal of Physical Chemistry.
J. pr. Chem.	Journal für praktische Chemie.
J. Russ. Phys. Chem. Soc.	Journal of the Physical and Chemical Society of Russia.
J. Soc. Chem. Ind.	Journal of the Society of Chemical Industry.
J. Soc. Dyers.	Journal of the Society of Dyers and Colourists.
Min. Mag.	Mineralogical Magazine and Journal of the Mineralogical Society.
Monatsh.	Monatshefte für Chemie und verwandte Theile anderer Wissenschaften.
Pharm. J.	Pharmaceutical Journal.
Pharm. Zeit.	Pharmazeutische Zeitung.
Phil. Mag.	Philosophical Magazine (The London, Edinburgh and Dublin).
Phil. Trans.	Philosophical Transactions of the Royal Society.
Phot. J.	Photographic Journal.
Proc. Roy. Soc.	Proceedings of the Royal Society.
Rec. trav. chim.	Receuil des travaux chimiques des Pays-Bas et de la Belgique.
Zeitsch. anal. Chem.	Zeitschrift für analytische Chemie.
Zeitsch. angew. Chem.	Zeitschrift für angewandte Chemie.
Zeitsch. anorg. Chem.	Zeitschrift für anorganische Chemie.
Zeitsch. Nahr. Genussm.	Zeitschrift für Untersuchung der Nahrungs-und Genussmittel.
Zeitsch. öffentl. Chem.	Zeitschrift für öffentliche Chemie.
Zeitsch. physikal. Chem.	Zeitschrift für physikalische Chemie, Stöchiometrie und Verwandtschaftslehre.
Zeitsch. physiol. Chem.	Hoppe-Seyler's Zeitschrift für physiologische Chemie.

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GRAIN LAC *v. Lac resins,* art. Resins.

GRAIN OIL *v.* Fusel oil.

GRAIN TIN *v.* Tin.

GRAINS OF PARADISE *v.* Cocculus indicus.

GRANITE. A holocrystalline acid rock of plutonic origin; *i.e.* it is a rock consisting wholly of crystalline minerals, and containing from about 60 to 80 p.c. of silica, partly free and partly combined, whilst its texture suggests that it has slowly consolidated from a molten condition, under great pressure, at considerable depth beneath the surface. Granite is essentially an aggregate of felspar, quartz, and mica. The usual felspathic constituent is orthoclase, or common potash-felspar, generally associated with more or less plagioclase; and the mica is either muscovite (white mica) or biotite (dark mica), whilst in many granites both micas are present. Biotite-granite is now frequently known by G. Rose's name of *granitite.* Granitic rocks may contain various accessory minerals, such as hornblende, augite, and tourmaline, thus giving rise to varieties often distinguished by special names; whilst, on the other hand, it sometimes happens that one of the minerals of typical granite may disappear, thus producing a binary granite. *Aplite* is a name occasionally applied to a rock consisting only of felspar and quartz; but sometimes extended to all muscovite-granites. If the quartz and felspar are so intergrown as to suggest they have crystallised simultaneously, the rock is termed *graphic granite* or *pegmatite.* Under the name of *greisen,* German miners recognise a rock composed of quartz and mica, usually carrying topaz, and associated with tin-stone. An aggregate of orthoclase and black mica is known as *mica-syenite*; the typical *syenite,* sometimes distinguished as *hornblende-syenite,* being composed essentially of orthoclase and hornblende. Hornblende-granites are often called, by English writers, 'syenitic.' Schorl, or black tourmaline, is not unfrequently present in granite, especially near the margin of intruded masses. Garnet is an occasional constituent, but not so commonly in true granite as in *granulite,* a rock consisting mainly of quartz and felspar in small grains, so that microscopic sections present between crossed nicols a characteristic mosaic structure. When a granitic rock becomes foliated, or its constituent minerals exhibit more or less elongation in definite directions, it is said to acquire a 'gneissoid' structure, and may pass into a true *gneiss.*

Granite occurs frequently in the form of intrusive masses, which, while coarsely crystalline in the centre, may present a fine texture towards their margin. From the main mass, veins or apophyses are thrown off into the neighbouring rocks; and these veins, having cooled less slowly, are often fine-grained, and may pass into micro-granites and quartz-porphyries. It has been asserted that certain granites may have resulted from the extreme alteration of stratified rocks; and hence geologists who hold this view recognise two types of granite, one igneous, and the other metamorphic.

It is not uncommon to find in granite nodular masses which appear as dark patches on the fractured or polished surface of the rock. Whilst some of these inclusions seem to be fragments of foreign rock which have been caught up in the granitic magma and altered, others may be regarded as parts of the original magma differentiated during consolidation; and it is notable that the inclusions are usually more basic than the matrix. (For comparative analyses of the granite and its inclusions, *v.* J. A. Phillips in Quart. Journ. Geol. Soc. 1880, 36, 1.)

Granite is extensively employed for constructive purposes where massive work is required, as in the foundations of buildings, in docks, sea walls, the piers of bridges, and lighthouses. The specific gravity of granite is about 2·6; a cubic foot weighing about 166 lbs., and a cubic yard 2 tons.

Granite rocks are always divided by joints, which usually run in three directions, thus splitting the rock into masses of roughly cuboidal form. The stone is blasted in the quarry, and the blocks split up by 'plug and feather' wedges. When the surface is required to be dressed smooth, it is 'fine-axed' by continued tapping, at right angles to the face, with a special form of axe. Solid cylinders are turned on a lathe, and columns measuring as much as 8 feet in diameter may be thus wrought. The polishing of granite is effected by means of cast-iron planes worked over the smooth surface, first with sand and water, and then with emery, the final polish being given with putty powder applied on thick felt. In this way even elaborate mouldings may be readily polished. (For granite working, *v.* G. W. Muir, Journ. Soc. Arts. 1866, 14, 471; and G. F. Harris, Granite and our Granite Industries, London, 1888.)

Granite rocks are extensively developed and quarried in Cornwall and Devon, where they occur as a series of bosses protruding through the killas or clay-slate. The largest of these intrusions are, proceeding westwards, those of Dartmoor, Brown Willy or St. Breward district, Hensbarrow or St. Austell, Carn Menelez or Penryn, and the Land's End or Penzance district. In addition to these principal exposures there are numerous smaller masses. The granite of Devon and Cornwall is usually grey and coarse-grained, but red granite also occurs, as at Trowlesworthy in the western part of Dartmoor. A local variety, termed by R. N. Worth *Trowlesworthite*, and described by Prof. Bonney, is composed of red felspar, with a tourmaline, purple fluorspar, and a little quartz. A handsome red granitic rock occurring near Luxullian, in Cornwall, and hence called by Bonney *Luxullianite*, consists of red orthoclase, in large crystals, with schorl, or black tourmaline, and quartz. This is the rock of which the Duke of Wellington's sarcophagus, in St. Paul's, is formed.

The nearest exposure of granite to London is at Mount Sorrel, in Leicestershire, where pink and grey biotite-granite, rather hornblendic, is worked for kerb-stones, paving setts, and road metal. The hornblende granites of the Channel Islands are quarried for similar purposes. Shap Fell, in Westmoreland, yields a beautiful biotite-granite, with large crystals of salmon-coloured orthoclase, which is now largely used as an ornamental material, and has been employed, for example, in the posts around St. Paul's. The granites of Scotland are of much industrial importance. Aberdeen granite was brought to London for paving in the 18th century, but the great development of the trade dates from about 1850. The Aberdeen stone, which is of grey or blue tint, is valued for monumental work; the Peterhead granite is usually of a fine pink colour. The Ross of Mull, in Argyllshire, furnishes a handsome red granite, yielding blocks of exceptional size. Granite is also worked in Kirkcudbrightshire, where it occurs in bosses surrounded by slates; the grey granite of Dalbeattie being well known in commerce.

In Ireland, granite is very extensively developed, the chief districts being in counties Wicklow, Galway, Mayo, Donegal, and Down. The largest quarries are those near Dalkey, which yielded the stone for Kingstown Harbour. The quarry near Castlewellan, Co. Down, which was opened to supply granite for the Albert Memorial, in Hyde Park, has since been closed. Granite is also found in the Isle of Man, Arran, Anglesea, Lundy I., and the Scilly Isles.

It is needless to specify the numerous European localities in which granite is worked. Of late years a green 'granite' (gabbro) from Warburg, in Sweden, has been imported as a monumental stone. In the United States, workings are established in a large number of localities, the granite-producing States being, in order of relative importance, Massachusetts, Maine, Rhode Island, Connecticut, Virginia, and New Hampshire.

For a large collection of analyses of granites, *v.* J. Roth's Beiträge z. Petrographie d. plutonische Gesteine (Berlin, 1873–84); H. S. Washington, U. S. Geol. Survey, Prof. Paper, No. 14, 1903; No. 28, 1904. F. W. R.

GRANITE BLACK *v.* AZO- COLOURING MATTERS.

GRAPE. The berry of *Vitis vinifera* (Linn.). There are many varieties differing in size, shape, colour and composition.

König gives as the average percentage composition—

Water	Nitrogenous substances	Free acid	Invert sugar	Other carbohydrates	Fibre	Ash
79·1	0·7	0·7	15·0	1·9	2·1	0·5

The sugar (glucose) in particular is liable to considerable variation, ranging from 9 to 18 or 19 p.c.

This variation, as well as that in the acidity—due to tartaric acid or acid potassium tartrate—is influenced not only by the variety, but also by the climate and soil; a wet winter and a hot, dry summer being generally favourable to the production of sweet grapes, suitable for wine making, whilst much rain during the ripening period dilutes the juice and leads to the bursting and consequent injury of the berries.

The proportion of skin and seeds shows considerable variation in different varieties, averaging about 2·2 p.c. of the whole fruit, and of this the seeds usually constitute about one-fourth. The skin contains tannin, and, according to Malvezin (Compt. rend. 1908, 147, 384), a yellow colouring matter, which, on oxidation either by exposure to air in aqueous solution, or by the action of an enzyme, present in red, but absent in white grapes, changes to a red substance.

Sostegni (Gazz. chim. ital. 1902, 32, ii. 17) states that the red colouring matter is a tannin derived from protocatechuic acid and has the formula $C_6H_3(OH)_2CO{\cdot}C_6H_3(OH)O{\cdot}C_6H_3(OH)_2$.

The skin and seeds of grapes, in a moist condition, were analysed by Balland (Rev. intern. falsif, 1900, 13, 92), who found them to have the following percentage composition:—

	Water	Nitrogenous substances	Fat	Soluble carbohydrates	Crude fibre	Ash
Skin .	76·5	1·5	0·9	18·4	2·1	0·6
Seeds .	38·7	5·5	8·6	18·9	27·6	0·7

Wittmann found about 0·4 p.c. pentosans in grapes.

The ash, according to König, contains—

	Per cent. of ash in dry substance	K_2O	Na_2O	CaO	MgO	Fe_2O_3	P_2O_5	SO_3	SiO_2	Cl
Whole fruit	3·95	53·0	3·7	6·9	3-3	1·2	21·3	5·0	3·6	1·8
Skin .	4·03	44·2	1·9	21·0	5·7	1·5	17·6	3·7	3·0	0·6
Seeds .	2·81	28·7	—	33·9	8·6	0·6	24·0	2·5	1·1	0 3

About 0·2 p.c. of manganese oxide is also usually present.

Boric acid has been found in grapes (Crampton, Amer. Chem. J. 11, 227; Baumert, Ber. 21, 3290). Salicylic acid also occurs especially in the stalks (Mastbaum, Chem. Zeit. 1903, 27, 829).

Dried grapes constitute raisins and currants and are extensively used. Their average composition, as given by König, is respectively—

	Raisins	Currants
Water	24·5	25·4
Nitrogenous substances .	2·4	1·2
Fat	0·6	—
Free acid . . .	1·2	1·5
Invert sugar . . .	59·3	61·8
Cane sugar . . .	2·0	—
Other carbohydrates .	1·3	5·9
Crude fibre and seeds .	7·0	2·4
Ash	1·7	1·8

American analyses give considerably less water and more ash than these figures.

H. I.

GRAPE SEED OIL is obtained from grape seeds (*Vitis vinifera* [Linn.]) by expression or by extraction. The oil is only of local importance, and is expressed only for local consumption. Thus, in Italy and in the south of France (and even in south Germany) it is said to be used as an edible oil. The cold expressed oil has a golden-yellow colour, and is free from odour. If the seeds have been stored for some time the expressed oil is dark, and acquires a slightly bitter flavour. The chemistry of this oil is not fully known, as the *data* obtained by the several observers who examined grape seed oil are very conflicting. At first this oil was credited with a very high acetyl value, and was compared in this respect with castor oil, so that its use for the manufacture of Turkey red oil had been proposed. More recent examinations have shown that grape-seed oil has a very high iodine value, so that accordingly the oil would seem to belong to the semi-drying or drying oils. A fresh examination of this oil is desirable in order to remove the doubts existing as to its composition. J. L.

GRAPHIC TELLURIUM *v.* TELLURIUM.

GRAPHITE, a crystallised form of carbon, known also as *plumbago,* and popularly as *black lead.* It occurs usually in compact and crystalline masses, but occasionally in six-sided tabular crystals which cleave into flexible laminæ parallel to the basal plane. The crystals were referred to the hexagonal system until A. E. von Nordenskiöld, in 1855, after studying the crystals from Pargas, in Finland, declared them to be monoclinic. Kenngott, however, afterwards showed that they were truly rhombohedral (Pogg. Ann. 96, 110).

Graphite is a mineral of iron-black or steel-grey colour, with metallic lustre, having a sp.gr. of 2·2. In consequence of its softness (H.=1) and the ease with which it produces a metallic streak when rubbed on paper, it is largely used in the manufacture of pencils, whence the name 'graphite' given to it by Werner, from γράφω (I write). It was formerly called *molybdæna,* and confused with molybdenite (MoS_2), a mineral which also gives a metallic mark on paper. (On the history of these names, and of plumbago, *v.* J. W. Evans, Trans. Philological Soc. 1908, 133.) Graphite seems to have been first recognised as a distinct mineral by Gesner, who figured a lead pencil in 1565 (Roscoe). Scheele in 1779 showed that graphite was a kind of mineral carbon, since it could be converted into carbon dioxide by the action of nitric acid. As the carbon is usually associated with more or less iron, the older mineralogists described the mineral as a 'carburet of iron,' but Vanuxem demonstrated that the iron is present as ferric oxide and not as a carbide. The ash left on the combustion of graphite usually contains, in addition to the ferric oxide, silica, alumina, and lime.

Exposed on platinum foil to the flame of the blowpipe, graphite burns, but often with more difficulty than diamond. When heated with a mixture of potassium dichromate and sulphuric acid, it disappears. In order to obtain perfectly pure graphite, the mineral is first ground and washed to remove earthy matter, and then treated, according to Brodie's method, with potassium chlorate and sulphuric acid; on subjecting the resulting product to a red heat, pure carbon is obtained in a remarkably fine state of division.

The following analyses are selected from a large number by C. Mène (Compt. rend. 64, 1091):—

—	I	II	III	IV
Carbon . .	91·55	81·08	79·40	78·48
Volatile matters	1·10	7·30	5·10	1·82
Ash . .	7·35	11·62	15·50	19·70
	100·00	100·00	100·00	100·00

I. Very fine Cumberland graphite, sp.gr. 2·345. II. Graphite from Passau, Bavaria, sp.gr. 2·303. III. Crystallised graphite, from Ceylon, sp.gr. 2·350. IV. Graphite, from Buckingham, Canada, sp.gr. 2·286.

Graphite when used for pencils is frequently mixed, in a powdered state, with pure clay, and the mixture consolidated by hydraulic pressure. It is also sometimes mixed with sulphur or with antimony sulphide. Brockedon first suggested the use of the hydraulic press as a means of obtaining from powdered graphite a homogeneous and coherent mass, which could be readily sawn into pieces of convenient size. The finest pencil lead was yielded by the ancient mine at Borrowdale in Cumberland, where it occurred in pipes, strings, and irregular masses, or 'sops,' associated with a dyke of diorite and with intrusive masses of diabase, in the Cambro-Silurian volcanic series known as 'the green slates and porphyries.' The Cumberland graphite was formerly termed 'wad,' a name sometimes applied also to native oxide of manganese. (For description of the old Borrowdale workings *v.* J. C. Ward in Geol. Survey Mem. on Lake District, 1876.) A small amount of graphite, about 100 tons per annum, is obtained from the Craigman mine, near Cumnock in Ayrshire; here the mineral usually exhibits a columnar structure, and it has been produced by the baking action of dykes of igneous rock on seams of coal.

Excellent graphite is found in Siberia, especially at the Mariinoskoi mine, in the Tunkinsk Mountains, Government of Irkutsk. This deposit, discovered in 1838, occurs in gneiss, associated with diorite; it has been largely worked by M. Alibert to supply Faber's pencil factory. In 1860 graphite was discovered in granite near the river Nischne Tungusska, and workings were undertaken by M. Siderov. (For Russian graphite *v.* N. Koksharov, Materialien z. Mineralogie Russlands, 1862, 4, 153, where analyses are given.)

The best quality of graphite found in large quantities is that from Ceylon. The mineral is widely distributed through the western and north-western provinces of the island, and is obtained from a large number of small pits, there being but few mines of any size. The output amounts to about 30,000 tons per annum, with a value of rather over half a million pounds sterling. (On the graphite deposits of Ceylon *v.* A. K. Coomaraswamy, Mineralogical Survey of Ceylon, 1903, etc.; Quart. J. Geol. Soc. 1900, 56, 590.) In India, graphite is found at several localities, chiefly in the Madras Presidency, the best coming from Travancore, but even this is far inferior to that from Ceylon.

In the United States, graphite is widely diffused, but rarely in sufficient quantity to be worked. The principal locality is Ticonderoga, in Essex Co., New York, where the Dixon Crucible Co. have worked a schist containing about 10 p.c. of graphite. It has also been worked to a limited extent near Raleigh, North Carolina; at Stourbridge, Mass.; at Cumberland Hill in Rhode I.; and at Sonora in California. The graphite 'ores' are crushed or stamped, and then washed, whereby the flakes of graphite are readily separated from the denser matrix. In the Laurentian gneiss of Canada, graphite is of frequent occurrence, and has occasionally been worked, as at the Buckingham Mines. The mineral is usually found in veins and nodular masses, or finely disseminated through bands of limestone.

In Europe, extensive deposits of graphitic schists occur in the Eastern Alps and in the mountainous region between Bohemia and Bavaria (Böhmerwald). These are extensively mined in Austria (in Moravia, Styria, and particularly in the east of Bohemia), where the annual output reaches 50,000 tons; but the material is of inferior quality, containing often 50 p.c. of ash. Considerable amounts are also obtained in the north of Italy, but the well-known locality at Passau in Bavaria is now little worked. (On Alpine Occurrences of Graphite *v.* E. Weinschenk, Abh. bayer. Akad. Wiss. 1898, 19, 509, 521; 1901, 21, 279.)

Daubrée has obtained graphite artificially by decomposing carbon disulphide in contact with metallic iron at a high temperature; while H. Sainte-Claire Deville prepared it by passing vapour of carbon tetrachloride over fused cast iron. Crystalline graphite is often formed in blast furnace slag during iron smelting, and is known to workmen as *kish*; and it is present in grey pig iron. Considerable quantities of graphite are now produced commercially, together with carborundum, in the electric furnace. The artificial production of graphite (as well as various properties of the natural mineral) is dealt with by H. Moissan (The Electric Furnace, London, 1904). Graphite also occurs in certain meteoric irons, such as that of Toluca in Mexico. A cubic form of graphitic carbon, discovered in a meteoric iron from Youndegin, Western Australia, has been described by Fletcher under the name of *Cliftonite* (Min. Mag. 1887, 7, 121).

In consequence of its refractory character, graphite is largely used in the manufacture of crucibles, retorts, twyers, and other objects required to withstand high temperatures. For crucibles, the powdered mineral is mixed with Stourbridge fire-clay, and made into a paste with water; the kneaded mass is allowed to lie for many weeks before the crucible is moulded; the vessel when moulded is slowly dried, and carefully fired in a seggar.

As a lubricating agent graphite is highly valued, since it diminishes friction and tends to keep the moving surfaces cool. To obtain the best results the powdered mineral should be carefully selected and sized. For steam cylinders it is used dry; for heavy bearings it is mixed with grease; and for light bearings with oil. Made into a paint with linseed oil, it has been advantageously employed as a coating for metal work. Graphite is also used dry for polishing stoves and other objects of cast iron, the thin flakes forming a lustrous coating which protects the metal. Blasting powder and heavy ordnance powders are likewise glazed with graphite, for though it slightly diminishes the explosive force of the powder it protects it from damp. Being a good conductor of electricity, graphite is used in electrotyping, as originally suggested by Murray; the moulds upon which the metal is to be deposited receiving a conducting surface by being coated with finely divided graphite.

E. Donath, Der Graphit, eine chemisch-technische Monographie, Leipzig and Wien, 1904; Graphite, its Occurrence and Uses, Bull. Imp. Inst. London, 1906, 4, 353; 1907, 5, 70; F. Cirkel, Graphite, its Properties, Occurrence, Refining, and Uses, Dept. of Mines, Ottawa, 1907; A. Haenig, Der Graphit, eine technische Monographie, Wien and Leipzig, 1910.

L. J. S.

GRASSES. The term 'grass' is used by the agriculturist to denote, not only plants which belong to the *gramineæ*, but also other pasture or meadow plants, or even certain weeds common on cultivated land.

The true grasses are characterised by a somewhat low content of nitrogenous substances and by the richness of the ash in silica and its poverty in lime and magnesia, whilst clovers and other leguminous crops possess the exactly opposite features.

H. I.

GREASES. The term 'grease' was applied originally to all kinds of fats having a buttery consistence. At present, however, the term 'grease' is restricted to low-class material, chiefly obtained from waste products, such as kitchen grease, ship's grease, tripe tallow, slaughter-house grease ('tankage' grease), bone grease, skin grease, greases from carcase-rendering establishments, and garbage fats. All these greases must be looked upon as varieties and (or) mixtures of lard, tallow, bone fat, horse fat, fish stearines, &c.

Greases are characterised by a dark colour, by a high percentage of free fatty acids, and a correspondingly high proportion of unsaponifiable matter. They are also characterised by an objectionable odour.

Black grease is the dark, almost black, fatty matter which is recovered from cotton seed mucilage, on decomposing the latter with mineral acids (*see* Cotton Seed Oil). This black grease is used in the manufacture of low-class candle materials, after a purification by distillation with superheated steam, and further treating the distillate in the same manner as the fatty acids of the candle industry are worked up (*see* Saponification). J. L.

GREEN EBONY. Green ebony is a yellow dyewood formerly employed to some extent in this country, but now almost entirely replaced by other colouring matters. It is a native of Jamaica or West India, and is obtained from the *Excœcaria glandulosa* (Siv.) or *Jacaranda ovalifolia* (R. Br.). The trunk of the tree is about 6 inches in diameter; the wood is very hard, and of an orange-brown colour when freshly cut and stains the hands yellow. References to this dyestuff are meagre, and it does not appear to have been ever largely employed. Bancroft (Philosophy of Permanent Colours, 1813, ii. 106) states that green ebony contains a species of colouring matter very similar to that of *Chlorophora tinctoria* (Gaudich) (old fustic), and is sometimes employed in its stead; and O. Neill (Dictionary of Calico Printing and Dyeing, 1862) mentions that it is used in dyeing greens and other compound shades. Until recently it had a limited sale in Yorkshire as a dye for leather, but appears to have entirely passed out of use as a woollen dyestuff. It is little used in silk dyeing, but was formerly employed for greening blacks.

Green ebony contains two crystalline colouring matters, which are distinguished by the fact that whereas one, excœcarin, is not precipitated by lead acetate solution, the second, jacarandin, is completely deposited by this reagent (Perkin and Briggs, Chem. Soc. Trans. 1902, 81, 210).

Excœcarin $C_{13}H_{12}O_5$ crystallises in lemon-yellow needles, sparingly soluble in cold alcohol, and melting with effervescence at 219°–221°. It is soluble in aqueous and alcoholic alkaline solutions with a violet-red colouration, and these liquids, on exposure to air, are rapidly oxidised, and assume a brown tint.

Excœcarin does not dye mordanted fabrics, but is a substantive dyestuff in that it has a weak but decided affinity for the animal fibres with which it gives, preferably in the presence of tartaric or oxalic acid, yellow shades. *Benzoyl excœcarin* $C_{13}H_9O_5(C_7H_5O)_3$, colourless needles, m.p. 168°–171°; and *excœcarindimethyl ether* $C_{13}H_{10}O_5(CH_3)_2$ yellow needles, m.p. 117°–119°. On fusion with alkali excœcarin gives *hydroquinonecarboxylic acid* ($CO_2H : OH : OH = 1 : 2 : 5$) and a substance melting at 124°, which is probably *hydrotoluquinone*

$$(CH_3 : OH : OH = 1 : 2 : 5).$$

By the action of bromine upon a solution of excœcarin in alcoholic potassium acetate *excœcarone* $C_{13}H_{10}O_5$, flat copper coloured needles or leaflets, melting at about 250°, is produced, and this by the action of sulphurous acid is readily converted into excœcarin. With alcoholic quinone solution excœcarin gives the compound $C_6H_4O_2 \cdot C_{13}H_{12}O_5$, minute green-coloured leaflets, melting with decomposition at 190°, and from this sulphurous acid also regenerates excœcarin. From these results it appears evident that excœcarin contains free hydroquinone hydroxyls.

Jacarandin $C_{14}H_{12}O_5$, yellow plates or leaflets, m.p. 243°–245°, dissolves sparingly in alcohol and the usual solvents to form pale yellow liquids having a green fluorescence. With caustic alkali solutions it gives orange-red liquids; with alcoholic lead acetate a bright orange coloured precipitate; and with alcoholic ferric chloride a dark greenish-black solution. It dyes mordanted woollen fabrics the following shades :—

Chromium	*Aluminium*	*Tin*	*Iron*
Dull yellow-brown	Orange-brown	Bright golden yellow	Deep olive

Acetyl jacarandin $C_{14}H_{10}O_5(C_2H_3O)_2$, pale-yellow needles, melts at 192°–194°, and when digested with boiling alcoholic potassium acetate gives the salt $(C_{14}H_{12}O_5 \cdot C_{14}H_{11}O_5)K$, yellow needles. *Benzoyljacarandin* $C_{14}H_{10}O_5(C_7H_5O)_2$ forms yellow prismatic needles, m.p. 167°–169°.

As indicated by Bancroft (*l.c.*) the colours given by green ebony are similar in character to those yielded by old fustic. Employing mordanted woollen cloth the following shades are produced :—

Chromium	*Aluminium*	*Tin*	*Copper*	*Iron*
Dull yellow-brown	Dull brown-yellow	Golden yellow	Pale brown	Olive green

With 40 p.c. of the dyewood the iron mordant gives greener and brighter shades than with larger amounts, in which case a browner colour is produced. Possibly from this green shade, and the extremely hard and compact nature of the wood, the name 'green ebony' has originated. A. G. P.

GREEN ALIZARIN *v.* Madder.

GREEN CINNABAR. A mixture of chrome yellow and Prussian blue.

GREEN EARTH, *Terre verte, v.* Pigments.

GREEN, EMERALD, *v.* Chromium.

GREEN, GUIGNET'S, *v.* Chromium.

GREEN SMALT, *Cobalt green, v.* Pigments.

GREEN ULTRAMARINE, *Chromium sesquioxide, v.* Chromium.

GREEN VITRIOL, *Ferrous sulphate, v.* Iron.

GREENLAND SPAR *v.* Cryolite.

GREENOCKITE, *Cadmium sulphide, v.* Cadmium.

GRENAT BROWN *v. iso*-Purpuric acid.

GREY ANTIMONY ORE, *Antimony sulphide, v.* Antimony.

GRI-SHI-BU-ICHI. Japanese name for an alloy of copper and silver of a rich grey colour.

GRISOUTINE. An explosive consisting of a mixture of nitroglycerin, nitrocellulose, ammonium nitrate, and kieselguhr.

GROSSULARITE *v.* Garnet.

GUACAMPHOL, GUAIACETIN, GUAIAFORM, GUAIAKINOL, GUAIAMAR, GUAIASANOL, GUATANNIN *v.* Synthetic drugs.

GUAIACENE *v. Guaiacum,* art. Resins.

GUAIACIC ACID *v. Guaiacum,* art. Resins.

GUAIACOL (*Monomethoxycatechol*)

$$OH \cdot C_6H_4 \cdot OMe$$

is a constituent of guaiacum resin (Herzig and Schiff, Monatsh. 1898, 19, 95), and occurs in beechwood tar from which it can be separated by treating the fraction of the tar that comes over at 200°–205° with ammonia to remove acids; it is then again fractionated, and the lower boiling fraction is dissolved in ether and treated with potassium hydroxide. The potassium salt of guaiacol is filtered, washed with ether, and recrystallised from alcohol, after which it is decomposed with sulphuric acid, and the guaiacol redistilled. (For other methods of separation, *cf.* D. R. PP. 87971, 56003, 100418, Chem. Zentr. 1899, i. 764.) Guaiacol is prepared from *o*-anisidine. 500 grams *o*-anisidine are diazotised, and the solution of the diazo salt is then poured into a boiling solution of 600 grams of copper sulphate in 600 c.c. of water. The guaiacol is then separated by distillation in steam (D. R. P. 167211; Frdl. 1905–7, 128; *cf.* also D. R. P. 95339; J. Soc. Chem. Ind. 1898, 269, 314).

Pure guaiacol can be obtained by dissolving catechol (55 parts) in ethyl alcohol (2000 parts) and adding nitrosomonomethyl urea. The mixture is cooled to 0° and 20 parts of sodium hydroxide dissolved in a small quantity of water is added, drop by drop, with constant stirring. The solution is filtered, the alcohol distilled off, and the residue is fractionated *in vacuô* (D. R. P. 189843; Frdl. 1905–7, 1151).

Guaiacol is also prepared by heating an equimolecular mixture of catechol, potash and potassium methyl sulphate in tightly closed vessels at 170°–180°, or by heating catechol and methyl iodide in methyl alcohol. Thompson (Eng. Pat. 5284, 1893) suggests the purification of guaiacol by treatment with a freezing mixture.

Guaiacol has a characteristic odour and crystallises in long vitreous transparent prisms, which appear rose-red in sunlight; m.p. 28·5°, b.p. 202·4°/738 mm. (Freyss, Chem. Zeit. 1894, 18, 565); sp.gr. 1·140 at 25°. When quite pure it is non-caustic and non-poisonous (Béhal and Choay, Compt. rend. 1893, 116, 197; Kuprianow, J. Soc. Chem. Ind. 1895, 57).

It is soluble in most organic solvents, and to a less extent in water. With a trace of ferric chloride its alcoholic solution gives a blue colour, which becomes emerald-green on the addition of more ferric chloride. Guaiacol also gives a blue colour with traces of hydrogen peroxide (Denigès, J. Pharm. 1909, 31).

Guaiacol is employed in pharmacy as an expectorant and intestinal antiseptic; also in pulmonary tuberculosis in cases of typhoid and other fevers, and for the relief of superficial neuralgia.

Kuprianow (Centralbl. f. Bakteriol. 1894, 15, 933, 981) has suggested the use of pure guaiacol in the internal treatment of cholera, since he found that a solution of 1 in 500 of this reagent completely prevents the development of the cholera bacillus.

Guaiacol should be preserved in amber-coloured bottles protected from the light, and should only be used in pharmacy when quite pure.

Tests.—(1) 2 c.c. of guaiacol mixed with 4 c.c. of light petroleum, should separate at once into 2 layers. (2) 1 c.c. of guaiacol should dissolve in 2 c.c. of N. sodium hydroxide when heated; on cooling the mixture should congeal to a white saline mass, which gives a clear solution with 20 c.c. of water. (3) 1 c.c. of guaiacol treated with 10 c.c. of N. sulphuric acid should give a pure yellow colour. For other tests, *v.* Marfori, J. Soc. Chem. Ind. 1891, 487; Fonzes Diacon, Bull. Soc. chim. 1898, 19, 191; Guérin, J. Pharm. Chim. 1903, [vii.] 17, 173.

Guaiacol can be estimated approximately by conversion into catechol, by heating with water in a current of hydrobromic acid; or 0·5 gram of the guaiacol is dissolved in a little water, 10 c.c. of alcohol added, and the solution made up to 1000 c.c., and 20 c.c. of this solution are mixed in a test-tube with 1 c.c. of sodium nitrite solution (1 : 100), and 1 c.c. dilute nitric acid (1 : 200). A characteristic red-brown colour is produced, which is compared within about 10 minutes with the colourations given by suitable standard solutions (Adrian, Zeitsch. anal. Chem. 1901, 40, 624).

Guaiacol, when treated with hydrogen cyanide, in the presence of sodium or zinc chloride, yields vanillin (Roesler, D. R. P. 189037; Frdl. 1905–7, 1280; Guyot and Gry, Compt. rend. 1909, 149, 928; Bull. Soc. chim. 1910 [iv.] 7, 902).

Guaiacol monosulphonic acids can be obtained by treating guaiacol with sulphuric acid at 30°–60°, the ortho- and para- acids formed being separated by converting them into the basic salts of the alkaline earths, or of the heavy metals, the ortho- salts being readily soluble in water, whereas the para- salts are insoluble or sparingly soluble. By the action of sulphuretted hydrogen, or some suitable acid, the salts are then converted into their respective acids (D. R. P. 188506; Frdl. 1905–7, 936; D. R. P. 132607; Frdl. 1900–02, 1113; Hähle, J. pr. Chem. 1902, [ii.] 65, 95; Lamière and Perrin, Bull. Soc. chim. 1903 [iii.] 29, 1228; Rising, Ber. 1906, 39, 3685; Paul, *ibid.* 2773, 4093; Ginhorn, Fr. Pat. 391601, 1908; J. Soc. Chem. Ind. 1908, 1176; Andrè, J. Pharm. Chim. 1898, 7, 324).

The most striking difference between the ortho- and the para- acids is their action with calcium or barium chloride, with which the para-acid yields a white precipitate, whereas the ortho- remains unchanged. With nitric acid the para- acid forms yellow dinitroguaiacol (m.p. 122°), whilst the ortho- acid merely gives a dark-red colouration. It is important that when the ortho- acid is used therapeutically, it should be free from the para- compound, as the latter gives rise to secondary reactions (Ellis, J. Soc. Chem. Ind. 1906, 335).

The alkali guaiacol sulphonates are employed as drugs (Alpers, U.S. Pat. 692588; J. Soc. Chem. Ind. 1902, 364). Tagliavini has prepared salts of the sulphonates with antipyretic and analgesic bases (Boll. Chim. farm. 1909, 48, 6).

Carbonyl chloride condenses with the alkali guaiacol sulphonates in alkaline solutions, giving derivatives such as *potassium carbonatodiguaiacol disulphonate* $CO[OC_6H_3(OMe)SO_3K]_2$, and *potassium carbonatodiguaiacol sulphonate*

$$C_6H_4(OMe)O{\cdot}CO_2C_6H_3(OMe)SO_3K$$

(Einhorn, D. R. P. 203754, 1909).

Guaiacol 5-sulphonic acid is obtained by sulphonating an acetyl derivative of guaiacol with or without the addition of dehydrating agents, the resulting acetyl guaiacol sulphonic acid is hydrolysed, neutralised, and the resulting acid is isolated as such, or in the form of its salts D. R. P. 212389; J. Soc. Chem. Ind. 1909, 1005). The corresponding *carbonate*

$$(MeO{\cdot}C_6H_3SO_3H)_2CO_3$$

is formed by treating guaiacol carbonate with sulphuric acid in the cold until the product is soluble in water. It melts at 115°–117°, with evolution of carbon dioxide (D. R. P. 215050; J. Soc. Chem. Ind. 1909, 1223).

Triphenyl guanidine guaiacol sulphonate is obtained by the action of triphenyl guanidine sulphate on barium guaiacol sulphonate. It crystallises in leaflets, m.p. 50°, and can be used as a local anæsthetic (Goldschmidt, Chem. Zeit. 1901, 25, 628).

A number of important compounds of *o*-guaiacol sulphonic acids with alkaloids are described by Schaefer (J. Soc. Chem. Ind. 1910, 928). They are used in medicine and are also of scientific interest. The alkaloid salts are prepared by neutralising the guaiacol sulphonic acid with the required alkaloid, and purifying the product by filtration and recrystallisation, or the amorphous salt is obtained by evaporation at low temperature or *in vacuô*. The salts may also be obtained by double decomposition between a soluble alkaloid, and a readily soluble salt of the acid in molecular proportions, using alcohol, water, &c., as a solvent. Most of the alkaloid salts are non-crystalline or crystallise with difficulty. The most important of the salts described by Schaefer are:

Quinine guaiacol bisulphonate (guaiaquin) $[C_6H_3(OH)(OMe)SO_3H]_2,C_{20}H_{24}N_2O_2$ is a yellowish crystalline powder, soluble in water, alcohol, and dilute acids. The solution is coloured blue by a drop of ferric chloride solution. It softens at about 80°, and becomes liquid at 130°.

Codeine-o-guaiacol sulphonate

$$C_6H_3(OH)(OMe)SO_3H,C_{18}H_{21}NO_3,$$

m.p. 164°–165°, is a well-crystallised neutral salt. It is readily soluble in hot water and in alcohol, but almost insoluble in ether and chloroform. It gives the characteristic blue colouration of *o*-guaiacol sulphonic acid with ferric chloride, and when its aqueous solution is treated with an alkali, codeine is precipitated. Other opium and cinchona compounds, as well as compounds with strychnine, brucine, atropine, hyoscine, hyoscyamine, and cocaine, are described.

Guaiacol iron and lithium sulphonates have been prepared (Schaefer, Eng. Pat. 21747, 1899).

Guaiakinol, quinine derivative of bromo-guaiacol, $C_{20}H_{24}N_2O_2,2HBr,C_6H_4(OH)(OMe)$, forms fine crystalline yellow scales, readily soluble in water. It is said to be practically non-toxic, and its aqueous or alcoholic solution is readily absorbed by the skin (Pharm. J. 1901, 66, 132; Schaefer, Eng. Pat. 8227, 1897).

Guacamphol, the camphoric acid ester of guaiacol $C_8H_{14}(CO{\cdot}OC_6H_4{\cdot}OMe)_2$, obtained by the action of camphoric acid chloride on sodium derivative of guaiacol. Forms white, odourless, tasteless needles, and has been recommended for the relief of night sweats in phthisis.

Guaiacol benzoate (benzosol, benzoyl guaiacol) $C_6H_5{\cdot}CO{\cdot}OC_6H_4{\cdot}OMe$ is prepared by heating an alcoholic solution of potassium derivative of guaiacol with the requisite amount of benzoyl chloride, and purifying the substance by crystallisation from alcohol. It is a colourless, odourless, tasteless powder, almost insoluble in water, readily soluble in organic solvents. It has m.p. 56°, and is used in the treatment of pulmonary tuberculosis (Eng. Pat. 5366, 1890; J. Soc. Chem. Ind. 1891, 383; Walzer, Chem. Zeit. Rep. 1891, 15, 165).

Guaiacol cinnamate (styracol, cinnamyl guaiacol) $C_8H_7{\cdot}CO{\cdot}OC_6H_4{\cdot}OMe$ is formed by the interaction of molecular weights of guaiacol and cinnamyl chloride. It forms colourless needle-shaped crystals, m.p. 130°, which are employed in catarrhal affections of the digestive tracts, and in the treatment of phthisis.

Guaiacol combines with tannin and cinnamic acid to form a compound which is said to be of use in medicine. It melts above 300°, is insoluble in most organic solvents, and dissolves in alkalis and also in pyridine, from which the pyridine derivative crystallises in well-shaped rhombic needles (D. R. P. 133299; Frdl. Nissel. 1900-02, 1111).

Guaiacol valerate $C_4H_9{\cdot}CO{\cdot}OC_6H_4{\cdot}OMe$, a yellowish oily liquid, b.p. 245°–265°, is used in medicine under the name of *geosote* (Rieck, J. Soc. Chem. Ind. 1897, 632). It is prepared by the action of valeryl chloride on sodium derivative of guaiacol.

Guaiacol salicylate (guaiacol salol)

$$C_6H_4(OH)CO{\cdot}OC_6H_4{\cdot}OMe$$

is a white crystalline, odourless, tasteless powder; m.p. 65°. It is formed by the action of phosphorus oxychloride on a mixture of sodium guaiacol salicylate, and is used as an intestinal antiseptic.

Guaiacol succinate $C_2H_4(CO{\cdot}OC_6H_4{\cdot}OMe)_2$ is formed by the action of phosphorus oxychloride on a mixture of guaiacol and succinic acid in molecular proportions. It forms fine silken crystalline needles; m.p. 136°.

Guaiamar, the *glyceryl ether of guaiacol* $C_6H_4(OMe)OC_3H_7O_2$, is formed by the action of anhydrous glycerol on guaicol. It is a white crystalline body, m.p. 75°, soluble in water and in most organic solvents. It has a bitter aromatic taste, and is employed in medicine as an antiseptic for internal and external application (J. Soc. Chem. Ind. 1900, 371; 1902, 1346).

Guaiasanol (diethylglycocollguaiacol hydrochloride) $MeO,C_6H_4O{\cdot}CO{\cdot}CH_2NEt_2,HCl$, m.p. 184°, is non-poisonous, and said to possess slight anæsthetic, antiseptic, and deodorising properties (Einhorn, Chem. Zeit. Rep. 1900, 24, 33; J. Soc. Chem. Ind. 1900, 464). By the action of the monochloracetic esters of phenols with secondary amines of the fatty series, many compounds, similar to the above, have been prepared (Einhorn and Heinz, Arch. Pharm. 240 [8] 631; D. R. P. 105346). They are non-poisonous, odourless, and strongly antiseptic substances.

Guaiaperol (piperidine derivative of guaiacol) is prepared by dissolving 85 parts of piperidine and 248 parts of guaiacol in benzene or light petroleum, and allowing the solution to evaporate (Tunnicliffe, Chem. Soc. Trans. 1898, 145).

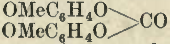
Valuable albuminous products said to be applicable in medicine for tuberculous and other cases are obtained by the interaction of guaiacol with egg or other albumin in aqueous or alcoholic solution (D. R. P. 162656; Frdl. 1905-7, 931).

Guaiacol, when treated with ethoxyacetyl chloride, bromide, or iodide, reacts thus:

$$MeO{\cdot}C_6H_4{\cdot}O\boxed{H+Cl}COCH_2OEt \\ \rightarrow MeO{\cdot}C_6H_4CO{\cdot}OCH_2OEt.$$

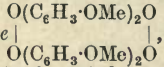
The product is a colourless, odourless oil; b.p. 150°/10 mm. The corresponding methoxy derivative boils at 170°–171°/10 mm., and has very similar properties to the ethoxy derivative. Both substances are non-poisonous, and can be used therapeutically as external remedies (D. R. P. 171790; Frdl. 1905–7, 933).

Guaiaform (geoform) is produced by the condensation of guaiacol (2 mols.) with formaldehyde (1 mol.). It is a tasteless, yellow, non-irritant and non-toxic powder, but on keeping it acquires the vanilla flavour. It is insoluble in water, but readily soluble in ether, benzene, or alcohol (Ehlert, Pharm. J. 1902, 68, 61).

Guaiacol carbonate  $\begin{matrix}OMeC_6H_4O\\OMeC_6H_4O\end{matrix}\!\!>CO$ is prepared by passing phosgene into a solution of guaiacol in sodium hydroxide. The substance is filtered off, washed with sodium hydroxide solution, and recrystallised from alcohol. It is a white crystalline powder, m.p. 84°–87°, of neutral reaction, and almost odourless and tasteless, soluble in most organic solvents, but insoluble in water. Its alcoholic solution yields no characteristic colour with ferric chloride. When taken internally its action is very similar to that of guaiacol, but it is less liable to derange the stomach. It is employed as an expectorant in the treatment of tuberculosis and bronchitis, and also as an intestinal antiseptic in the treatment of typhoid fever and intestinal indigestion (D. R. PP. 99057, 58129, 117346, of 1901; D. R. P. 224160; Einhorn, Chem. Zentr. 1910, ii. 518).

Guaiacol chlorocarbonate is a colourless oil; b.p. 112°/25 mm. It is prepared by the interaction of antipyrine, carbonyl chloride and guaiacol (D. R. P. 117624 of 1901; Einhorn, D. R. P. 224108, 1910; Chem. Zentr. 1910, ii. 517).

Guaiacol carboxylic acid $C_6H_3(OH)(OMe)CO_2H$ is formed by the action of carbon dioxide on sodium derivative of guaiacol, previously heated; the product is heated for some time, and is then acidified with hydrochloric acid, the free acid being recrystallised from water or dilute alcohol. It is a white, odourless crystalline powder; m.p. 148°–150°. It has a bitter taste, is readily soluble in hot water, and its aqueous solution is coloured blue by ferric chloride. The acid and its salts have been recommended as antiseptics and antirheumatics (Pharm. J. 1890, 977).

Guaiacol, when oxidised with laccase, yields *tetraguaiacoquinone*  $\begin{matrix}O(C_6H_3{\cdot}OMe)_2O\\|\qquad\qquad|\\O(C_6H_3{\cdot}OMe)_2O\end{matrix}$, a fine crystalline powder, m.p. 135°–140°, having a purplish-red colour with a faint green metallic lustre. It is insoluble in water, but gives mahogany-red solutions with chloroform and with acetic acid. It also forms coloured solutions in alkalis (Bertrand, Compt. rend. 1903, 137, 1269).

Dimethylamino ε-guaiacylamyl ether, the corresponding piperido derivative and the piperido-γ-guaiacyl-propyl ether are formed by the interaction of a halogen hydrocarbon alkyl ether of guaiacol with a secondary amine, thus:

$$x(CH_2)_nO{\cdot}R+NHMe_2=Me_2N(CH_2)_nOR;\text{ or}$$
$$x(CH_2)_nO{\cdot}R+NHC_5H_{10}=C_5H_{10}N(CH_2)_nO{\cdot}R$$

(where x=halogen). They are employed in medicine as anæsthetics (D. R. P. 184986; Frdl. 1905–7, 1050).

Hexamethylenetetraminetriguaiacol crystallises in brilliant needles, which become soft at 80°, and melt to a turbid liquid at about 95°. When distilled in steam it yields guaiacol (Eng. Pat. 24072, 1908; J. Soc. Chem. Ind. 1909, 490).

Chloroacetyl guaiacol $OMeC_6H_4O{\cdot}CO{\cdot}CH_2Cl$ is prepared by treating a mixture of guaiacol monochloroacetic acid and pyridine with phosphorus oxychloride. It forms white needles, m.p. 58°–60° (Einhorn and Hentz, *l.c.*).

Guaiacol chloroformic ester is a colourless oil; b.p. 112°/25 mm. (D. R. P. 117624; Frdl. 1900-02, 1165).

Benzyl guaiacol is a yellow, beautifully fluorescent oil; b.p. 269°–270°/430 mm. (Boscogrande, Chem. Zentr. 1898, i. 207).

Guaiacol picrate forms orange-red needles; m.p. 80°. Many other guaiacol derivatives have been prepared, some of which have been recommended for use in medicine (Eng. Pat. 5856, 1894; Ruhemann, Chem. Soc. Trans. 1902, 421; D. R. P. 120558; Frdl. 1900–02, 1112; D. R. P. 157355; Frdl. 1902–04, 616; Knapp and Suter, Chem. Zentr. 1904, i. 391; Moureu and Lazennec, Compt. rend. 1906, 142, 894; Bischoff, Ber. 1906, 39, 3846; Gattermann, Annalen, 1907, 357, 313; Fourneau, J. Pharm. Chim. 1910, [vii.] 1, 55, 97; Manchot, Ber. 1910, 43, 949; Wohl and Berthold, *ibid.* 2175; Hoffmann, D. R. P. 255924; Chem. Zentr. 1910, ii. 1105).

A number of azo derivatives of guaiacol are described by Leonardi (Atti R. Accad. Lincei. 1907 [v.] 16, ii. 639); some nitro and amino derivatives by Reverdin and Crepieux, Ber. 1903, 36, 2257; 1906, 39, 4232; Paul, *ibid.* 2773; Kühling, *ibid.* 1905, 38, 3007; Fichter and Schwab, *ibid.* 1906, 39, 3339).

Thioguaiacol and *thioguaiacol xanthate* have been prepared by Mauthner (Ber. 1906, 39, 1347).

Guaiacol forms mono-, di-, tri-, and tetrahalogen derivatives (Cousin, Compt. rend. 1898, 127, 759; Tassily and Lerride, *ibid.* 1907, 144, 757; Bull. Soc. chim. 1908, [iv.] 3, 124; Mameli, Gazz. chim. ital. 1907, 37, ii. 366; Robertson, Chem. Soc. Trans. 1908, 791). The iodo derivatives are said to be applicable to medicine (Mameli and Pinna, Chem. Zentr. 1907, ii. 2044).

Guaiacol phosphite, m.p. 75·5°, is a white crystalline powder, with a piquant non-caustic taste and slight odour, soluble in most organic solvents, but only sparingly in water (Bollard, D. R. P. 95578; J. Soc. Chem. Ind. 1897, 632; Ellis, Eng. Pat. 27527, 1896). Its medicinal properties are similar to those of guaiacol.

Another *guaiacol phosphite*, m.p. 59°, is described by Dupuis (Compt. rend. 1910, 150, 622).

Guaiacol phosphate $(C_6H_4OMe)_3PO_4$ is prepared by the interaction of phosphorus oxychloride and sodium derivative of guaiacol. It forms colourless crystals; m.p. 98°, insoluble in water and alcohol, but soluble in ether, chloroform, and acetone. It is used as an intestinal antiseptic and in hectic fever.

A number of other phosphorus compounds of guaiacol are described by Auger and Dupuis (Compt. rend. 1908, 146, 1151), and by Dupuis (*ibid.* 1910, 150, 622).

Guaiacol-cacodylate $AsMe_2O_2{\cdot}C_6H_4OMe$ is a white hygroscopic, crystalline, very unstable salt (Astruc and Murco, J. Pharm. Chim. 12, 553).

GUAIACONE *v. Guaiacum*, art. Resins.

GUAIACONIC ACID *v. Guaiacum*, art. RESINS.

GUAIACUM *v.* RESINS.

GUAIENE *v. Guaiacum*, art. RESINS.

GUAIOL *v. Guaiacum*, art. RESINS.

GUANIDINE $HN:C(NH_2)_2$ occurs in small quantities in etiolated vetch seedlings, 3 kilos. of dried material yielding 1 gram of the nitrate (Schulze, Ber. 1892, 25, 658); and in beet juice (Lippmann, *ibid.* 1896, 29, 2651).

Guanidine was first prepared by Strecker (Annalen, 1861, 118, 159) by oxidising guanine with potassium chlorate and hydrochloric acid; and it is obtained in small quantity by oxidising egg albumen with potassium permanganate, or gelatin with barium or calcium permanganate (Lossen, J. Pharm. Chim. [iii.] 31, 32; Kutscher and Kickgraf, Sitzungsber. K. Akad. Wiss. Berlin, 1903, 28, 624); it is formed synthetically (1) by heating biuret and hydrogen chloride at 160°–170° (Finckh, Annalen, 1862, 124, 332); (2) from chloropicrin and alcoholic ammonia at 100° (Hofmann, Ber. 1868, 1, 145); (3) from ethyl orthocarbonate and aqueous ammonia at 150° (Hofmann, Annalen, 1866, 139, 111); (4) from carbonyl chloride and ammonia (Bouchardt, Zeitsch. Chem. 1870, 58); (5) from ammonium chloride and alcoholic cyanamide at 100° (Erlenmeyer, Annalen, 1868, 146, 259); (6) from cyanogen iodide and alcoholic ammonia at 100° (Bannow, Ber. 1871, 4, 161); (7) by the action of *aqua regia* on dicyanodiamide, when a quantitative yield of the nitrate is obtained (Ulpiani, D. R. P. 209431).

Guanidine is usually prepared by heating ammonium thiocyanate for 20 hours at 180°–190°, treating the fused mass with water and allowing the guanidine thiocyanate to crystallise from the solution; it is then purified by animal charcoal and recrystallised from alcohol and water. The thiocyanate is converted into the carbonate by treating the concentrated aqueous solution with one equivalent of potassium carbonate, the solution is evaporated and the residue extracted with hot alcohol in which the guanidine carbonate is insoluble, and this is afterwards recrystallised from water (Delitsch, J. pr. Chem. 1871, [ii.] 9, 2; Volhard, *ibid.* 15). According to Goldberg, Siepermann, and Flemming (D. R. P. 1898, 97820), a better yield of guanidine salts is obtained when the ammonium thiocyanate is mixed with wood charcoal and the oxide or salt of a heavy metal, and the mixture heated in a current of ammonia,

$$(1)\ 2NH_4CNS+ZnO =CH_5N_3,HCNS+ZnS+H_2O\ ;$$

$$(2)\ 2NH_4CNS+ZnO+PbCl_2 =2NH_3+2CH_5N_3,HCl+ZnS+PbS+H_2O\ ;$$

or guanidine thiocyanate can be prepared by heating the thiocyanate of a heavy metal under pressure in an atmosphere of ammonia at 180°

$$Pb(CNS)_2+2NH_3=PbS+CH_5N_3,HCNS.$$

Guanidine is a deliquescent crystalline solid, readily soluble in alcohol or water; it is volatile and strongly alkaline, absorbs carbon dioxide from the air and forms crystalline salts. The thermal value of the basic function of guanidine is +32·1 Cal., intermediate between that of barium hydroxide +31·7 Cal. and sodium hydroxide +36·4 Cal. (Matignon, Compt. rend. 1892, 114, 1432). Guanidine is decomposed into ammonia and urea on boiling with baryta water or dilute sulphuric acid (Ossikowsky, Bull. Soc. chim. 1872, [ii.] 18, 161; Baumann, Ber. 1873, 6, 1376); and is completely decomposed into carbon dioxide and ammonia by heating with concentrated acids or alkalis. Guanidine is decomposed, evolving two-thirds of its nitrogen, when mixed with sodium hypochlorite or hypobromite (Fenton, Chem. Soc. Trans. 1879, 14).

When the hydrochloride is heated at 180°, ammonia is evolved and *biguanide* is formed, the reaction being similar to the formation of biuret from urea:

$$2HN:C(NH_2) =NH_3+HN:C(NH_2)NH{\cdot}C(NH_2)NH.$$

In its physiological action, guanidine is highly toxic; doses smaller than poisonous ones are in rabbits excreted unchanged in the urine (Pommerrenig, Beitr. Chem. Physiol. Path. 1902, i. 561); it acts on frog's muscles, producing spontaneous twitching and affecting their contractility, and it is supposed that the guanidine acts by combining with two different substances in the muscle, one of which is responsible for the twitching, and the other for the changes in contractility (Camis, J. physiol. 1909, 39, 73). Although guanidine does not appear to be a normal oxidation product of arginine in the body (Pommerrenig, *l.c.*), it is found among the products of pancreatic autodigestion (Kutscher and Otori, Zeitsch. physiol. Chem. 1904, 43, 93). Small quantities of guanidine, 0·1 per thousand, are injurious to chlorophyllous plants, whilst fungi utilise it as a source of nitrogen but not of carbon (Kawakita, Bull. Coll. Agr. Tōkyō, 1904, 6, 181).

Many salts of guanidine give a yellowish-white flocculent precipitate with Nessler's reagent, which can thus be used as a test for small quantities of the salts of the base, a 0·05 p.c. aqueous solution of guanidine nitrate gives a bulky precipitate and a 0·01 p.c. solution is rendered turbid (Schulze, Ber. 1892, 25, 661). Another test for guanidine is the development of a deep yellow to orange red colouration with alkali hypochlorites (de Coninck, Compt. rend. 1898, 126, 142). Guanidine is usually estimated as the picrate, the salt being collected on a Gooch asbestos filter, dried at 110° and weighed (Vozarik, Zeitsch. angew. Chem. 1902, 15, 670); or it can be converted into the strongly alkaline carbonate and titrated with standard acid (Grossmann and Schück, Chem. Zeit. 1906, 30, 1205).

Guanidine forms crystalline salts with mineral and with organic acids; it also forms characteristic double salts. The *hydrochloride*

$$CH_5N_3,HCl$$

forms double salts with *mercuric chloride*

$$CH_5N_3,HCl,2HgCl_2$$

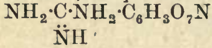
(Byk, J. pr. Chem. [ii.] 20, 233); with *gold chloride* $CH_5N_3,HCl,AuCl_3$, deep yellow, sparingly soluble needles (Hofmann, Ber. 1868, 1, 146); with *platinic chloride* $(CH_5N_3,HCl)_2,PtCl_4$, yellow needles, soluble in water, sparingly so in alcohol (Strecker, Annalen, 1861, 118, 160). The *nitrate*, CH_5N_3,HNO_3, crystallises in large plates, m.p. 214°, 10·75 parts dissolve in 100 parts of water at 15·9°. The *compound* with silver nitrate $CH_5N_3,AgNO_3$ crystallises in needles. The *nitrite* CH_5N_3,HNO_2 forms glittering prisms, m.p. 76°–78·5° (Lossen, Annalen, 1891, 265, 129). The *sulphate* $(CH_5N_3)_2,H_2SO_4$ crystallises in the regular system and is soluble in water (Bodewig, J. 1876, 763); it forms a double salt with *aluminium sulphate*

$$(CH_5N_3)_2,H_2SO_4,Al_2(SO_4)_3,12H_2O$$

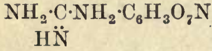
crystallising in large, well-developed hexagonal prisms belonging to the scalenohedral class of the rhombohedral system, and having sp.gr. 1·806 at 13·5° (Ferraboschi, Proc. Camb. Phil. Soc. 1908, 14, 471). The *carbonate* $(CH_5N_3)_2,H_2CO_3$ forms octahedral or tetragonal prisms; sp.gr. 1·238–1·251 (Schröder, Ber. 1880, 13, 1072). The *metaphosphate* CH_5N_3,HPO_3 forms a fine crystalline precipitate (Pohl, Zeitsch. physiol. Chem. 1889, 13, 296). The *perchromate*

$$(CH_5N_3)_3CrO_8,H_2O$$

forms small brownish-yellow, double-refracting prisms, and yields the usual blue solution with ether and dilute sulphuric acid (Hofmann and Buchner, Ber. 1909, 42, 2773). The *thiocyanate* $CH_5N_3,HCNS$ has m.p. 118°, and 100 parts of water dissolve 73 parts at 0°, or 134·9 parts at 15° (Engel, Bull. Soc. chim. 1885, 44, 424). The *platinothiocyanate* $(CH_5N_3)_2,H_2Pt(CNS)_6$ forms beautiful red crystals that blacken at 170°–175° (Guareschi, Chem. Zentr. 1891, ii. 620). The *cyanurate* $(CH_5N_3)_3,(CNHO)_3$ forms silky needles (Bamberger, Ber. 1887, 20, 71). The *dioxalate* $CH_5N_3,C_2H_2O_4,H_2O$ is sparingly soluble (Strecker, *l.c.*). The *picrate* $CH_5N_3,C_6H_2(NO_2)_3OH$ is a sparingly soluble, yellow, crystalline salt, 1 part dissolves in 2630 parts of water at 9°, and it does not melt at 280° (Emich, Monatsh. 1891, 12, 24). According to von Cordier (Chem. Zentr. 1906, i. 340), guanidine picrate exhibits stereoisomerism. The salt, as usually prepared, forms dark yellow plates that, owing to repeated twinning, have a hook-like structure, but when guanidine prepared by decomposing methylguanidine sulphate with barium hydroxide is used, the picrate crystallises in rosettes of bright yellow needles. The two forms are identical in composition, sp.gr., temperature of decomposition and electric conductivity, but differ in colour, crystalline form and solubility, 100 parts of water dissolve 0·037 parts of the plates at 0°, 0·061 at 20°, and 0·574 at 80°. The solubility of the needles is 0·043, 0·060, 0·800 at these temperatures respectively. One form cannot be converted into the other by crystallisation, and the author suggests that they are stereoisomerides, the plates being the stable modification,

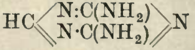


$\underset{\ddot{N}H}{NH_2\cdot C}\cdot NH_2\cdot C_6H_3O_7N_3$, and the needles the labile



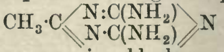
$\underset{H\ddot{N}}{NH_2\cdot C}\cdot NH_2\cdot C_6H_3O_7N_3$. The *benzenesulphonate* has m.p. 200°, the *p-toluene-sulphonate*, m.p. 206°, and the α- and *β-naphthalenesulphonates*, m.p. 257° (Remsen and Garner, Amer. Chem. J. 1901, 25, 173). The 4-*nitroacetylanthranilate* has m.p. 247° (corr.) (Bogert and Klaber, J. Amer. Chem. Soc. 1908, 30, 807). The *acetate* $CH_5N_3\cdot C_2H_4O_2$ forms shining needles, m.p. 229°–230° (Ostrogovich, Gazz. chim. ital. 1897, 27, i. 223). The *picrolonate* $CH_5N_3\cdot C_{10}H_8O_5N_4$ is soluble in alcohol (Schenck, Zeitsch. physiol. Chem. 1905, 44, 427).

Guanamines. When the guanidine salts of the first seven of the fatty acid series are heated at 220°–230°, water and ammonia are eliminated and heterocyclic bases called *guanamines* are formed: these are well characterised crystalline compounds. *Formoguanamine*



$$HC\left\langle\begin{matrix}N{:}C(NH_2)\\ N\cdot C(NH_2)\end{matrix}\right\rangle N$$

melts and decomposes at a high temperature; *acetguanamine*



$CH_3\cdot C\left\langle\begin{matrix}N{:}C(NH_2)\\ N\cdot C(NH_2)\end{matrix}\right\rangle N$ melts at 265°; *propionoguanamine* blackens at 300°; *œnanthoguanamine* melts at 130° (Nencki, Ber. 1874, 7, 1584; Haaf, J. pr. Chem. 1891, [ii.] 43, 75).

Chloroguanidine CH_4ClN_3, obtained by the action of bleaching powder solution on guanidine carbonate in ice water, forms a pale yellow crystalline powder that decomposes at 150° (Kamenski, Ber. 1878, 11, 1602).

Bromoguanidine CH_4BrN_3, formed from equimolecular proportions of bromine and guanidine carbonate, crystallises in yellow needles. By the action of 3 mols. bromine on 1 mol. guanidine carbonate, the *compound*

$$CH_5N_3\cdot HBr\cdot Br_2$$

is formed, crystallising in dark red prisms. The corresponding *iodine compound* $CH_5N_3\cdot HI\cdot I_2$ crystallises in prisms the colour of iodine (Kamenski, *l.c.*).

Nitroguanidine $NH:C(NH_2)NH\cdot NO_2$ was first prepared by Jousselin (Compt. rend. 1877, 85, 548; 1879, 88, 814, 1086) by the action of fuming nitric acid and nitric oxide on guanidine nitrate, and called by him nitrosoguanidine. Pellizzari (Gazz. chim. ital. 1891, 21, ii. 405) showed that it was the *nitro* compound, and his results were confirmed by Thiele (Annalen, 1892, 270, 1), who also prepared it by the action of fuming nitric acid and sulphuric acid on guanidine thiocyanate. It crystallises from water in colourless needles, melts and decomposes at 230° with evolution of ammonia; it dissolves in 372–375 parts of water at 19·3°, or in 11 parts of boiling water. The heat of combustion at constant pressure is +210·3 Cal. and the heat of formation from its elements is +22 Cal. (Matignon, Compt. rend. 1892, 114, 1432). The *silver* derivative $CH_3N_4O_2Ag$ is colourless and almost insoluble in water; the *nitrate* $CH_4O_2N_4\cdot HNO_3$ is crystalline and melts at 147°; the *hydrochloride* $CH_4O_2N_4.HCl$ crystallises in plates or prisms.

Nitrosoguanidine $NH:C(NH_2)NH\cdot NO$ is obtained by the partial reduction of nitroguanidine with zinc dust and sulphuric acid. It forms yellow needles, explodes violently at 160°–165°, is soluble in alkalis and reprecipitated by carbon dioxide; it also gives the Liebermann reaction. The alkali solutions give a beautiful purple colouration with ferrous salts. The *silver salt* CH_3ON_4Ag is a colourless explosive precipitate; the *copper salt* $(CH_3ON_4)_2Cu$ is reddish brown, and the *nickel salt* $(CH_3ON_4)_2Ni$ is vermilion red (Thiele, Annalen, 1893, 273, 133). According to Hantzsch, Schümann, Engler (Ber. 1899, 32, 575, 1703), nitrosoguanidine is a true nitrosamine and its constitution is represented by the formula $NH:C(NH_2)NH\cdot NO$, since it has a neutral reaction, yields mainly nitrous acid and not nitrogen when decomposed by acids, and does not interact with phosphorus pentachloride or acetyl chloride. On the other hand, Whiteley (Chem. Soc. Trans. 1903, 31) and Tschugaeff

(Ber. 1906, 39, 3383) consider that the coloured metallic derivatives are salts of the tautomeric diazo-hydrate form HN : C(NH_2)N : N·OH.

Aminoguanidine HN : C(NH_2)NH·NH_2, is obtained by reducing nitroguanidine with zinc dust and acetic acid at 40° until a test portion develops no colouration with ferrous sulphate and an alkali (Thiele, Annalen, 1892, 270, 23). The mixture is filtered, the filtrate evaporated till it is only feebly acid, and the aminoguanidine bicarbonate precipitated in the cold by adding a concentrated solution of alkali bicarbonate (D. R. P. 59241). Also prepared by heating an alcoholic solution of hydrazinehydrochloride, and cyanamide in a reflux apparatus (Pellizzari and Cuneo, Gazz. chim. ital. 1894, 24, i. 450). A yield of 81 p.c. of the theoretical is obtained by the electrolytic reduction of the nitro compound, suspended in water slightly acidified with sulphuric acid, using a tin cathode and a current density of 250 amperes per square metre and a temperature of 10° (Boehringer and Söhne, D. R. P. 167637).

Aminoguanidine is crystalline, soluble in water or alcohol, decomposes on boiling with dilute acids or alkalis, yielding first semicarbazide and finally ammonia, carbon dioxide, and hydrazine (Curtius, Ber. 1896, 29, 759). Aminoguanidine forms crystalline salts with mineral acids: the *hydrochloride* CH_6N_4,HCl forms large prisms, m.p. 163°; the *double salt* with platinic chloride $(CH_6N_4,HCl)_2,PtCl_4$ is a yellow precipitate, m.p. 145°–146°; the *nitrate* CH_6N_4,HNO_3 forms large shining plates, m.p. 144°; 100 parts of water dissolve 12·01 parts at 15·9°; the *sulphate* $(CH_6N_4)_2,H_2SO_4,H_2O$ crystallises in needles, m.p. 207°–208°; the *bisulphate*

$$CH_6N_4,H_2SO_4$$

crystallises in large plates, m.p. 161°; the *picrate* $CH_6N_4,C_6H_3O_7N_3$ is precipitated as yellow needles from hot water. The *copper compounds* $Cu(CH_5N_4)_2,2HNO_3$ and

$$Cu(CH_5N_4)_2,H_2SO_4$$

are violet crystalline precipitates; the *bicarbonate* CH_6N_4,H_2CO_3 (Thiele, Annalen, 1898, 302, 332) melts at 172° and is almost insoluble in cold water.

Acetaminoguanidine $CH_5N_4(C_2H_3O)$ forms a crystalline *nitrate*, m.p. 85°–90° and *picrate*; *formylaminoguanidine nitrate*

$$HNO_3,H_2N{\cdot}C(NH)NH{\cdot}NH{\cdot}CHO$$

melts at 143°, the *picrate* melts at 193°; *oxalylaminoguanidine* HN : C(NH_2)NH·NH·CO·CO_2H melts at 231°–232° (Thiele and Manchot, Annalen, 1898, 303, 37).

Aminoguanidine and its alkyl and aryl derivatives contain the grouping —NH·NH_2, present in hydrazines, and semicarbazide, and like them readily form condensation products with aldehydes, ketones, sugars, and ketonic acids; these are usually well characterised crystalline compounds, forming crystalline salts with mineral and organic acids. For the condensation products with aldehyde, chloraldehyde, chloral, *v.* Thiele and Dralle (Annalen, 1898, 302, 278); with benzaldehyde, *v.* Thiele (*ibid.* 1892, 270, 1), Wedekind (Ber. 1897, 30, 444); with diacetyl, acetylacetone, acetonylacetone, *v.* Thiele and Dralle (*l.c.*); with galactose, glucose, and lactose, *v.* Wolff (Ber. 1895, 28, 2613); with glyoxylic acid, *v.* Thiele and Dralle (*l.c.*), Doebner and Gärtner (Annalen, 1901, 315, 1); with pyruvic acid, *v.* Wedekind and Bronstein (*ibid.* 1899, 307, 297). For the preparation and properties of *alkyl* and *aryl* substituted derivatives of aminoguanidine, *v.* Pellizzari and Cuneo (Gazz. chim. ital. 1894, 24, i. 450), Pellizzari and Rickards (*ibid.* 1901, 31, i. 526).

Diaminoguanidine HN : C(NH·NH_2)$_2$ does not exist in the free state; its *hydrobromide* CH_7N_5,HBr is formed by the action of cyanogen bromide (1 mol.) on hydrazine (2 mols.); it crystallises in plates, m.p. 167°; the *picrate*, $CH_7N_5,C_6H_3O_7N_3$, melts at 191°; the *hydrochloride* at 185°; the *platinochloride* at 172°–173°; all the salts reduce Fehling solution and ammoniacal silver nitrate solution. *Dibenzylidenediaminoguanidine* HN : C(NH·N : CHPh)$_2$ yellow crystals, m.p. 180°; the *hydrobromide* melts at 243°, and the *hydrochloride* at 230° (Pellizzari and Cantoni, Gazz. chim. ital. 1905, 35, i. 291).

Dihydroxyguanidine hydrobromide

$$HN : C(NH{\cdot}OH)_2,HBr$$

is formed by the interaction of cyanogen bromide and hydroxylamine in methyl alcohol and ether at −20°; it forms colourless, flat, hygroscopic needles that decompose at 95° (Wieland, Ber. 1905, 38, 1445).

Methylguanidine HN : C(NH_2)NHMe has been isolated from extract of muscle (Gulewitsch, Zeitsch. physiol. Chem. 1906, 47, 471), and is prepared by boiling creatine with mercuric or lead oxide and dilute sulphuric acid (Dessaignes, Annalen, 1854, 92, 407; 1856, 97, 340). It can be synthesised from methylamine hydrochloride and cyanamide (Erlenmeyer, Ber. 1870, 3, 896). It is a strongly alkaline, volatile, crystalline substance, and liberates ammonia and methylamine on heating with potassium hydroxide. The *aurichloride* $C_2H_7N_3,HCl,AuCl_3$ melts at 198°–200°; the *platinichloride* $(C_2H_7N_3,HCl)_2,PtCl_4$ melts at 194°–195° (Schenck, Arch. Pharm. 1909, 247, 466). The *oxalate* $(C_2H_7N_4)_2,C_2H_2O_4,2H_2O$ is crystalline and soluble in water. The *picrate* crystallises from water in two distinct modifications (Gulewitsch, *l.c.*). The *picrolonate*

$$C_2H_7N_3,C_{10}H_8O_5N_4$$

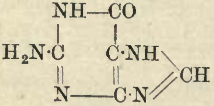
melts at 291° (Wheeler and Jamieson, J. Biol. Chem. 1908, 4, 111).

For other *alkyl* and *aryl* substituted derivatives of guanidine, some of which have therapeutic properties, *v.* Strakosch (Ber. 1872, 5, 692); Tatarinow (J. 1879, 401); Noah (Ber. 1890, 23, 2196); Hofmann (*ibid.* 1869, 2, 601); Fischer (*ibid.* 1897, 30, 2414); Alway and Vail (Amer. Chem. J. 1902, 28, 158); Kämpf (Ber. 1904, 37, 1681); Reidel (D. R. PP. 1892, 66550; 1898, 104361).

Guanidine forms condensation products with *dicarboxylic acids* (Traube, Ber. 1893, 26, 2551; Ruheman and Stapleton, Chem. Soc. Trans. 1900, 805; Kaess and Gruszkiewicz, Ber. 1902, 35, 3600); with *β-ketonic acids* (Jaeger, Annalen, 1891, 262, 365); with *β diketones* (Evans, J. pr. Chem. 1892, 45, 489; Wense, Ber. 1886, 19, 761); with *malononitrile* (Merck, D. R. PP. 165692, 165693); with *ethyl cyanacetate* (Traube, D. R. P. 1900, 115253).

Guanidine forms *compounds* with sugars containing 3 mols. of sugar and 1 mol. of guanidine; these exhibit mutarotation and have a lower optical activity than the sugars from which they are derived (Morrell and Bellars, Chem. Soc. Trans. 1907, 1010). M. A. W.

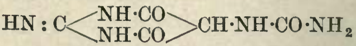
GUANINE, 2-*amino*-6-*oxypurine*,



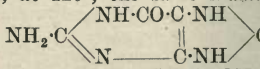
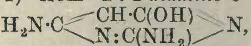
was discovered by Unger in guano in 1844 (Annalen, 51, 395; 58, 18; 59, 58), and though Hoppe-Seyler failed to find it in the excrement of fowls and geese, Haeter obtained it from the excrement of a heron (*Ardea cinerea*) fed on fish and flesh (Med. Chem. Untersuch. 1871, 582); Will and Gorup Besanez found it in the excrement of a spider, in the organ of Bojanus of the mussel, and in the green gland of the crayfish (*cp.* Weinland, Zeit. Biol. 25, 390); and Pecile found 0·0068 gram of guanine per litre in the urine of a pig fed on bran, and in an unhealthy condition (Annalen, 1876, 183, 141). In addition to its occurrence among the excretory products of the animal, guanine is fairly widely distributed throughout the tissues; thus it occurs, together with hypoxanthine, in the protamine from salmon roe, forming 6–8 p.c. of the ripe organ (Piccard, Ber. 1874, 7, 1714); it occurs in the pancreas, spleen, liver, and muscle of the ox, in quantities varying from 0·020 to 0·746 p.c. (Braginsky, Zeitsch. physiol. Chem. 1883, 8, 395; Kossel, *ibid.* 404; Schindler, *ibid.* 1889, 13, 432); and it is found in the skin of fishes (Ewald and Kruckenberg, Chem. Zentr. 1883, 705). Guanine is widely spread throughout the vegetable kingdom, Schützenberger found it, together with other purine bases, in yeast extract (Compt. rend. 1874, 78; Chem. Zentr. 1877, 73); Schulze and Bosshard isolated it, together with hypoxanthine and xanthine, from young potato tubers, sugar beet, leaf buds of plane and maple, bark of plane, from lupins, red clover, vetch, young grass, and oats (Zeitsch. physiol. Chem. 1884, 9, 420); and v. Lippmann obtained it from beet juice (Ber. 1896, 29, 2645). According to Levene and Mandel (Biochem. Zeitsch. 1908, 10, 215) guanine is one of the cleavage products of nucleic acid, when the hydrolysis is effected by acetic acid in the presence of lead acetate at 150°.

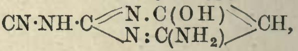
Guanine exists in guano partly as the calcium compound, partly in substances like nuclein, from these it is liberated by boiling for 4 hours with dilute sulphuric acid, the liquid is cooled and filtered, and the filtrate made alkaline with sodium hydroxide and again filtered. The guanine and uric acid are precipitated in the filtrate by the addition of ammoniacal silver solution, the precipitate washed with cold and hot water, and then decomposed by hot dilute hydrochloric acid, the silver chloride filtered off, the filtrate decolorised with animal charcoal, and the guanine precipitated by ammonia, a small quantity of urea in hot nitric acid is added, and the mixture set aside to crystallise. The guanine nitrate now free from uric acid is dissolved in dilute sodium hydroxide and the guanine precipitated by the addition of ammonium chloride, this last operation removing the xanthine (Wulff, Zeitsch. physiol. Chem. 1893, 17, 468).

Fischer (Ber. 1897, 30, 559) has shown that guanine is 2-amino-6-oxypurine from the fact that *imino-ψ-uric acid*



$$HN:C\left<\begin{matrix}NH\cdot CO\\ NH\cdot CO\end{matrix}\right>CH\cdot NH\cdot CO\cdot NH_2$$

obtained synthetically by Traube (Ber. 1893, 26, 2551) from guanidine and ethylmalonate, yields, on treatment with hydrochloric acid (sp.gr. 1·19), at 120°, the same 2-*amino*-6 : 8-*dioxypurine*  as is obtained from *bromoguanine* $C_5H_4BrON_5$ (Fischer and Reese, Annalen, 1883, 221, 342) by the action of hydrochloric acid at 130°. Further, a synthetic guanine, identical in every way with the natural product, is obtained when 6-*oxy*-2 : 8-*dichloropurine* is heated with alcoholic ammonia, and the resulting *chloroguanine* reduced by means of hydriodic acid (Fischer, Ber. 1897, 30, 2226). The synthetical production of guanine has also been effected by Traube (Ber. 1900, 33, 1371) from 2 : 4-*diamino*-6-*hydroxy*·*pyrimidine*  $H_2N\cdot C\left<\begin{matrix}CH\cdot C(OH)\\ N:C(NH_2)\end{matrix}\right>N$, obtained by the condensation of guanidine and ethyl cyanoacetate in the presence of sodium ethoxide. The nitroso derivative of this compound yields, on reduction with ammonium sulphide, 2 : 4 : 5-*triamino*-6-*hydroxypyrimidine*, which, when heated with an equivalent amount of sodium formate and 8–10 times its weight of anhydrous formic acid, is converted into guanine. A similar synthetic production of guanine from 2-*cyanamino*-4-*amino*-6-*hydroxypyrimidine*



$$CN\cdot NH\cdot C\left<\begin{matrix}N.C(OH)\\ N:C(NH_2)\end{matrix}\right>CH,$$

obtained by the condensation of dicyanodiamide and ethyl cyanoacetate in the presence of sodium ethoxide, forms the subject of certain patents of Merck (D. R. PP. 1905, 158591, 162336).

Guanine is an amorphous powder, insoluble in water, alcohol, or ether, but soluble in acids or alkalis, forming salts of a di-acid base, or dibasic acid respectively. It can be obtained in the form of small rhombic crystals when the freshly precipitated compound is dissolved in a large excess of ammonia at 30°–35°, and the filtered solution allowed to evaporate slowly (Drechsel, J. pr. Chem. 1881, 24, 44); or in crystals resembling those of creatinine zinc chloride, when a warm dilute alkaline solution (1 : 2000) is mixed with about one-third its volume of alcohol, acidified with acetic acid and allowed to cool (Horbaczewski, Zeitsch. physiol. Chem. 1897, 23, 226).

The administration of guanine as food to rabbits produces neither increase in purine excretion nor pathological changes in the kidney; but subcutaneous or intravenous injections of guanine dissolved in caustic soda, cause a great increase of purine substances, especially uric acid, in the urine (Schittenhelm, Chem. Zentr. 1902, i. 1306; Schittenhelm and Bendix, Zeitsch. physiol. Chem. 1905, 43, 365).

Guanine is converted to the extent of 60–70 p.c. into xanthine when heated with excess of 25 p.c. hydrochloric acid for 32 hours (Fischer, Ber. 1910, 43, 805); and undergoes profound decomposition, yielding ammonia, carbon dioxide, formic acid, and glycocoll on prolonged treatment with concentrated hydrochloric acid at 180°–200° (Wulff, Zeitsch. physiol. Chem. 1893, 17, 468). A micro-organism belonging to the class of coccus bacteria and found in the excrement of pigeons, flourishes in a culture containing guanine, which is decomposed into urea, guanidine, and carbon dioxide (Ulpiani and Cingolani, Atti. R. Accad. Lincei, 1905, [v.] 14, ii. 596).

The following derivatives of guanine have been described :—

Salts. (1) *With bases*, the *sodium*

$$Na_2O{\cdot}C_5H_5N_5O,6H_2O\,;$$

barium $C_5H_3N_5OBa$; and *copper*

$$C_5H_5N_5O{\cdot}Cu_2O \text{ and } C_5H_5N_5CuO$$

derivatives. (2) *With acids*, the *hydrochloride* $C_5H_5N_5O,HCl,H_2O$, forms double salts with zinc, cadmium, mercury, or platinic chloride ; *hydrobromide* $C_5H_5N_5O,HBr,2\frac{1}{3}H2O$; *hydriodide*

$$C_5H_5N_5O,HI,2\tfrac{1}{3}H_2O$$

forms a double salt with bismuth iodide ; *nitrates* $C_5H_5N_5O,HNO_3,1\frac{1}{2}H_2O$;

$$C_5H_5N_5O,2HNO_3,2H_2O\,;$$

$$3C_5H_5N_5O,4HNO_3,4H_2O\,;$$

and $3C_5H_5N_5O,5HNO_3,5\frac{1}{2}H_2O$;

sulphate $(C_5H_5N_5O)_2H_2SO_4,2H_2O$; *oxalate* $3C_5H_5N_5O,2C_2H_2O_4$; *tartrate*,

$$3C_5H_5N_5O,2C_4H_6O_6\,;$$

dichromate $C_5H_5N_5O,H_2Cr_2O_7$; *picrate*

$$C_5H_5N_5O,C_6H_3N_3O_7,H_2O\,;$$

picrolonate $C_5H_5ON_5,2C_{10}H_8O_5N_4$; *ferricyanide* $(C_5H_5N_5O)_4,H_3Fe(CN)_6,8H_2O$; *nitroferricyanide* $(C_5H_5N_5O)2H_2(CN)_5NOFe,1\frac{1}{2}H_2O$; *metaphosphate* $C_5H_5N_5O,HPO_3,xH_2O$. (3) *With salts*, *mercuric chloride* $C_5H_5N_5O,HgCl_2,2\frac{1}{2}H_2O$; *silver nitrate* $C_5H_5N_5O,AgNO_3$, the *silver picrate compound* $C_5H_4AgN_5O,C_6H_3N_3O_7 1\frac{1}{2}H_2O$ is insoluble in cold water. (*Cp*. Unger, *l.c.* ; Strecker, Annalen, 118, 152 ; Balke, J. pr. Chem. [ii.] 47, 539 ; Neubauer and Kerner, Annalen, 103, 268 ; Wulff, Zeitsch. physiol. Chem. 1893, 17, 468 ; Levene, Biochem. Zeitsch. 1907, 4, 320).

Acyl derivatives. *Acetylguanine*

$$C_5H_4N_5O(C_2H_3O)$$

is crystalline, sparingly soluble in water, alcohol, or ether, and may be heated at 260° without change. *Propionylguanine* $C_5H_4ON_5(C_3H_5O)$ is crystalline, and remains unchanged when heated at 260°. *Benzoylguanine*

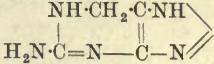
$$C_5H_4ON_5(C_7H_5O)$$

is also crystalline (*cp*. also Bayer & Co., D. R. P. 213711).

Azo derivatives. Guanine and other purine bases that are not substituted in position 7 react with diazobenzenesulphonic acid to form coloured *azo* compounds, in which the ·N : NR group is attached to carbon atom 8. Guanine and *p*-dichlorodiazobenzene chloride yield a dark-red dye, which forms 8-aminoguanine when reduced. The amino compound does not itself couple with diazo compounds, but can be diazotised at 40°, and then yields a violet dye with an alkaline solution of R salt (Burian, Ber. 1904, 37, 696, 708 ; Hans Fischer, Zeitsch. physiol. Chem. 1909, 60, 69). This reaction has been applied by Amatore de Giacomo (Zeitsch. wiss. Mikroscop. 1910, 27, 257) to a microchemical method for demonstrating the presence of guanine in the renal system of birds.

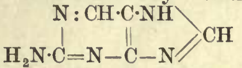
Bromoguanine $C_5H_4N_5OBr$ is a white crystalline powder, almost insoluble in water, alcohol, or ether. It forms crystalline salts with acids, *e.g.* $C_5H_4N_5OBr,HCl$, and also unites with lead or silver to form crystalline compounds, which, when heated with methyl iodide at 100°, yield bromocaffeine. Nitrous acid converts bromoguanine into bromoxanthine (Fischer and Reese, Annalen, 1883, 221, 336).

Deoxyguanine



$$\begin{array}{l} NH{\cdot}CH_2{\cdot}C{\cdot}NH \\ \;\;| \qquad\qquad\;\; \| \\ H_2N{\cdot}C{=}N{-}C{-}N \end{array}\!\!{>}CH$$

is obtained when guanine is electrolytically reduced in 60 p.c. sulphuric acid solution, it crystallises in microscopic needles, melts and decomposes at 204°, and has strongly basic properties combining with atmospheric carbon dioxide. It is oxidised by bromine to 2-*aminopurine*



$$\begin{array}{l} N{:}CH{\cdot}C{\cdot}NH \\ \;\;| \qquad\quad \| \\ H_2N{\cdot}C{=}N{-}C{-}N \end{array}\!\!{>}CH$$

a crystalline base more readily soluble than its isomeride, *adenine*.

Tests. Warm dilute solutions of guanine hydrochloride give with a saturated solution of picric acid, an orange-red crystalline insoluble precipitate ; xanthine and hypoxanthine give a similar reaction in very concentrated solutions only (St. Capranica, Zeitsch. physiol. Chem. 1880, 4, 233).

When guanine nitrate solution is evaporated it leaves a yellow residue, soluble in potassium hydroxide with a yellow colouration. On evaporating the yellow solution to dryness, it affords first a purple, then a violet colouration, and on exposure to air the original colour returns (Brücke, Montash. 1886, 7, 617).

Estimation. The formation of the insoluble picrate has been recommended by Wulff (Zeitsch. physiol. Chem. 17, 468) for the estimation of guanine. M. A. W.

GUANO *v.* FERTILISERS.

GUANOSINE, identical with *Vernin*

$$C_{10}H_{13}O_5N_5,2H_2O,$$

a compound of guanine and *d*-ribose, occurs in certain plants, and forms one of the products of hydrolysis of nucleic acid; it decomposes at 237°, and has $[\alpha]^{20}_{D}-60{\cdot}52°$ (Levene and Jacobs, Ber. 1909, 42, 2469 ; Schulze, Zeitsch. physiol. Chem. 1910, 66, 128 ; Schulze and Trier, *ibid.* 1910, 70, 143).

GUANYLUREA, *Dicyandiamidine*, *v.* DICYANDIAMIDE.

GUARANA (*Uarana*). Guarana is a dried paste prepared from the seeds of the *Paullinia Cupana* (H. B. and K.), a climbing shrub inhabiting the northern and western provinces of Brazil. It is made for the most part by different sections of the Guaranis, a tribe of South American Indians, and probably by different methods. Generally, however, the ground or powdered seeds are moistened by exposure to dew, or by the addition of water, kneaded into a paste, made into cylindrical or globular masses and dried before fires, in chimneys, or by the heat of the sun. These cakes as they appear in commerce are hard, with a rough reddish-brown exterior, and somewhat lighter colour inside. They evolve a chocolate-like odour, and have a bitter astringent taste. In South America guarana is an article of food used much in the same manner as we employ cocoa, and in European medicine it is administered as a nervous stimulant for the relief of certain kinds of headache. For further details as to its source, preparation, and uses *v.* Cooke (Pharm. J. [iii.] 1, 221); Hallawell (*ibid.* [iii.] 3, 773); Squibb (*ibid.* [iii.] 15, 165); Rusby (*ibid.* [iii.] 18, 1050); and Marsden (Annals Trop. Med., 4, 105).

The physiological activity of guarana depends upon the presence of an alkaloid at first termed 'guaranine' but afterwards found to be identical with *caffeine* (*v.* CAFFEINE) (Martius, Kastn. Archiv. 7, 266; Annalen, 36, 93; Berthemot and Dechastelus, J. Pharm. Chim. 26, 518). Stenhouse obtained the alkaloid by extracting powdered guarana with about fifty times its weight of boiling water, and treating the solution when cold with basic lead acetate. A precipitate of alkaloid and salts of lead falls from which repeated extraction with hot water removes the caffeine. The aqueous solution is freed from lead by sulphuretted hydrogen, evaporated to dryness, and the residue treated with hot alcohol. From this solution, on concentration, crystals of the alkaloid are obtained, which may be purified by recrystallisation (Pharm. J. [i.] 16, 212). For other methods *v.* Greene (*ibid.* [iii.] 8, 87), who prefers to extract a mixture of guarana and three times its weight of litharge with boiling water; C. J. Williams (Chem. News, 26, 97), who exhausts a moistened and slowly dried mixture of guarana and lime with benzene; Squibb, (Pharm. J. [iii.] 15, 165) and Bochefontaine and Gusset (Ch. Tech. C. Anzeiger, 4, 322), who treat a mixture of guarana and magnesia with weak alcohol and chloroform respectively. Kremel (Ph. Post. 21, 101) determines the caffeine in guarana by placing 10 grams in a flask with 100 c.c. of 25 p.c. alcohol, noting the total weight, and digesting for 1 or 2 hours at 100°. The weight lost by evaporation is made up with similarly diluted alcohol, and 50 c.c. of the solution, corresponding to 5 grams of guarana, is separated by filtration, mixed with calcium hydroxide, and evaporated to dryness. The residue is extracted with chloroform, from which the alkaloid is obtained in crystals, dried at 100° and weighed. The following percentages of caffeine are selected from published analyses of guarana; 5·10, 5·04 (Stenhouse); 5·05 (Greene); 4·20-5·00 (5 samples, Feemster, Pharm. J. [iii.] 13, 363); 4·5 (B. and Gusset); 3·12, 3·80 (Kremel). Feemster found in the seeds 5·08 p.c. and Peckolt (J. 1866, 709), in the shelled seeds 4·81 p.c.; seed shells 2·44 p.c. and pulp 4·29 p.c. Thoms (Pharm. Centh. 1890, 533) however states that the proportion of caffeine in guarana has been overestimated, and this has been confirmed by Kirmsse (Arch. Pharm. 236, 122), who found in three samples 2·68, 2·97, and 3·10 p.c. respectively.

Besides caffeine, guarana contains gum, starch, an acrid *green fixed oil*, a *concrete volatile oil*, and *tannin* (Fournier, J. Pharm. Chim. 1861, 291). The tannin further examined by Greene (Pharm. J. [iii.] 8, 328) was found to behave towards reagents unlike previously known varieties, and the term *paullinitannic acid* was, therefore, applied to it. It forms a yellowish-white amorphous mass, having an astringent taste. It is easily soluble in water or alcohol. By extraction of the crude tannin with ether, crystals are obtained identical with those of the catechin of Pegu catechu (Kirmsse, *l.c.*). Kremel found 1·3-2·0 p.c. of *ash* consisting chiefly of phosphates.

A specimen of guarana examined by Nierenstein, probably derived from *Paullinia trigonia* (Vell.), was found to contain an alkaloid, *β-guaranine.* This was obtained in the form of small needles, m.p. 217°-219°; after drying, the substance had the composition $C_{40}H_{47}O_{21}N_4$. The guarana contained 4·3 p.c. of tannic acid, which, after purification, was obtained in small colourless needles; m.p. 199°-201°. The tannin, *guaranatannic acid*, appears to resemble the chlorogenic acid obtained from coffee (Gorter, Annalen, 358, 327; 359, 217) rather than catechin, but is not identical with either of these substances (Annals Trop. Med. 4, 115). A. S.

GUAVA. The fruit of *Psidium Guajava* (Linn.). Prinsen-Geerligs (Chem. Zeit. 1897, 21, 719), gives the following data:—

Average wt. in grammes	The fruit consists of			The flesh contains		
	Flesh	Skin	Seeds	Glucose p.c.	Levulose p.c	Sucrose p.c.
65·0	85·0	12·0	3·0	2·0	0·5	1·7

H. I.

GUERNSEY BLUE. A colouring matter belonging to the INDULINE group (*q.v.*).

GUIGNET'S GREEN *v.* CHROMIUM.

GUINEA GREEN B. The sodium salt of the disulphonic acid of diethyl- dibenzyl- diamino- triphenyl- carbinol. Is a dark-green powder resembling Light-green S or Acid Green, *v.* TRIPHENYLMETHANE COLOURING MATTERS.

GULAUCHA, GULOE, and **GILOE.** Indian names for *Tinospora cordifolia* (Miers.). This plant flourishes in India, the drug being sold extensively in the bazaars as a tonic and antiperiodic, in the form of cylindrical pieces 2–5 cm. long and 1–5 cm. in diameter. It is a perennial creeper, climbing to the summits of the highest trees, its branches putting forth roots which, reaching to the ground, initiate a fresh growth. Roots, stems, and leaves are equally in demand as a drug. The Indian pharmacopœia commends its use as a tincture (4–8 c.c. *in die*); as an extract (0·6–1 gram *per diem*) in the form of pills; and as an infusion (1 : 10), of which 60-90 c.c. are to be taken thrice a day. The stems contain *verberin*, an uncrystallisable bitter substance, changed by dilute sulphuric acid into a glucoside, and a bitter kind of starch meal known as 'palo' (J. Soc. Chem. Ind. 6, 49).

GUM RESINS. This article includes the more important members of that group of products which consist essentially of a mixture of gum and resin. They are generally the exudated milky juice of plants dried by spontaneous evaporation. When triturated with water they give more or less perfect emulsions. Compare introduction to article RESINS.

Ammoniacum; *Gummi-resina ammoniacum. Gomme-résine ammoniaque*, Fr.; *Ammoniak gummi-harz*, Ger.

Persian ammoniacum. The ammoniacum of the early Greek physicians came from Africa, and was probably that variety known as African ammoniacum. The drug, which has however since the tenth century been an article of European commerce, is obtained from Persia and neighbouring districts, reaching our markets according to Dymock (Pharm. J. [iii.] 6, 321) now generally by way of Bombay. It is the inspissated juice collected from the stems of the *Dorema Ammoniacum* (D. Don). For plates *v.* Bentl. a. Trim. 131. This plant attains a height of 6–8 feet, and the flow of juice from its stem is caused by punctures made by beetles.

The gum-resin occurs in commerce as brittle grains or tears or roundish lumps, pale yellow externally and waxy milky-white within. It softens readily when warmed. In taste it is bitter and acrid, and it possesses a characteristic odour. Triturated with water it forms an emulsion. A very complete account of the literature of ammoniacum, including the result of the examination of some twenty specimens, will be found in the memoir of Hirschsohn (Pharm. Zeit. 1875, 225; Pharm. J. [iii.] 7, 612, 710, and 770). The sp.gr. of ammoniacum is 1·207, and 3 parts of it dissolve in 4 of alcohol. Hypochlorites, as for example a solution of bleaching powder, impart to it a bright-orange colour, a character that serves to distinguish it from the African variety which is not affected by these reagents. The allied gum-resin galbanum also gives no colour reaction with hypochlorites.

Ammoniacum consists essentially of *resin*, *gum*, and a small proportion of *volatile oil.* The *resin* constitutes 70 p.c. of good specimens of the drug. A sample of ammoniacum examined by Luz (Arch. Pharm. 233, 540) contained 4·5 p.c. of water, 69 p.c. of resin, 22·7 p.c. of substances soluble in water, and 3·5 p.c. of substances, other than resin, insoluble in water. A considerable amount of salicylic acid was present, but no aldehydes or terpenes. Normal butyric and valeric acids were also present largely in combination with a resin alcohol *ammoresinotannol* $C_{18}H_{30}O_3$, a chocolate-brown, tasteless and odourless powder, soluble in alkalis and acids. The resin consists essentially of ammoresinotannol salicylate. It melts at from 35° to 50°, is soluble in alcohol, chloroform, glacial acetic acid, sulphuric acid, and alkalis, partly soluble in carbon disulphide, benzene, and solution of ammonia, and insoluble in light petroleum. Sommer (J. 1859, 573) was unable to obtain umbelliferone from the gum-resin, but resorcinol, $C_6H_4(OH)_2$, and protocatechuic acid, $C_6H_3(OH)_2COOH$, are formed when it is fused with potash (Hlasiwetz and Barth, Annalen, 130, 354). It yields styphnic acid, trinitroresorcinol, $C_6H(NO_2)_3(OH)_2$, when treated with nitric acid (Will and Böttger, Annalen, 58, 269; *cf.* Schwanert, *ibid.* 128, 123).

Ammoniacum gum is partly soluble and partly insoluble in water. The insoluble portion, which constitutes a fourth of the gummy constituents, appears to be identical with the similar bassorin-like gums which occur in asafœtida and galbanum. When treated with 20 p.c. hydrochloric acid, besides humus substances, it yields lævulic acid, and, on oxidising with nitric acid, 31·3 p.c. of mucic acid (equivalent to 41·75 p.c. of galactose), but no saccharic acid. When distilled with dilute hydrochloric acid, it yields 9·35 p.c. furfuraldehyde (equivalent to 16·67 p.c. of arabinose), and when boiled with dilute sulphuric acid reducing sugars are obtained, consisting chiefly of galactose (Frischmuth, Chem. Zentr. 1897, ii. 1078).

Volatile oil of ammoniacum exists only to the extent of ⅓ p.c. Hirschsohn obtained no volatile oil by distillation with water, but light petroleum gave him 1·4–6·7 p.c. of volatile oily residues. Flückiger and Hanbury describe the oil as unlike that of galbanum, possessing in a high degree the odour of the drug, and being free from sulphur.

To test ammoniacum for galbanum resin 5 grams is boiled with 15 grams of strong hydrochloric acid for 15 minutes, 15 c.c. of water is then added, and the liquid filtered through a wetted, double filter; ammonia is added to the clear filtrate when a blue fluorescence reveals the presence of galbanum (Dieterich. Chem. Zentr. 1896, ii. 1137). For method of examination and table giving analytical constants, *see* Dieterich, *l.c.*, and Pharm. Centh. 40, 467.

Ammoniacum is employed in medicine internally as an expectorant, and externally as a constituent of plasters.

African ammoniacum. This, according to Hanbury (Pharm. J. [iii.] 3, 741), is the ammoniacum of Dioscorides and the older writers. It is derived, according to Lindley (Pereira, Mat. Med. 1853, 1715), from the *Ferula tingitana* (Linn.), a plant inhabiting the African coast of the Mediterranean Sea.

African ammoniacum, which is scarcely known in European markets, is described by Pereira as consisting of dark-coloured masses which internally have much the appearance of the Persian variety. The odour is, however, quite distinct. It forms an emulsion with water. Moss examined a specimen in 1873 (Pharm. J. [iii.] 3, 742) which consisted of *resin* 67·76 p.c., *gum* 9·01 p.c., *water* and *volatile oil* 4·29 p.c., and *bassorin* and *insoluble matter* 18·85 p.c. It contained 13·47 p.c. of *ash.* It softened between the fingers more readily than Persian ammoniacum. Similar results were obtained by Hirschsohn By distilling it, however, the last observer isolated *umbelliferone*

$$C_6H_3(OH)\Big<\begin{matrix}CH=CH-CO\\ O\text{————————}\end{matrix}.$$

Goldschmiedt (Ber. 11, 850) announces that by fusion with potash African ammoniacum yields resorcinol, together with *an acid* $C_{10}H_{10}O_6$. This acid is not produced when the Persian drug is similarly treated.

Asafœtida; *Gummi-resina Asafœtida. Asafœtida*, Fr.; *Asant, Stinkasant, Teufelsdreck*, Ger.

Gum-resin asafœtida is the dried juice of the roots of two large herbaceous plants which inhabit Tibet, Afghanistan, Turkestan, and the country from the Sea of Aral to the Persian Gulf. These are the *Ferula Narthex* (Boissier) and the *Ferula fœtida* (Regel). For drawings *v.* Bentl. a. Trim. 126–127, and Holmes (Pharm. J. [3] 19, 21, 41, and 365). Details of the mode of preparing the roots and of collecting the dried exudation are given by Flückiger and Hanbury (Flück. and Hanb. 316) and by Pereira (Mat. Med. 1853, 2, 1704). It is certain that asafœtida was known to the Arabian writers of the tenth century, and there is reason to believe that a knowledge of the drug is far more ancient.

Supplies of asafœtida are now almost entirely derived by way of India from Afghanistan. It occurs as tears more or less agglutinated, and sometimes as a honey-like mass. It is often largely mixed with earthy matter. A characteristic property of the drug is that when broken the milky white surface changes gradually to a pink, which passes into a brown hue. Touched with nitric acid (sp.gr. 1·2) it gives a green colour. With water it forms an emulsion. The tears are brittle, and may be powdered when cold. Asafœtida has a powerful alliaceous odour and an acrid bitter alliaceous taste.

The chief constituents of asafœtida are *resin, gum,* and *volatile oil.* For results of early investigations *v.* Gm. 17, 398. The analysis of Pelletier (Bull. Pharm. 3, 556) shows that the resin amounts to 65·0 p.c., the soluble gum 19·44 p.c., the insoluble gum 11·66 p.c., and the volatile oil 3·6 p.c., or, according to Flückiger and Hanbury, 6–9 p.c. The resin is only partly soluble in ether and chloroform, but is entirely dissolved without alteration by concentrated nitric acid (*cf.* Johnston, Phil. Trans. 1840, 354). Hlasiwetz and Barth (Annalen, 138, 64) discovered in the resin *ferulic acid,* the methylphenolic ether of hydroxycinnamic or caffeic acid,

$$C_6H_3(CH{:}CH{\cdot}COOH)(OCH_3)(OH)1:3:4$$

An alcoholic solution of asafœtida is precipitated by an alcoholic solution of lead acetate, and from the insoluble lead salt the ferulic acid is regenerated. It consists of needles melting at 168°–169° (Tiemann, Ber. 9, 416). Vanillin was shown to be present in asafœtida by Schmidt (Arch. Pharm. [3] 24, 534).

Pure drops of *Asafœtida amygdaloides* examined by Polásek (Arch. Pharm. 235, 125), gave the following results: resin, soluble in ether, *asaresinotannol ferulate,* 61·40; resin, insoluble in ether, free *asaresinotannol,* 0·60; gum, 25·1; essential oil, 6·7; vanillin, 0·06; ferulic acid, 1·28; moisture, 2·36 p.c. On hydrolysis with potassium carbonate, the soluble resin yields asaresinotannol and ferulic acid; with sulphuric acid, however, it is hydrolysed into the same tannol and umbelliferone. Asaresinotannol is a brownish-yellow amorphous substance, and has the composition $C_{24}H_{34}O_5$.

When asafœtida resin is distilled alone, *variously tinted oils* are obtained, with $\frac{1}{4}$ p.c. of umbelliferone (Sommer J. 1859, 573). Fused with potash, resorcinol and protocatechuic acid are formed (Hlasiwetz and Barth), and treated with nitric acid it yields trinitroresorcinol or styphnic acid (Will and Boettger, Annalen, 58, 269).

The gum of asafœtida consists of two portions, the one soluble and the other insoluble in water. The volatile oil is described by Flückiger and Hanbury as of a light-yellow colour with the odour of asafœtida. The taste is at first mild and then irritating, but it does not stimulate when applied to the skin like mustard oil. The oil is neutral, but becomes acid by exposure to the air, at the same time evolving sulphuretted hydrogen. By fractional distillation of the oil under reduced pressure, Semmler (Ber. 23, 3530; 24, 78) finds that it contains two *terpenes* $C_{10}H_{16}$; a *substance* $(C_{10}H_{16}O)_x$, which gives a *sesquiterpene* $C_{15}H_{24}$ when acted upon by sodium; an *oil* $C_7H_{14}S_2$ boiling at 210°–212° with slight decomposition; and an *oil* $C_{11}H_{20}S_2$, which decomposes on distillation under the ordinary pressure with evolution of most repulsive smelling gases.

Asafœtida is used in medicine as a nervous stimulant and antispasmodic, and in the East as a condiment.

Other varieties of asafœtida. The *Hing* used by the natives of Bombay is a variety of asafœtida. It is derived from *Ferula alliacea* (Boissier). It is more repulsive, and contains a larger proportion of volatile oil than asafœtida (Flückiger, Pharm. J. [iii.] 6, 401; Flück. a. Hanb. 319).

Bdellium.

Indian Bdellium; False Myrrh; Bdellium. This is the bdellium of the Bible, and is now used chiefly as an adulterant of myrrh. It is the product of *Balsamodendron Mukul* (Hooker) and, according to Dymock, also of the *B. Roxburgii* (Arnott) (*cf.* Pharm. J. [iii.] 6, 661). Both are indigenous to India, but grow perhaps also in Southern Arabia. The gum-resin breaks with a flat conchoidal fracture, and though somewhat darker in colour, it resembles myrrh in appearance. It may be distinguished from myrrh by its not giving the violet colour reaction (*v. Myrrh*). (For analytical constants of bdellium *v.* Dieterich Pharm. Centr. 40, 467.)

African Bdellium. A more highly esteemed bdellium, the product of *Balsamodendron africanum* (Arnott), a shrub indigenous to West Africa. It is used in France as a constituent of plasters. In fracture and other respects it resembles myrrh, but it does not give the violet colour reaction (*v. Myrrh*). African bdellium was analysed by Pelletier (Ann. Chim. Phys. [ii.] 80, 38), who found *resin* 59 p.c., *soluble gum* 9·2 p.c., *insoluble gum* 30·6 p.c., *volatile oil* and loss 1·2 p.c. The resin was further examined by Johnston (Phil. Trans. 1840, 368). *Cf.* Bley and Diesel (Arch. Pharm. [ii.] 43, 304).

Euphorbium. *Gomme-résine d'Euphorbe,* Fr.; *Euphorbium,* Ger. This extremely acrid drug has been known since the time of Dioscorides, but it is now very seldom employed in medicine. It is the inspissated milky juice of the *Euphorbia resinifera* (Berg), a cactus-like plant inhabiting Morocco and neighbouring districts of Northern Africa. A drawing is given by Bentl. a. Trim. 240. Euphorbium consists of irregular masses of a waxy-yellow or brown appearance, often inclosing spines and other fragments of the plant. It has a slight aromatic odour and an extremely acrid taste, its dust causing violent and even dangerous irritation to the nose or throat.

Flückiger (Flück. and Hanb. 560) found a selected specimen to consist of *amorphous resin,* 38 p.c.; *euphorbon,* 22 p.c.; *mucilage,* 18 p.c.; *malate of calcium, sodium,* &c., 12 p.c.; *mineral compounds,* 10 p.c. It contains no volatile oil.

Examined by Tschirch and Paul (Arch. Pharm. 234, 249) 100 parts of the drug were found to contain euphorbic acid, 0·7; euphorbone, 40; amorphous resins, 21; malates, 25; carbohydrate, 2; impurities and loss, 11. *Euphorbic acid,* which is extracted from an ethereal solution of the resin by 1 p.c. aqueous ammonium carbonate, is amorphous, has the m.p. 107°–108° and the composition $C_{24}H_{30}O_6$. *Euphorbone* $C_{30}H_{48}O$ is best obtained from the drug by extraction with light petroleum and crystallisation first from alcohol and then repeatedly from acetone. It melts at 115°–116°.

Euphorboresene $C_{33}H_{48}O_4$ remains as an amorphous mass, m.p. 74°–76°, after steam distillation for some weeks of the resin freed from euphorbone and mixed with aqueous potassium hydroxide. The residual alkaline liquid, on being acidified, gives an amorphous precipitate of *a-euphorboresene* $C_{28}H_{48}O$, which melts at about 75°, and is now insoluble in dilute aqueous potassium hydroxide. From an aqueous extract of the drug calcium malate was isolated; also a dextrorotatory carbohydrate precipitated by alcohol, and another, possibly a pentosan, which remained dissolved.

When a filtered light petroleum extract of euphorbium resin is floated on a solution of one drop of concentrated sulphuric acid in 20 c.c. of water, a very stable blood-red layer is formed at the surface where the two liquids touch; on shaking, the whole of the acid liquid becomes red, and this colour only slowly changes to brown. This reaction may be used for purposes of identification; an extract of the most suitable concentration is obtained from 0·1 gram of euphorbium and 10 c.c. of light petroleum.

Euphorbium is now used only in veterinary medicine. Applied externally to the human subject it is irritant and vesicating, and internally administered it causes violent vomiting and purging. It is said to be an efficient preservative of iron and steel against corrosion (Year Book Pharm. 1880, 344).

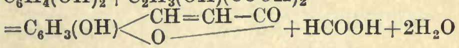
Galbanum; *Gummi-resina Galbanum. Galbanum*, Fr.; *Mutterharz*, Ger. Galbanum has entered into the constitution of incense, and has been employed in medicine from the earliest times. It was used by the Israelites, and was well known to Hippocrates, Theophrastus, and Dioscorides, also to the Arabians, and still retains its place in the official pharmacopœias of Europe and the United States. But notwithstanding its antiquity, the precise plant from which galbanum is derived still remains uncertain. It is most probably obtained from the *Ferula galbaniflua* (Boissier and Buhse), and perhaps from other allied species of *Ferula*, natives of Persia. For figure *v.* Bentl. a. Trim. 128 (*cf.* Holmes, Pharm. J. [iii.] 19, 365).

The gum-resin occurs in commerce in drops or tears, usually adhering into solid masses. In colour it exhibits various shades of light yellowish-brown, sometimes tinted with green. The odour of galbanum is aromatic, and the taste unpleasant, bitter, and alliaceous. Flückiger and Hanbury (Flück. a. Hanb. 323) note that when galbanum is warmed with concentrated hydrochloric acid a red colour is developed, which on the careful addition of spirit of wine, turns violet or bluish. Asafœtida treated in the same manner assumes a dingy colour, whilst ammoniacum gives no colour change at all. Further details of the characters of galbanum and its behaviour towards reagents are given in an elaborate memoir by Hirschsohn (Pharm. Zeit. 1875, 225; Pharm. J. [iii.] 7, 369, 389, 429, 531, and 571). This observer divides galbanum of commerce, according to its physical character, into three varieties, one coming from Persia and two from the Levant, or, according to its behaviour towards reagents, into four sorts—one from Persia and three from the Levant.

Galbanum resin examined by Conrady (Arch. Pharm. 232, 98) was found to contain 9·5 p.c. of ethereal oil; 63·5 p.c. of a resin soluble in alcohol; and 27·0 p.c. of impurities and gum. The pure resin obtained from the commercial product by extraction with alcohol and subsequent treatment with sodium salicylate contains 20 p.c. of combined umbelliferone; 50 p.c. of galbaresinotannol; and 0·25 p.c. of free umbelliferone. The resin which most probably consists of a galbaresinotannylic salt of umbelliferone is best hydrolysed by sulphuric acid since umbelliferone is unattacked by this reagent. *Galbaresinotannol* on analysis gives numbers agreeing with the formula $C_{18}H_{30}O_3$; on distillation with phosphoric anhydride it yields a hydrocarbon $C_{15}H_{20}$ and, on oxidation with nitric acid, camphoric and camphoronic acids. The volatile oil is obtained by distillation with water or by extraction with light petroleum. According to Flückiger and Hanbury, the crude oil possesses an aromatic taste and is dextrorotatory. On the addition of bromine to the oil extracted from Persian galbanum a red to violet or blue colour appears. The oil consists partly of a *hydrocarbon* $C_{10}H_{16}$ which gives a crystalline hydrochloride $C_{10}H_{16},HCl$. The chief part, however, is a mixture of heavier hydrocarbons (*cf.* Moessmer, Annalen, 119, 237).

When galbanum resin is distilled a small quantity of umbelliferone is obtained (Sommer, J. 1859, 573). This compound is now known to be a product of the distillation of many other resins or gum-resins, especially those of the *Umbelliferæ*. Galbanum yields 0·83 p.c., sagapenum 0·32 p.c., asafœtida 0·28 p.c. Synthetically, umbelliferone may be produced, as pointed out by Pechmann (Ber. 17, 932), by acting upon a mixture of resorcinol and malic acid with dehydrating agents such as sulphuric acid, thus:

$$C_6H_4(OH)_2+C_2H_3(OH)(COOH)_2$$



$$=C_6H_3(OH)\begin{cases}CH=CH-CO\\O\end{cases}+HCOOH+2H_2O$$

Another product of the destructive distillation of galbanum resin is a thick *brilliant blue oil.* The oil deposits in the cold crystals of umbelliferone. It has a bitter acrid taste and aromatic odour. Kachler (Ber. 4, 36) separated it into a *colourless hydrocarbon* $C_{10}H_{16}$ boiling at 240°, and a *blue oil* $C_{10}H_{16}O$ which boiled at 289°. The flowers of the wild chamomile *Matricaria Chamomilla* (Linn.) yield a blue oil very similar to that obtained from galbanum. Both oils are converted by potassium into the hydrocarbon $C_{10}H_{16}$, which on the addition of bromine vapour gives the blue colour reaction. Hlasiwetz and Barth (Annalen, 130, 354) have shown that by fusing galbanum resin with potash as much as 6 p.c. of resorcinol is formed (*cf.* Goldschmied, Ber. 11, 850); and by treatment with nitric acid, Will and Boettger (Annalen, 58, 269) obtained styphnic acid (*cf.* Schwanert, Annalen, 128, 123).

Hirschsohn in his experiments, after removal of the volatile oil and resin and a little saccharine and astringent matter, by extraction of galbanum with light petroleum, ether, and 85 p.c. alcohol, successively, treats the residue with water to obtain the gum. The yield was 6–17 p.c. The sugar obtained from this gum by the action of dilute acids is optically distinct from that produced in the same way from gum arabic.

Galbanum is administered in medicine internally as an expectorant, and externally it is applied in the form of plasters.

A table of the acidity, ether, and saponification numbers of galbanum resin is given by Dieterich (Pharm. Centh. 40, 467).

Gamboge. *Cambogia, Cadie Gum, Gummi Gambogia, Gummi Gutti. Gomme Gutte*, Fr.; *Gutti, Gummigutt*, Ger. This beautiful orange-red gum-resin comes to us from Camboja, Siam, and Cochin China, where it is the product of a laurel-like tree, the *Garcinia Hanburyi* (Hook.); *v.* Bentl. a. Trim. 33. Gamboge was known to the Chinese in the thirteenth century, but it was not until the seventeenth century that it appeared in European markets. For the purpose of collecting it the trees are incised, and sections of bamboo are attached to collect the milky juice, which, hardening by evaporation, takes the cylindrical shape of the receiving vessel. Gamboge as it occurs in commerce is brittle, and may be powdered readily. In presence of water it forms at once a yellow emulsion. It has a disagreeable and acrid taste.

Among the earlier investigators who analysed gamboge are Braconnot (Ann. Chim. Phys. [i.] 68, 33), John (Chem. Schriften, 4, 193), Unverdorben (N. Jour. Trommsdorf. 8, 1, and 60), Christison (Annalen, 23, 185), Johnston (Phil. Trans. 1839, 281), and Büchner (Annalen, 45, 72). Costelo (Amer. J. Pharm. 1879, 174), finds the *resin* to vary from 68 to 79 p.c., and the *gum* from 19 to 27 p.c. (*cf.* Hurst, Pharm. J. [iii.] 19, 761). The gum is extracted by water. Its solution, like arabic, is not precipitated by neutral lead acetate, but its behaviour towards other reagents shows it to be a different gum. By the action of dilute acids it yields a *non-fermentable sugar*, and when oxidised by nitric acid, mucic acid $C_4H_4(OH)_4(COOH)_2$ is formed.

Alcohol dissolves the resin. It combines with bases, and is called by Johnston *gambodic acid.* By fusion with potash, Hlasiwetz and Barth (Annalen, 138, 68) obtained a number of interesting products. Besides several acids of the fatty series, these observers isolated phloroglucinol $C_6H_3(OH)_3(1:3:5)$; pyrotartaric acid $CH_3{\cdot}CH(COOH)CH_2{\cdot}COOH$; and *isomesidic, isouvitic*, or *isovitinic acid* $C_6H_4{\cdot}CH_2(COOH)COOH$. This last-mentioned acid has since been produced by the action of hot dilute alkali on benzylcyanide-*o*-carboxylic acid $CN{\cdot}CH_2{\cdot}C_6H_4{\cdot}COOH$, which converts the cyanogen into a carboxylic group (Wislicenus, Annalen, 233, 106).

For the detection of gamboge in mixtures, *v.* Hirschsohn (Pharm. Zeit. 24, 609). In medicine gamboge is employed as a drastic purgative, usually in combination with other substances. It is also an important colouring agent.

Ivy gum resin. *Gummi-resina Hederæ.* In Southern Europe and in the Levant a gum-resin is obtained from the old trunks of the common ivy, *Hedera Helix* (Linn.). It consists of irregular masses of a reddish or yellowish-brown colour externally, but showing a deep red by transmitted light. The taste is bitter and acrid, but when heated it evolves a balsamic odour. Pelletier (Bull. Pharm. 4, 504) found the gum-resin to consist of *resin* 23 p.c., *gum* 7 p.c., and 70 p.c. of woody fibre. Examined by Sommer (Arch. Pharm. [ii.] 98, 11) it gave no umbelliferone.

Besides the gum-resin the leaves, berries, and the wood itself of ivy have been used in medicine and they have been examined by chemists. Hartsen (J. 1875, 827) found ivy leaves to contain a glucoside allied to saponin, and this was afterwards studied by Davies and Hutchinson (Pharm. J [iii.] 7, 275), Davies (*ibid.* [iii.] 8, 205), Kingzett (*ibid.* [iii.] 8, 206), Vernet (J. 1881, 91), Vincent (Bull. Soc. chim. 35, 231), and Block (Arch. Pharm. [iii.] 26, 953). Most of these observers obtained the glucoside from ivy berries. Davies and Hutchinson regard it as identical with the *hederic acid* which, together with *hederotannic acid*, Posselt found in ivy berries (Annalen, 69, 62).

Hederic acid or *ivy glucoside* $C_{32}H_{54}O_{11}$ is deposited in needles from the alcoholic extract of ivy berries that have been previously exhausted with ether (D. and H.), or the berries may be exhausted with alcohol, and the residue, after the alcohol has been removed by distillation, washed in the cold with benzene and extracted with hot acetone. On concentrating the solution a crystalline mass is obtained which is purified by recrystallisation from alcohol (Vernet; Vincent). The glucoside forms silky needles which melt at 233°. It is insoluble in water, chloroform, or light petroleum, is slightly soluble in cold acetone, benzene, or ether, and very soluble in hot alcohol and alkalis. It is inodorous, but possesses the taste of the berries. By the action of dilute acids it breaks up into a crystalline *compound* $C_{20}H_{42}O_6$ (?), which melts at 278°–280° and a non-fermentable *sugar* which reduces Fehling's solution.

Houdas (Compt. rend. 128, 1463) has separated from ivy a glucoside *hederin* $C_{64}H_{104}O_{19}$, which crystallises from alcohol in thin needles, melting at 248°. When hydrolysed with dilute sulphuric acid hederin gives rise to an insoluble product hederidin, and to two sugars hederose and rhamnose. *Hederidin* $C_{26}H_{40}O_4$ crystallises from boiling alcohol in sparkling prisms, which melt at 324°, and sublime undecomposed. *Hederose* $C_6H_{12}O_6$ crystallises in shining needles, and is very soluble in water or boiling alcohol. It melts at 155°, and is dextrorotatory.

The physiological action of ivy and hederin has been studied by Joanin (Compt. rend. 128, 1476).

Myrrh. *Myrrha*; *Heerabol Myrrh*; *Gummi-resina Myrrha. Myrrhe*, Fr.; *Myrrhe*, Ger. Together with olibanum, myrrh has been used as a constituent of incense from the earliest times. It is mentioned in Genesis and in other places in the Bible. The Egyptians employed it not only in fumigations, but also in embalming and in medicine. It has retained its place down to the present day, and is included in all the pharmacopœias. Myrrh is the spontaneous gum-resinous exudate of the shrubs or small trees of the *Balsamodendron Myrrha* (Nees), an inhabitant of the Somali coast of the Gulf of Aden and of the Red Sea coast of Arabia (Trimen, Pharm. J. [iii.] 9, 893). A drawing of the tree is given by Bentl. a. Trim. 60. The exudate is allowed to harden on the tree before collection. It occurs in irregular-shaped masses of a red-brown colour and dusty appearance. When cold it is brittle, and breaks with an uneven, waxy, oily-looking fracture, often exhibiting lighter-coloured semicircular striations. With water it readily yields an emulsion. The odour of myrrh is fragrant and agreeable, and the taste bitter, aromatic, and acrid.

The chief constituents of myrrh are *gum*, *resin*, and *volatile oil.* The relative proportions, even in the case of true myrrh, vary greatly in different specimens. Generally the gum constitutes 40–65 p.c., the resin 25–40 p.c., and the volatile oil is said to reach 4·4 p.c. Flückiger and Hanbury (Flück. a. Hanb. 143) found 27 p.c. of resin in a good specimen, and Köhler (Arch. Pharm. 228, 291) found 7–8 p.c. of volatile oil. Brückner's analysis (Neues Rep. Pharm. 16, 76) gave: soluble in water, gum, 67·76 p.c.; resin soluble in carbon disulphide, 14·06 p.c.; resin soluble in ether, 12·57 p.c.; resin insoluble in ether, 4·81 p.c.; substances soluble in diluted alcohol, 0·43 p.c.; insoluble (sand, bark, &c.), 0·38 p.c.

Myrrh resin is soluble in alcohol or chloroform, but it is only partly soluble in ether, carbon disulphide, or alkalis. According to Köhler (*l.c.*) it is a mixture of several resins, the greater portion of which is a soft resin $C_{26}H_{34}O_5$ soluble in ether. There are also present two dibasic acids $C_{13}H_{16}O_{18}$ and $C_{26}H_{32}O_9$ respectively.

Tschirch and Bergmann (Arch. Pharm. 243, 641) have made an examination of *Myrrha electa*, which is the true or Heerabol myrrh obtained by sorting from the other resins mixed with which myrrh is imported into the United Kingdom. By extraction of the ethereal solution with 1 p.c. aqueous potassium hydroxide two amorphous greyish-yellow neutral substances were obtained: *α-heerabo-myrrhol* $C_{17}H_{24}O_5$, m.p. 158°–165°, which is precipitated from alcoholic solution by lead acetate, and *β-heerabo-myrrhol* $C_{19}H_{28}O_4$, m.p. 116°–124°, not precipitated in this way. From the residue insoluble in ether, alcohol extracted two brown amorphous substances, *α-heerabo-myrrholol* $C_{15}H_{22}O_7$ or $C_{30}H_{44}O_{14}$, m.p. 207°–220°, and *β-heerabo-myrrholol* $C_{29}H_{36}O_{10}$, m.p. 205°–213°. These differ in their behaviour towards lead acetate. The portion of the resin soluble in ether but insoluble in alkali consists of *heeraboresene* $C_{29}H_{40}O_4$, m.p. 98°–104°. From the portion of the resin of *Myrrha electa*, insoluble in light petroleum, but soluble in ether, von Friedrichs (Arch. Pharm. 245, 427) isolated the following compounds: *α-commiphoric acid* $C_{14}H_{18}O_4$, m.p. 201°–203°; *β-commiphoric acid* $C_{14}H_{18}O_4$, m.p. 205°; *γ-commiphoric acid* $C_{17}H_{22}O_5$, m.p. 169°–172°; *α-herrabo-myrrhol* $C_{18}H_{26}O_5$, m.p. 248°–250°; *β-heerabo-myrrhol* $C_{20}H_{26}O_6$, m.p. 168°; *commiphorinic acid* $C_{28}H_{36}O_8$, m.p. 135°; a yellow *alcohol* $C_{14}H_{22}O_2$, b.p. 264°; and *herraboresene* $C_{42}H_{56}O_8$, m.p. 100°–102°; and from the portion of the resin insoluble both in light petroleum or ether, *α-heerabo-myrrhololic acid* $C_{15}H_{22}O_7$, m.p. 220°–225°, and *β-heerabo-myrrhololic acid* $C_{25}H_{32}O_6$, m.p. 187°–190°.

Myrrh resin gives a violet colour when a fragment moistened with alcohol is treated with nitric acid, but the colour is not so marked as in the case of galbanum (*cf.* Ruickholdt, Arch. Pharm. [ii.] 41, 1; Held, Annalen, 63, 59; Hager, Pharm. Centh. 1865, 58). Distilled, it gives no umbelliferone, but by fusion with potash Hlasiwetz and Barth (Annalen, 139, 78) obtained small quantities of catechol and protocatechuic acid. The property of giving a violet colour when oxidised by nitric acid, or better, by bromine vapour, is confined to that resin which dissolves in carbon disulphide, and which, according to Brückner, contains 75·6 p.c. of carbon.

The gum of myrrh on analysis gives numbers agreeing with the formula $C_6H_{10}O_5$. On treatment with hydrochloric acid it yields levulic acid (Köhler). It contains an enzyme which has the properties of an oxydase (Tschirch and Bergman; von Friedrichs).

The quantity of volatile oil in myrrh varies very greatly. The oil, according to Ruickholdt, has the composition $C_{10}H_{14}O$. Gladstone (Chem. Soc. Trans. 17, 11) describes it as a viscid brownish-green oil that, boiling at 266°, gave an oxidised product. Its sp.gr. was 1·0189. The oil prepared by Flückiger (*cf.* Ber. 9, 471) was lighter than water, the sp.gr. at 13° being 0·988, and the boiling-point 270°–290°. Redistilled in a current of carbon dioxide it passed over between 262° and 263°. After redistillation the oil, on addition of a drop of nitric acid, gave after an hour or two a permanent violet hue, but this is better observed when bromine vapour is applied to a solution of the crude oil in carbon disulphide.

Samples of the oil examined by Lewinsohn (Arch. Pharm. 244, 412) contained cuminaldehyde up to 1 p.c. and small quantities of eugenol and *m*-cresol, and of acetic and palmitic acids. By distillation over sodium, pinene, dipentene, and limonene were isolated, and in one commercial sample, a fourth *terpene* $C_{10}H_{16}$, b.p. 78°–80° (20 mm.). Two other possibly new *sesquiterpenes* $C_{15}H_{24}$, b.p. 151°–154° (15 mm.) and b.p. 163°–168° (12 mm.) respectively, were obtained from two other samples of the oil. Von Friedrichs (*l.c.*) obtained from the essential oil, formic and acetic acids; a crystalline *acid*, m.p. 159°; *m*-cresol; cuminaldehyde and cinnamaldehyde; crystalline monobasic *myrrholic acid* $C_{17}H_{22}O_5$, m.p. 236°; and the sesquiterpene *heerabolene* $C_{15}H_{24}$, b.p. 130°–136° (16 mm.).

According to Flückiger, the *bitter constituent* of myrrh is a glucoside. v. Bolton (Zeitsch. Elektrochem. 14, 211), by extracting myrrh with alcohol, evaporating to dryness and then extracting with water, obtained a substance *burseracin*, which forms 1·5–2 p.c. of the original drug. It is a yellow hygroscopic powder, m.p. 78°, and has the composition $C_{20}H_{28}O_8$. It is not a glucoside. On treatment with hydrogen peroxide a compound is obtained, which appears to be radioactive.

Myrrh is a reputed stimulant and tonic, but its employment in medicine depends chiefly on its aromatic properties.

Other varieties of myrrh. Several gum-resins more or less resembling true myrrh are occasionally found in commerce. Two are described by Flückiger and Hanbury. One of these, often incorrectly called *East Indian myrrh*, but which is really an African drug, is known as *bisabol* or *hebbakhade.* In outward appearance it is very similar to true myrrh, but it is more acrid, and its resin, soluble in carbon disulphide, gives no violet colour with bromine vapour. An analysis of bisabol-myrrh from Somaliland gave the following results: gum soluble in water, 22·1; gum soluble in soda, 29·85; resin, 21·5; bitter principles, 1·5; volatile oil, 7·8; water, 3·17; and inorganic matter, &c., 13·4 p.c. (Tucholka, Arch. Pharm. 235, 289).

The other variety is *Arabian myrrh.* It is collected in Southern Arabia east of Aden, and is probably the product of a distinct species (Hanbury). It is very nearly related to true myrrh in appearance, and some specimens give the violet colour reaction.

Olibanum. *Frankincense*; *Gummi-resina Olibanum*; *Thus masculum. Encens*, Fr.; *Weirauch*, Ger. Olibanum or frankincense has been the favourite basis of incense from the earliest times. It is frequently referred to in the Bible, and the Egyptians employed it for fumigations and for embalming.

Duemichen, in his book on the Paintings of the Temple of Dayr el Báhri in Upper Egypt, which represent the traffic between Egypt and a land called Punt as early as the seventeenth century B.C., has shown that these paintings include, not only representations of olibanum in bags, but boxes or tubs containing living olibanum trees. Tribute offerings of frankincense were common throughout the ancient world. At the present day the incense of the Roman and Greek Chruches is largely composed of olibanum.

The gum-resin is the dried exudated juice of several species of *Boswellia.* These trees, the fragrance of which is noticeable even at a distance, inhabit Eastern Africa, near Cape Gardafui, and the southern coast of Arabia. They were studied by Birdwood (Trans. Linn. Soc. 27, 111, 148). One of them is figured by Bentl. and Trim. 58 (Flück. a. Hanb. 134). Olibanum is a solid which softens in the mouth, and has a slightly terebinthinous, not disagreeable, taste. It consists of tears of various shapes, generally detached. The odour, especially on heating, is pleasantly aromatic. It has a pale yellow or brown colour, and the larger fragments are more or less milky and translucent. Triturated with cold water it yields an emulsion.

The chief constituents of frankincense are *resin*, *gum*, and *volatile oil.* The oil is obtained by distillation; alcohol dissolves the resin and water the gum. Braconnot (Ann. Chim. Phys. [i.] 68, 60) found resin 56 p.c., soluble gum 30 p.c., insoluble gum 6 p.c., and volatile oil 8 p.c.; whilst the analysis of Kurbatow gave resin 72 p.c., gum 21 p.c., and volatile oil 7 p.c. (Zeitsch. Chem. [ii.] 7, 201). From the resin Tschirch and Halbey (Arch. Pharm. 236, 487) obtained *boswellic acid* $C_{32}H_{52}O_4$, a white powder, m.p. 150°, which shows little tendency to crystallise. The resin probably contains boswellic acid in the form of an ethereal salt, and also *olibano-resene* $(C_{14}H_{22}O)_n$, a powder insoluble in sodium hydroxide and melting at 62°. According to Kurbatow, an *oil* boiling at 360° is obtained when the resin is subjected to destructive distillation. No umbelliferone is obtained (Sommer, J. 1859, 573).

The gum of olibanum behaves towards reagents exactly as gum arabic (Heckmeijer, J. 1858, 482).

Volatile oil of olibanum, examined by Stenhouse (Annalen, 35, 306), boils at 179·4°, and has a sp.gr. of 0·866. This oil Kurbatow has succeeded in separating into a hydrocarbon $C_{10}H_{16}$ *olibene*, which boils at 156°–158°, has the odour of turpentine, and the sp.gr. at 12° of 0·863, and an *oxidised oil* boiling above 175°. Olibene is soluble in alcohol and ether, and gives a crystalline hydrochloride $C_{10}H_{16},HCl$, which melts at 127°. Wallach (Annalen, 252, 94) finds that olibene is identical with *lævopinene*, and that *dipentene* is contained in the higher boiling fractions. At the present day olibanum is seldom employed in medicine. It is used almost exclusively in the preparation of incense.

Opopanax. A bright orange-brown gum-resin occurring in hard nodular or earthy-looking lumps. It was used by Hippocrates, and several varieties were known to Theophrastus and Dioscorides. It is said to be derived from the *Opopanax Chironium* (Koch), a native of Southern Europe.

Opopanax consists essentially of *resin*, *gum*, and a little *volatile oil.* The most recent examination of opopanax is that by Tschirch and Knitl (Arch. Pharm. 237, 256) who found a specimen from the *Opopanax Chironium* (Koch) to contain: resin soluble in ether 51·8, resin insoluble in ether 1·90, gum 33·8, volatile oil 8·3, free ferulic acid 0·22, vanillin 0·0027, moisture 2·0, bassorin and plant remains 2·0 p.c. The resin soluble in ether is the ferulate of a resinotannol, and on hydrolysis ferulic acid and *oporesinotannol* are obtained. The latter is a light brown powder having the composition $C_{12}H_{13}O_2(OH)$. The resin of opopanax insoluble in ether consists of free oporesinotannol. The purified gum contained 3·53 p.c. of ash, and an arabic acid was prepared from it containing C 43·17, H 6·42 p.c. From the volatile oil a product was obtained in needles, which melted at 133°-134° and had the composition C 66·6, H 2·7 p.c. This substance is named *oponal.*

A sample of opopanax examined by Baur (Arch. Pharm. 233, 209) contained plant fragments which showed it to be derived from some member of the genus *Balsamodendron*, order *Burseraceæ*, probably from *B. Kafal* [*Commiphora abyssinica* (Engl.)]. It contained 19 parts p.c. of resin, 6·5 of ethereal oil, and 70 of gum, besides plant fragments.

The resin of opopanax gives no umbelliferone when distilled. When fused with potash, Hlasiwetz and Barth found the resin to yield catechol, together with protocatechuic acid (Annalen, 139, 78). The substance formerly known by the name of opopanax was altogether different in odour and appearance from the resin described above. It was probably derived from a Persian member of the *Umbelliferæ* (Powell, Economic Products of the Punjab, 1, 402; Flück. a. Hanb. 327). This resin differs from the usual variety by yielding umbelliferone on dry distillation, also the volatile oil obtained from it contains sulphur.

Opopanax was highly esteemed in ancient medicine, but it has now gone entirely out of use.

Sagapenum. This gum-resin, which, like galbanum and asafœtida, has been known from the earliest times, is now seldom met with. Its botanical origin is not known with certainty.

Flückiger and Hanbury (Flück. a. Hanb. 324) describe sagapenum as consisting of a tough, softish mass of closely agglutinated tears. The tears are brownish, not milkwhite like asafœtida, and when broken do not acquire a pink tint, and are without alliaceous odour. The specimen of sagapenum examined by these observers contained no sulphur, but yielded umbelliferone. Seven out of the eight specimens examined by Hirschsohn (Pharm. Zeit. 1875, 225; Pharm. J. [iii.] 7, 771), however, contained sulphur, and this character served to distinguish sagapenum from ammoniacum, galbanum, and opopanax. Umbelliferone was always obtained. Resorcinol is formed when sagapenum is fused with potash (Hlasiwetz and Barth, Annalen, 139, 78), and styphnic acid by treatment with nitric acid (Boettger and Will, *ibid.* 58, 269). When some specimens of sagapenum are immersed in hydrochloric acid (sp.gr. 1·13) they acquire a permanent blue colour, but others do not exhibit this behaviour.

A specimen of sagapenum investigated by Hohenadel (Arch. Pharm. 233, 259) was found on examination of the plant fragments contained in the drug to have been obtained from the stems and fruits of a Persian species of *Ferula*, order *Umbelliferæ*. It contained resin, 56·8; volatile oil, 5·8; water, 3·5; gum, 23·3; and impurities, 10·6 p.c. The purified resin is yellowish-brown, and melts at 74°–76°; when hydrolysed by boiling with sulphuric acid it is decomposed into umbelliferone and *sagaresinotannol*, a brown substance having the composition $C_{24}H_{28}O_5$. The 56·8 parts of purified resin contained 40 of sagaresinotannol, 15·7 of combined, and 0·11–0·15 of free umbelliferone. The ethereal oil contains 9·7 p.c. of sulphur.

Scammony. *Scammonée*, Fr.; *Scammonium*, Ger. A purgative gum-resin derived from the *Convolvulus Scammonia* (Linn.), a native of Greece, Asia Minor, Syria, and Southern Russia.

The gum resin obtained by incision from the living root, and known as scammony or 'virgin scammony,' has been used medicinally for many centuries. The value of this drug depends on its resinous constituent, which, however, is now usually prepared by extracting the dried scammony root with alcohol, and precipitating the resin from the solution with water; but the resin from both of these sources appears to have been displaced in the market, to a large extent, by the resin obtained from the root of *Ipomoea orizabensis* (Ledanois), commonly known as 'Mexican scammony root,' and until lately these two resins have usually been considered to be chemically identical.

An investigation of scammony root and scammony made by Power and Rogerson (Chem. Soc. Trans. 1912, 101, 398) shows that the resins obtained from the root by the methods of incision and extraction, although similar, are not identical, while both these resins differ very considerably from that obtained from the root of *Ipomoea orizabensis*, which has also been examined by Power and Rogerson (*ibid.* 101, 1). Both of these resins are exceedingly complex in character, but consist to a large extent of glucosides and methylpentosides of jalapinolic acid and its methyl ester, and, whilst the methylpentose obtained by the hydrolysis of the resin of scammony root appears to be identical with rhamnose, that from the resin of *Ipomoea orizabensis* yields a crystalline tetra-acetyl derivative not hitherto described. The resin from the last-mentioned source also contains small proportions of hentriacontane and cetyl alcohol, which are not present in the resin from scammony root; also, differences are observed in extracting with various solvents both the crude resins and the products of their alkaline hydrolysis.

Jalapinolic acid $C_{15}H_{30}(OH)CO_2H$ was first obtained by Mayer (Annalen, 95, 149) from 'jalapin,' the name given to that portion of the resin of *Ipomoea orizabensis*, which is soluble in ether. Jalapinolic acid, subsequently investigated by Kromer (J. pr. Chem. [ii.] 57, 448), has been studied by Power and Rogerson (*l.c.*). It forms silky needles, m.p. 67°–68°, and is slightly dextrorotatory. The *methyl ester* boils at 220° (20 mm.) and crystallises in laminæ, which melt at 47°–48°.

Earlier investigations of scammony resin were made by Johnston (Phil. Trans. 1840, ii. 341); Keller (Annalen, 104, 63; 109, 209); Spirgatis (*ibid.* 116, 289); Kromer (Chem. Zentr. 1893, i. 310), who have assigned formulæ to the resins obtained, but in view of their complexity, it is evident that they cannot be regarded as definite substances (*cf.* Power and Rogerson, J. Amer. Chem. Soc. 32, 112).

The sugars contained in scammony root and those obtained by hydrolysis of the resin and of 'jalapin' have been investigated by Votoček (Zeitsch. Zuckerind. Böhm. 27, 257; 30, 20, 117; Ber. 37, 3859, 4615): Requier (J. Pharm. Chim. [vi.] 20, 148, 213; [vi.] 22, 435, 492, 540). For assay of scammony resin, *v.* Guigues (J. Pharm. Chim. [vi.] 22, 241; Bull. Soc. chim. [iv.] 3, 872). A. S.

GUMS. Gums are amorphous substances, composed of carbon, hydrogen, and oxygen, which are characterised by the property of either dissolving in water, or of taking up enough of that solvent to become glutinous and form a mucilage. They are either derived from plants by spontaneous exudation, or are extracted by means of solvents. The gum usually contains some inorganic matter and occasionally a small proportion of nitrogen (*cf.* Stevens, Amer. J. Pharm. 77, 255). For a long time, the gums were considered to be carbohydrates. It is now known, however, from the researches of O'Sullivan on gum arabic (Chem. Soc. Trans. 45, 41; 57, 59), Gedda gum (*ibid.* 59, 1029), and gum tragacanth (*ibid.* 79, 1164), that the gums are acids of high molecular weight, composed of an acid nucleus to which is attached a number of residues of various hexoses, pentoses, and bioses by means of ethereal oxygen linkings.

The proportions of the sugars united to the nucleus acid to form the natural complex gum acid, and the proportions of the complex acids in the mixture that constitute the natural gum, appear to vary in different seasons, since investigations have shown that the properties of the gum of a given plant are not always the same.

The finer gums are used in pharmacy in the preparation of emulsions and pastilles, and as a constituent of emollient medicines, whilst the commoner qualities are used in the arts as adhesive agents, in the finishing of cloth, in the preparation of ink, of water colours, and in calico printing.

Many drugs, known as gums in commerce and not included in this article, will be found by reference to Balsams or Gum resins.

One of the most important factors in determining the quality of a gum is the viscosity of the solution it forms with water, and as no standard method is yet in use the results recorded by different investigators are usually not comparable. The simplest method of determining the viscosity is to allow a quantity of the solution to flow by its own weight out of a tube, provided with a capillary orifice, and to note the time of flow. The results obtained by this method are of little value, since the pressure under which the liquid flows varies continuously, but the method is still in use as affording a rough comparison of viscosities. For more accurate work, recourse may be had to the use of a viscometer, such as that described by Ostwald (Physico-Chemical Measurements, 162).

In addition to the viscosity determination, it is generally necessary to ascertain the percentage of moisture present in a sample of gum, the acidity, the amount of ash, the colour, taste, odour, and character of the solution it forms with water. The amount of moisture present should be merely enough to prevent the gum being excessively friable; as a rule it varies between 12 and 16 p.c. The ash should be merely that due to the bases combined with the natural gum acid and in good samples is generally about 3 p.c. The solution should be free from marked taste or odour and not very dark in colour.

In the early part of the 19th century, a good many gums were known, and the work then done resulted in the description of the properties of a few gum substances to which the names *bassorin*, *cerasin*, and *arabin* were given; and chemists, dominated by the idea that the number of organic compounds was only small, on investigating a gum, identified its constituents with one or more of these substances. It now appears that the number of gum compounds is very considerable, and it cannot be safely inferred that the arabin, or cerasin, &c., found in one gum, is the same substance as the compound, given the same name, found in another natural product. For further particulars, *see* Robinson (Brit. Assoc. Reports, 1906, 227; and the Imperial Institute Bulletin, 6, 29), from which much of the information embodied in this article has been obtained.

Acacia and Allied Gums.

Acacia gum. *Gum arabic*; *Acacia gummi. Gomme arabique*, Fr.; *Arabisches gummi*, Ger. Acacia gum is the exudation from the stems and branches of various species of acacia, notably the *A. Senegal* (Willd.), which inhabit Africa from Senegambia in the West to Kordofan, Southern Nubia, and the region of the Atbara in the East (Bentl. a. Trim. 94; Höhnel, Pharm. J. [iii.] 18, 1089; Flück. a. Hanb. 233). The drug has been known from the earliest times, having been an article of Egyptian commerce in the 17th century B.C.

The most esteemed variety is *Picked Turkey* or *white Senaar gum*. This gum, also known as *Sudan or Kordofan gum*, is collected from the grey barked acacia tree, *Acacia Senegal* (Willd.), known locally as 'hashab.' In Kordofan, the gum is obtained both from gardens of acacia trees which are private property and from wild trees. In the gardens, the gum is obtained by artificially incising the trees soon after the end of the rainy season, the bark is removed in strips from the principal branches of all trees which are three years old or upwards; the strips should be 1 to 3 inches wide, according to the size of the branch, and 2 to 3 feet in length. The incision should not penetrate into the wood, and a thin layer of the inner bark should be left. About 60 days afterwards, the first collection of gum is made, and after that the gum is collected every fourth day until the rains recommence and new leaves appear; at this stage the exudation ceases. The gum obtained from the wild or uncultivated trees is slightly darker in colour and of less value than that derived from trees under cultivation. It exudes naturally from the wild trees and usually dries into pear-shaped pieces which vary in size, according to the length of time between successive collections. Young hashab trees, 8 to 10 feet high and 6 to 8 inches in girth, will produce gum, and the limits of age for this purpose may be taken as 3 to 15 or 20 years; probably trees of from 8 to 12 years old are the most productive. The gum consists of lumps of various sizes, sometimes as large as a walnut, and of a white or nearly white colour. The unbroken masses are rounded in shape, and traversed by numerous minute fissures. They are brittle and break with a vitreous fracture, exposing a transparent and in the finer varieties quite colourless interior.

Suakin, Talca, or Talha gum is derived from the 'red' and the 'white' barked acacia trees, both of which are varieties of *Acacia Seyal* (Delile). It is collected chiefly in the forests of the Blue Nile. The red talha tree is more abundant than the white and consequently most of the talha gum is derived from that variety. The trees are said not to be barked or wounded by the collectors, who gather the gum they find exuding. Talha gum is so brittle that commercial specimens have usually, for the most part, fallen to powder. The particles exhibit a great variety of colour.

Senegal gum, collected in the French colony of Senegal, is obtained almost entirely from the same species of acacia which yields the Kordofan gum, but it is probable that the poorer qualities are procured from other species. The gum exudes naturally through fissures produced by the rapid and unequal desiccation of the barks of the trees by the hot winds experienced immediately after the wet season, but in recent years incisions have been made. Senegal gum is much darker in colour than the Sudan gum, and the surface of the lumps is unbroken by cracks or fissures. It is chiefly imported into France. A considerable quantity of this is, however, exported to other European countries.

Morocco, Mogador, or **Brown Barbary gum** is exported from Morocco. It is stated to be obtained from *Acacia arabica* (Willd.), and *Acacia gummifera* (Willd.), but according to some authorities, much of the gum now exported is merely Senegal or Sudanese gum, brought to Morocco by caravans from the interior. It consists of light dusky brown tears or vermiform pieces; they show numerous superficial fissures.

Cape gum is the product of the *Acacia horrida* (Willd.), a native of Cape Colony. Its colour is amber brown.

Aden and **East Indian gum** is produced in Abyssinia and Somaliland and is exported from the towns on the Somali coast principally to Aden and Bombay. From these two ports, it is reshipped to Europe as 'Aden gum' and 'East Indian gum' respectively. The source of the gum is not known with certainty but some of it is doubtless collected from *Acacia abyssinicia* (Hochst.) and *Acacia glaucophylla* (Steud.), which are known to occur in those regions. It consists of tear-shaped masses, often as large as an egg, and of a pale amber or pinkish hue. The best qualities approach the better classes of Kordofan gums in appearance, solubility, and other characters, but these gums are usually darker in colour.

Australian or **Wattle gum**, the product of several Australian species of Acacia known locally as 'Wattles,' occurs in large hard globular tear-like masses or lumps, varying in colour from deep yellow to deep reddish-brown (*v.* Maiden, Pharm. J. [iii.] 20, 86; *cf.* Flück. a. Hanb.).

Gum arabic is not much more soluble in hot than in cold water. In alcohol it is insoluble. The aqueous solution is precipitated by basic lead acetate, but not by neutral acetate. It is also thickened or rendered turbid by the addition of solutions of borates or ferric salts or alkaline silicates. Salts of mercury or silver have no action on the solution, neither is it coloured blue by iodine. Gum arabic yields about 3 p.c. of ash, consisting of calcium magnesium and potassium carbonates. For analytical distinctions between pure gum arabic and gums with which it may be associated, *v.* Hager (Zeitsch. anal. Chem. 11, 350; Pharm. Centh. 1885, 388); Schlosser (Chem. News, 20, 120); Roussin (J. Pharm. Chim. [iv.] 7, 251); Elwood (Pharm. J. [iii.] 19, 339); Hefelmann (Zeitsch. öffentl. Chem. 11, 195); Palladino (Bull. Soc. chim. [iii.] 9, 578); Vamvakus (Ann. Chim. anal. 12, 12). Methods of valuation of gum arabic are given by Fromm (Zeitsch. anal. Chem. 40, 143); Dieterich (*ibid.* 40, 408), and a method for detecting the presence of gelatin is given by Trillat (Compt. rend. 127, 724).

The chief constituent of gum arabic is *Arabin, Arabic acid*, or *Gummic acid*, combined with calcium and also perhaps with magnesium and potassium. The crude acid is precipitated when alcohol is added to an aqueous solution of gum arabic previously acidified with hydrochloric acid. By successively redissolving in water and reprecipitating, the product can be obtained pure. Arabic acid is amorphous, soluble in water and insoluble in alcohol. Heated to 100° it is converted into insoluble *meta-arabic acid* (Neubauer, J. 1854, 624; Annalen, 102, 105; Gelis, J. 1857, 496), or the same change may be effected by treatment with concentrated acid (Fremy, J. 1860, 503). Meta-arabic acid is readily changed back again to soluble arabic acid by the action of alkalis. Heat of combustion, *v.* Stohmann (J. pr. Chem. [ii.] 31, 298). Action of light, *v.* Eder (*ibid.* 19, 299).

The constitution of arabin has been investigated by O'Sullivan (*l.c.*) who showed that it contains the acid nucleus, $C_{23}H_{38}O_{22}$, to which he gave the name *λ-arabinosic acid*, but afterwards unfortunately called it *arabic acid*, the name already given to the naturally occurring gum acid, arabin, which is a compound of arabinosic acid with the sugar residues, arabinan and galactan, the termination 'an' indicating the anhydride of the corresponding sugar. On complete hydrolysis, arabin yields arabinose, galactose, and arabinosic (arabic) acid.

When oxidised with ordinary nitric acid, gum arabic yields oxalic, mucic, tartaric, and racemic acids (Guerin, Annalen, 4, 255; Liebig, *ibid.* 113, 4; Kiliani, Ber. 15, 35; Hornemann, J. 1863, 381; Maumene, Bull. Soc. chim. [iii.] 9, 138; Béchamp, *ibid.* [iii.] 7, 587). The so-called nitro derivatives of arabin are, like those of starch and cellulose, nitrates (Béchamp, J. 1860, 521; *l.c.*). Acetic anhydride also reacts forming acetyl derivatives (Schutzenberger and Naudin, Zeitsch. Chem. 1869, 265).

Gums from various species of *Acacia* grown in known localities have been examined by Meininger (Arch. Pharm. 248, 171).

Allied gums. The gum known in commerce as *Gedda gum*, in appearance very similar to the inferior kinds of gum arabic, has also been examined by O'Sullivan. He found that it is a mixture of several gum acids, which are constituted of the radicles of galactose and of arabinose or arabinan, attached in considerable numbers to a nucleus acid to which the name geddic acid is given. Geddic acid is an isomeride of arabic acid, $C_{23}H_{38}O_{22}$. *Chagual gum* is obtained from Chile, where it is produced by the *Puza lanuginosa* (Schult.). It is partly insoluble in water. Chagual gum has been investigated by Winterstein (Ber. 31, 1571). *Feronia* or *wood apple gum* is derived from the Indian tree *Feronia elephantum* (Correa) (*cf.* Flück. a. Hanb. 239). *Ghati gum* is the name given in India to gum produced in India itself, as distinguished from East Indian gum of exotic origin. In European commerce, however, the name 'Ghatti' or 'Gatty' is practically restricted to the partially soluble and viscous gum derived from *Anogeissus latifolia* (Wall.) and certain other species. It is derived from various trees and no attempt is made to keep the products of the different species separate. The result of this is that the gum may differ considerably in properties. *Hog* or *Doctor gum* consists of reddish tears. It is derived from the *Rhus Metopium* (Linn.), or perhaps the *Moronobea grandiflora* (Choisy), natives of South America. This gum is quite distinct from the Hogg or Kuteera gum of India (*cf. Tragacanth*). Plants containing gums similar to acacia (*v.* Gm. 15, 195). *Para* and other gums (Pharm. J. [iii.] 18, 623, 745, and 1009).

TRAGACANTH AND ALLIED GUMS.

Tragacanth. *Tragacantha. Gomme adragante*, Fr.; *Traganth*, Ger. A gummy exudate consisting in part of altered cells obtained either spontaneously or by means of incisions from the stems of various species of *Astragalus*, some of which occur in South Western Europe, while others are found in Greece and Turkey. The largest number, however, are indigenous in the mountainous regions of Asia Minor, Syria, Armenia, Kurdistan, and Persia. The tragacanth of commerce is produced in the last-named countries. In July and August, the shrubs are stripped of their leaves and short longitudinal incisions or slits are made in the trunks. The gum flows out, and, drying spontaneously, is ready for gathering in three or four days. If the weather is fine during the drying process, the 'white leaf' form of gum is obtained which is the most prized variety. If, however, rain falls or the wind rises, particles of dust collect on the surface of the gum which thereby loses its whiteness and becomes the 'yellow leaf' form, the second quality. The form of the pieces is determined by the shape of the incision; longitudinal incisions produce 'leaf' or flake tragacanth, punctures yield 'thread' tragacanth, while irregular shaped incisions give knob-like masses, generally coloured, and of relatively low value. Another form, known in Persia as 'Arrehbor,' exudes from branches which have been cut by a saw (Imp. Inst. Reports, 1909, No. 63).

When tragacanth is treated with water, one part dissolves and the other swells up, absorbing water, to the extent of even fifty times the weight of the gum used, the whole forming a thick mucilage. This may be diffused through more water when, on filtering, a soluble gum passes through, and there remains on the filter a slimy non-adhesive mucilage, *bassorin*, *tragacanthin*, or *adraganthin*. In presence of alkalis, the whole of the gum dissolves readily in water (Flück. a. Hanb. 178; Sandersleben, Phytochem. Untersuch. Leipzig, 1880, 90; Fremy, J. 1860, 504). On hydrolysis of three samples of white tragacanth, Widtsoe and Tollens (Ber. 33, 132) obtained fucose and arabinose, whilst fucose and xylose were obtained from two samples of brown tragacanth. Five different samples of tragacanth examined by Helger and Dreyfus (Ber. 33, 1178) were found to contain 9·4 to 15·4 p.c. of water; 3·1 to 2·7 of ash, also 15·1 to 22·4 p.c. of galactose (estimated as mucic acid) and 30 to 42 p.c. of arabinose (estimated as furfuraldehyde phenylhydrazone). A specimen of vermicelli tragacanth contained 4 p.c. of cellulose and 3 p.c. of starch. The samples obtained by artificial incision contain the larger proportions of water and ash.

Tragacanth gum, investigated by O'Sullivan, was found, like Gedda gum, to be a mixture of several gum acids. It can be separated into a group of acids which remain in solution in dilute alcohol, and an insoluble portion, for which the name *bassorin* is appropriated. The acids of the soluble group were found to be built up on a nucleus acid, very similar if not identical with geddic acid, by its union with galactose and arabinose residues. The constitution of the insoluble portion has not been completely worked out; but it yields a nucleus acid of the formula $C_{14}H_{20}O_{13}$, to which the name *bassoric acid* is given, and also intermediate acids formed of bassoric acid united to the residues of xylose, and of a new pentose sugar, *tragacanthose*.

Allied gums. *Bassora*, *Kuteera*, or *Caramania gum*, *Hogg gum tragacanth*, consists of yellow or brown waxy masses. It comes from Persia where it is said to be derived from almond and plum trees, and is employed in Smyrna in the adulteration of tragacanth (Flück a. Hanb.). The *Cochlospermum Gossypium* (D.C.), a small deciduous tree growing abundantly in India, furnishes a gum which occurs in irregular rounded translucent lumps of a pale buff colour. The gum is sold in the Indian bazaars as a substitute for tragacanth, which it closely resembles. This gum has the property of slowly giving off acetic acid when exposed to moist air, a property also possessed by the gum of *Sterculia urens* (Roxb.) (Gurbourt, Pharm. J. 15, 57). A stable acid, *gondic acid*, $C_{23}H_{36}O_{21}$, has been obtained from the gum of *Cochlospermum Gossypium* (D.C.) in the same manner as the arabic and geddic acids of O'Sullivan. On hydrolysis, the gum yields 18 p.c. of acetic acid, calculated on the dry and ash-free substance, and is thus an acetyl derivative. Xylose and a hexose are among the other products (Robinson, Chem. Soc. Trans. 89, 1496). *Cashew gum* is the exudation of the *Anacardium occidentale* (Linn.), a small tree indigenous to tropical America. *Cherry tree gum* behaves towards water in a similar manner to tragacanth. The insoluble portion consists of *cerasin*, combined with metals of the alkalis or alkaline earths (Fremy, J. 1860, 504). For hydrolysis of cherry tree gum, *v.* Hauers and Tollens (Ber. 36, 3306). *Linseed*, *marshmallow*, and *fleaseed gums* closely resemble tragacanth (Schmidt, Annalen, 51, 50; Frank, J. pr. Chem. [ii.] 95, 494; Kirchner and Tollens, Annalen, 175, 215; Hilger, Ber. 36, 3197). *Persian gum* (*v.* Pharm. J. [3] 20, 793) is of a hard glassy type and its solutions in water are intermediate in character between those of tragacanth and gum arabic. The trade in this gum is considerable, but the commercial value is lower than that of either tragacanth or fine gum arabic (Imp. Inst. Report). *Wood gum* has been extracted from various woods, straw, loofah, and similar materials. It resembles cherry tree gum. On hydrolysis it yields xylose, and in some cases arabinose (Th. Thomsen, J. pr. Chem. [ii.] 19, 146; Poumarède and Figuer, Annalen, 64, 338; J. Soc. Chem. Ind. 1890, 335; Wheeler and Tollens, Ber. 22, 1046; 23, 137; Annalen, 254, 320; Allen and Tollens, *ibid.* 260, 289; Bader, Chem. Zeit. 19, 55; Johnson, Amer. Chem. J. 18, 24; Browne and Tollens, Ber. 35, 1457; Salkowski, Zeitsch. physiol. Chem. 34, 162).

OTHER GUMS.

Agar agar gum, *Bengal isinglass gum*, the dried jelly of seaweed, which, under the name of agar agar, is obtained from China, forms with water, is largely composed of the gum *gelose* (Payen, J. 1859, 562) or *pararabin* the latter being contained also in the carrot and the sugar beet (*cf. sugar beet gum*). Gelose is insoluble in cold water, alcohol, dilute acids, and alkalis. 1 part in 500 of boiling water forms a jelly on cooling (Morin, J. 1880, 1010; Porumbara, J. 1880, 1011; Bauer, J. pr. Chem.

[ii.] 30, 375) (*v.* Agar Agar). *Galactin*, a very similar gum to gelose, is found in the seeds of the *Leguminosæ* (Müntz, Bull. Soc. chim. 37, 409).

Amyloid gums. These are distinguished from most gums by being coloured blue by iodine. The more important are: *Amyloid* (distinct from that derived from cellulose), the soluble gum of the cotyledons of the tamarind and other plants; *Quince gum*, which breaks up into cellulose, gum, and sugar when heated with dilute sulphuric acid; and *Salep gum*, derived from the bulbs of orchids (Frank, J. pr. Chem. [ii.] 95, 479; Hilger, Ber. 36, 3197).

Animal gum. A gummy substance having the composition $C_{12}H_{20}O_{10},2H_2O$ has been isolated from the secretions of the salivary glands, from the brain, pancreas, kidneys, and other parts of the body. It is unaffected by the digestive ferments but is converted into sugar by dilute acids. It reduces ammoniacal silver nitrate solution with formation of a mirror. With water, it gelatinises, forming a mucilage. It is insoluble in alcohol and ether (Landwehr, Zeitsch. physiol. Chem. 8, 122; 9, 367; 13, 122; Zeitsch. anal. Chem. 23, 601; 24, 640; Pouchet, Compt. rend. 20, 21; Folin, Zeitsch. physiol. Chem. 23, 347).

Fermentation gum. This gum, *Dextran* or *Viscose*, which occurs in the unripe sugar beet (Scheibler, Wag. J. 1875, 790), is formed in the lactic fermentation of cane sugar by the action of the bacterium *Streptococcus* (*Leuconostoc*) *mesenteroides* (van Teighem, Jahresb. Agrik. Chem. 1879, 544; Béchamp, J. Th. 1881, 85; Brüning, Annalen, 104, 197). Formed also in mucic fermentation (Nägeli, J. pr. Chem. [ii.] 17, 409). Dextran $C_6H_{10}O_5$ is amorphous, soluble in water and precipitated therefrom as an elastic thread-like mass by alcohol. By treatment with dilute sulphuric acid, sugar is obtained, and when oxidised with nitric acid, oxalic but no mucic acid.

Dextrin *v.* Dextrin.

Gum from German yeast (*v.* Salkowski, Ber. 27, 497, 925, 3325; Hessenland, Zeit. Vereins. Rübenzuch-Ind., 1892, 671).

Iceland moss gum. Two gums have been isolated from the jelly of Iceland moss, *Cetraria islandica* (Acharius). The one, *lichenin* $C_6H_{10}O_5$, is unaffected by iodine, while the other, *isolichenin*, is coloured blue by that reagent. Lichenin is a transparent brittle mass which dissolves in hot water, the solution gelatinising on cooling. It is soluble in solution of ammonio-copper sulphate; combines with bases; is converted by dilute acids into sugar; oxidised by nitric acid, it yields oxalic acid, and it reacts with glacial acetic acid, forming *triacetyl lichenin* $C_6H_7Ac_3O_5$ (Knop and Schnedermann, Annalen, 55, 165; J. 1847–8, 831; Errera, Inaug. Dis. Brussels, 1882, 18; Mulder, Annalen, 28, 279; Helger and Buchner, Ber. 23, 461). *iso*Lichenin is soluble in water, and unlike lichenin forms no acetyl derivative, nor is it soluble in ammonio-copper sulphate solution (Berg, J. 1873, 848; Errera; Hönig, Monatsh. 8, 452).

The lichen, *Evernia Prunastri* (Ach), contains a gum resembling lichenin, *everniin* $C_9H_{14}O_7$ (Stüde, Annalen, 131, 241).

Irish moss gum. The Irish moss, *Chrondus crispus* (Linn.), contains a gum which is soluble in water, insoluble in ammonio-copper sulphate, is not coloured blue by iodine and yields mucic acid when oxidised with nitric acid (Blondeau, J. 1865, 659; Flückiger and Obermeyer, J. 1868, 805; Painter, Pharm. J. [iii.] 18, 362).

Sterculia gum, derived from various species of *Sterculia* (*v.* Maiden, Pharm. J. [iii.] 20, 381).

Sugar beet gum. Several forms of gum have been separated from the juice of the sugar beet. *Arabic* or *meta-arabic acid* (*cf. gum acacia*), *dextran* (*cf. fermentation gum*), *pararabin* (Reichardt, Ber. 8, 808), and *lævulan* (v. Lippmann, *ibid.* 14, 1509). Pararabin is a powder which forms a jelly with water of quite a different appearance from that obtained with meta-arabin. It is soluble in dilute acid solutions from which alkalis or alcohol precipitate it. Lævulan is a by-product in the extraction of crystallisable sugar from beet sugar molasses. When anhydrous, it is insoluble in water, but in its hydrated form it dissolves readily. When oxidised by nitric acid it yields mucic acid, and heated with dilute sulphuric acid it is entirely converted into lævulose.

Wine gum (*v.* Béchamp, J. 1875, 987; Chancel, J. 1875, 987; Neubauer, Zeitsch. anal. Chem. 15, 194). A. S.

GUM ACACIA *v.* Gums.

GUM AMMONIACUM *v.* Gum resins.

GUM ARABIC *v.* Gums.

GUM ASAFŒTIDA *v.* Gum resins.

GUM BENJAMIN *v.* Balsams.

GUM BENZOIN *v.* Balsams.

GUM, BRITISH, *v.* Dextrin.

GUM ELASTIC *v.* Rubber.

GUM GALBANUM *v.* Gum resins.

GUM GAMBOGE *v.* Gum resins.

GUM KINO *v.* Kino.

GUM LAC or **LAC RESIN** *v.* Resins.

GUM MYRRH *v.* Gum resins.

GUM THUS *v.* Resins.

GUMMIC ACID *v.* Gums.

GUN COTTON *v.* Explosives.

GUN METAL *v.* Tin.

GUNPOWDER *v.* Explosives.

GURHOFITE *v.* Dolomite.

GURJUN BALSAM. *Wood-oil* *v.* Oleo-resins.

GURJUNIC ACID *v.* Oleo-resins.

GUROLITE or **GYROLITE** *v.* Calcium

GUTTA PERCHA is the product obtained by coagulating the latex of certain species of *Palaquium* and *Payena*, belonging to the natural order *Sapotaceæ*, which are natives of the Malay Peninsula and Archipelago. The name is derived from two Malay words: *getah* and *percha* or *pertja*. The word *getah* is applied to any exudation from a tree, whilst *percha* or *pertja* refers either to the local name of the tree which was erroneously thought at first to furnish the product, or to the Malay name for Sumatra ‘Pulau Percha.’

The introduction of gutta percha into commerce dates from 1843, when specimens were forwarded to London independently by two doctors resident in Singapore, Dr. William Montgomerie and Dr. José D’Almeida, and the remarkable properties of the material at once attracted attention. In 1847 the principal tree yielding gutta percha was described and named by Sir W. J. Hooker, and in the same year Dr. Ernst Werner von Siemens employed the material for insulating underground telegraph wires.

The principal trees yielding gutta percha of the best quality are *Palaquium Gutta*, Burck, *P. oblongifolium*, Burck, and *P. borneënse*, Burck. *P. oblongifolium* is considered by some botanists to be only a variety of *P. Gutta*; the common name for both in the Malay peninsula is Taban. A number of other species of *Palaquium* furnish gutta percha of second quality, the chief of these being *P. obovatum*, King (Taban putih), *P. Maingayi*, King and Gamble (Taban simpor), and *P. oxleyanum*, Pierre (*Dichopsis pustulata*, Hemsley), which is variously known as Taban sutra, Taban putih, and Taban chaier in different parts of the Malay peninsula. *Payena Leerii* (Hook. and Benth.); and *P. Havilandi* (King & Gamble), furnish the white gutta percha known as Getah sundek or soondie.

There has been considerable confusion regarding the botanical identity of the trees yielding gutta percha, which has been increased by the fact that the same native name is frequently applied to distinct species in different districts.

Palaquium Gutta is a large forest tree which usually attains a height of about 60 feet and has a straight cylindrical trunk. Trees up to 150 feet or more in height and 4 to 5 feet in diameter have been recorded. The tree is easily recognised by its leaves which are a beautiful coppery gold colour on the under surface and dark glossy green on the upper. They vary considerably in size, the leaves of mature trees being about 2 inches long, whereas those of young trees are much longer.

The geographical distribution of the trees which furnish gutta percha is curiously restricted, as they only occur naturally in a small area comprising the southern portion of the Malay peninsula, Sumatra, Banca, Borneo, Celebes, the Susu Islands, and the Philippines. The trees are not indigenous in Java but have been introduced and are now being cultivated there.

The latex is contained in isolated sacs which occur chiefly in the inner layers of the bark and also in the leaves. On making incisions in the bark the latex exudes and quickly coagulates, so that only a small yield of gutta percha can be obtained at one tapping. In consequence of this fact the Malays have adopted the destructive method of felling the trees in order to collect the gutta percha. The tree is cut down and incisions extending right round the trunk are made at intervals of 9 to 12 inches or even less. In the case of the best kinds of gutta percha, the latex exudes into the incisions where it quickly coagulates and in about half an hour can be rolled off on a stick or scraped off with a knife. The latex of the inferior varieties does not coagulate so rapidly; it is collected in vessels placed underneath the incisions and is afterwards coagulated by gentle heating. The gutta percha is subsequently boiled in water and made into blocks of various shapes.

The amount of gutta percha obtained per tree by the native method has been very variously stated, but it seems probable that the average return from 15 to 20 year old trees is not above 14 ozs. Large forest trees have, however, been known to yield over 2 lbs. of gutta percha and a tree 160 feet high, in the Philippines, is stated to have furnished 8½ lbs.

In view of the serious destruction of the trees which is involved in the native method of obtaining the gutta percha, attempts are now being made in Perak and in Java to collect the product by tapping the standing trees. The average yield by this method is not yet definitely determined, but in Perak a tree 59½ inches in girth has yielded 1 lb. 3¾ ozs. of gutta percha in 21 tappings extending over 6 weeks. Gutta percha is also being extracted by mechanical processes from the leaves of the trees. The older methods, involving the use of solvents, which were first employed for this purpose, have been abandoned, as it was found that the chemical treatment adversely affected the durability of the gutta percha when exposed to air and light.

Gutta percha resembles rubber in consisting essentially of a hydrocarbon, having the formula $(C_{10}H_{16})_n$, associated with resinous substances. It differs widely, however, from rubber in its physical properties. At ordinary temperatures it is hard, very tenacious, and cannot be stretched like rubber. On immersion in hot water it becomes soft and plastic so that it can be readily moulded; on cooling, it retains the shape given to it when soft and becomes hard but not brittle. When heated in the air, gutta percha decomposes and then takes fire, burning with a luminous smoky flame and giving off a characteristic odour resembling that of burning rubber. When submitted to destructive distillation, it yields a mixture of liquid hydrocarbons, including isoprene, similar to those obtained by the distillation of caoutchouc.

Gutta percha is not affected by weak mineral acids, strong hydrochloric or acetic acids, or strong alkalis, but is readily attacked by strong nitric or sulphuric acid. It is partially soluble in ether, alcohol, acetone, and cold petroleum spirit, which dissolve the resin; and completely soluble in carbon disulphide, chloroform, carbon tetrachloride, and hot petroleum spirit.

The hydrocarbon present in gutta percha, known as *gutta*, is the essential constituent and exhibits in an enhanced degree the characteristic properties of the product. When dissolved in chloroform and treated with chlorine, bromine, or iodine, *gutta* forms addition products, with some evolution of the halogen acid; and by the action of nitrogen oxides, nitrosites resembling those obtained from caoutchouc are formed.

Gutta percha slowly absorbs oxygen when exposed to air and light, and in the process the *gutta* is converted into a brittle resin. Gutta percha is, however, not energetically attacked by ozone like caoutchouc. Harries has shown that if gutta is dissolved in chloroform and treated with ozone, an ozonide $C_{10}H_{16}O_6$ is formed which, when decomposed by steam, gives a mixture of lævulic aldehyde and acid and lævulic aldehyde peroxide like the corresponding ozonide prepared from caoutchouc, but in different proportions. Harries concludes that the hydrocarbons of rubber and gutta percha are identical, both being probably 1 : 5 dimethyl*cyclo*octadiene (Ber. 1905, 38, 3985).

The resinous bodies associated with the gutta are oxygenated substances. They were separated by Payen in 1852 into two portions: (1) a crystalline white resin, soluble in hot but insoluble in cold alcohol, which he named *albane*; and (2) an amorphous yellow resin, soluble in cold alcohol, which he named *fluavile.* It seems probable from recent investigations that these substances are mixtures and not single compounds. In 1892 Oesterle discovered in gutta percha a fourth constituent, which he named *guttane* and found to contain C 86·4 p.c. and H 12·0 p.c. For information on the composition and chemical properties of gutta percha see papers by Ramsay, Chick, and Collingridge, and by Caspari in J. Soc. Chem. Ind. 1902, 21, 1367; 1905, 24, 1274.

In the analysis of crude gutta percha, it is customary to determine the moisture, the resin, the gutta, and the insoluble matter (dirt). The moisture is usually determined by heating a weighed quantity in an air or water oven, or *in vacuô*, until no further loss in weight occurs; sometimes the water given off is collected and weighed. The resins are determined by extraction with hot acetone in a Soxhlet apparatus, or by ether or petroleum spirit in the cold; the solvent is distilled off and the resin weighed. The residue left after removal of the resin is treated with chloroform which dissolves the gutta leaving the insoluble matter; the latter is removed by filtration, washed with chloroform, dried, and weighed. The gutta may be weighed after distilling off the chloroform or it may be precipitated from the chloroform solution by the addition of alcohol and then dried and weighed.

The composition of several representative specimens of gutta percha, derived from trees belonging to a single species, which have been examined at the Imperial Institute and by Dr. Obach, is given in the following table:—

Variety of gutta percha	Botanical source	Gutta	Resin	Dirt	Moisture	Ash
Getah taban merah[1]	*Palaquium Gutta* . .	70·6	13·9	0·7	14·8	0·95
,, ,, ,,	,, ,,	68·3	13·4	8·1	10·2	0·89
Getah taban putih .	Uncertain . . .	35·6	49·5	7·4	7·5	0·72
Getah taban chaier .	,,	52·0	43·4	3·4	1·2	1·61
Getah simpor . .	*Palaquium Maingayi* .	44·9	45·5	8·4	1·2	2·13
Getah taban sutra[2] .	*Palaquium oblongifolium*	84·3	10·7	3·7	1·3	—
Getah sundek[2] .	*Payena Leerii* . .	43·9	37·6	5·1	13·4	—

The commercial brands of gutta percha vary very considerably in composition and quality. They are usually designated by the names of the countries in which they are produced or of the ports from which they are shipped. Obach has classified the 12 principal brands into four groups as follows:—

I. First quality—genuine from *P. Gutta* or *oblongifolium* and allied species: (1) Pahang from the Malay peninsula, (2) Bulongan red, and (3) Banjer red from Borneo;

II. Second quality—Soondie from *Payena* spp.: (4) Bagan goolie soondie, (5) Goolie red soondie, both from Borneo, and (6) Serapong goolie soondie from Sumatra;

III. Third quality—white, botanical source not definitely known: (7) Bulongan white, (8) Mixed white, (9) Banjer white, all from Borneo;

IV. Fourth quality—mixed and reboiled: (10) Sarawak mixed, (11) Padang reboiled, and (12) Banca reboiled.

Obach has given the average results of 751 analyses of these varieties, representing 2282 tons of raw gutta percha (*see* Cantor Lectures on Gutta Percha, published by the Society of Arts, Appendix v. 90–92). The figures for the genuine varieties may be given for comparison with those recorded above:—

—	Quantity represented by analyses		Percentage composition			
	Lots	Tons	Gutta	Resin	Dirt	Water
Pahang .	93	233	57·0	13·3	11·5	18·2
Bulongan red	37	60	51·8	18·2	10·8	19·2
Banjer red .	91	232	40·7	20·0	17·4	21·9

The treatment which crude gutta percha undergoes in the factory previous to its technical use may be briefly described. The lumps, after slicing if necessary, are softened by immersion in hot water and are then freed from impurities by treatment in a washing machine with hot water. The washed gutta percha while still soft is forced by pressure through wire gauze in order to remove any solid impurities which have not been eliminated in the washing process. The strained product is usually rewashed and is then transferred to the masticator or kneading machine, where the mechanically enclosed water and air are eliminated and the material rendered homogeneous. It is afterwards passed through a rolling mill and formed into sheets from ⅛ to ¼ inch thick, which are cut into convenient lengths and stored in cellars until required for use. If it is desired to mix various kinds of gutta percha in order to obtain a product of a required composition, or to incorporate pigments, &c., the operation is conducted by means of a mixing machine fitted with specially shaped rollers which can be heated by steam.

In certain cases the crude gutta percha is washed with a hot 5 p.c. solution of sodium hydroxide in order to improve the colour. After treatment in this way, the product must be thoroughly washed with water to remove all trace of alkali.

The loss which results on cleaning raw gutta percha (*i.e.* the quantity of dirt and water present) is considerable, usually amounting to from 30 to 40 p.c. and sometimes to as much as 50 p.c.

[1] Obtained by tapping standing trees.

[2] Analyses by Dr. Obach.

For some purposes a very hard gutta percha is required, and this can be obtained by removing the resin from the ordinary material by extraction with solvents.

The physical and mechanical properties of gutta percha depend very largely on the proportions of gutta and resin present. Thus the temperature at which it softens; the time required to harden on cooling; the tensile strength; and the degree of elongation before breaking are all related to the value of the ratio gutta : resin.

The electrical properties, *i.e.* the insulation resistance, the inductive capacity and the dielectric strength, depend principally on the nature of the gutta and on the amount of water present, and are affected very little by the removal of the resin. (For determinations of the electrical properties of gutta percha, *see* Obach, *l.c.* 62–65.)

Gutta percha is employed for a variety of purposes, the chief of which are the insulation of submarine cables, and the manufacture of the covers of golf balls.

The amount of gutta percha which has been used in the cable industry forms a very large percentage of the total consumption. It was stated by Obach that of the 71,933 tons of raw gutta percha used in the United Kingdom from 1845 to 1896, at least two-thirds, and probably more, had been utilised for electrical purposes. The gutta percha employed for cable manufacture has to be specially selected for the purpose, as the insulating power of the different commercial brands varies enormously.

The gutta percha used for the covers of golf balls is 'hardened' by removal of the resin in order to render it as tough and elastic as possible.

Gutta percha is also utilised for the manufacture of driving belts; rings, valves, &c., for pumps and hydraulic presses; boot soles; tubes, funnels, bottles, buckets, &c., for use with acid liquids; for cements (such as Chatterton's compound); for taking casts; and for surgical and many other minor purposes.

H. B.

GYNOCARDIN *v.* Glucosides.

GYNOVAL *v.* Synthetic drugs.

GYPSUM (Fr. *Gypse*; Ger. *Gyps*; Ital. *Gesso*). A common mineral composed of hydrated calcium sulphate $CaSO_4,2H_2O$, crystallising in the monoclinic system. The name *selenite* is sometimes applied to the clear crystallised variety, *satin-spar* to the finely fibrous variety, and *alabaster* (*q.v.*) to a compact, marble-like variety used for carving. The low degree of hardness (No. 2 on the scale) is a very characteristic feature; the mineral can be readily scratched with the finger-nail. Sp.gr. 2·32. The mineral is usually white, but sometimes greyish, yellowish, or reddish; and the glistening cleavage surfaces are usually conspicuous on a broken surface. The crystals possess a highly perfect cleavage in one direction parallel to the plane of symmetry; on the smooth, bright cleavage surfaces the lustre is pearly, and coloured bands (Newton's rings) are often to be seen. Cleavage flakes are flexible but not elastic (thus differing from mica), and when bent a fibrous cleavage is developed parallel to the faces of a pyramid: this fibrous cleavage is seen as silky striations on the principal cleavage, and is a very characteristic feature of gypsum.

Single crystals of gypsum, with a rhomb-shaped outline, are of common occurrence, embedded in clays. Fine groups of water-clear crystals are found in the sulphur mines of Sicily, the salt mines of Bex in Switzerland, and at many other localities. Enormous crystals, a yard in length, have been found in a cave in Wayne Co., Utah. Various types of twinned crystals are of common occurrence. The deposits of massive gypsum, such as are mined for economic purposes, occur as thick beds and nodular masses in sedimentary rocks of various geological periods. Those of the midlands of England are interbedded with the red marls and sandstones of Triassic age; those worked near Battle, in Sussex, belong to the later Purbeck beds; many of the deposits of the United States are of Palæozoic (Silurian, Devonian, and Carboniferous) age; whilst the important deposits in the Paris basin are of Tertiary (Eocene and Oligocene) age. These more extensive deposits of gypsum have been formed by the evaporation of water in inland lakes and seas; and they are often associated with beds of rock-salt. The mineral has, however, in many cases originated by the action of water containing sulphuric acid and soluble sulphates (produced by the weathering of iron-pyrites and other sulphides) on limestone and other calcareous rocks. It is also formed by the action of volcanic vapours on the surrounding rocks.

The output of gypsum in England amounts to about a quarter of a million tons per annum; about half of this amount is mined in Nottinghamshire, considerable quantities in Staffordshire, Sussex, and Cumberland, and less in Derbyshire, Yorkshire, Westmoreland, and Somersetshire. The value ranges from 6 to 10 shillings per ton. In France, the output reaches 1½ million tons per annum, and about the same amount is produced in the United States. Nova Scotia and New Brunswick are also large producers. The French gypsum is remarkable in containing some admixed calcium carbonate and soluble silica, and for this reason it makes a harder plaster.

The principal use of gypsum is for the manufacture of plaster of Paris, stucco, and various kinds of wall plaster. Hence the popular name '*plaster-stone.*' The employment of plaster of Paris for making the moulds in the potteries has given rise to the name '*potter's stone*' for gypsum. The coarser grades of material are used as fertilizers (land plaster). Alabaster is used for carvings for inside decorations; and satin-spar is cut as beads and other small personal ornaments. Under the names 'terra alba,' 'annaline,' and 'satinite,' ground gypsum is used for adulterating paints and as a mineral loading in the manufacture of paper (*v.* Calcium).

L. J. S.

GYROPHORIC ACID $C_{16}H_{14}O_7$ is found in *Umbilicaria pustulata* (Hoffm.), *Gyrophora vellea* [(Linn.) Ach.], *Gyrophora spodochroa* [(Ehrh.) Ach.] and other lichens. It crystallises in needles from ether or dilute alcohol, melting at 202° with decomposition. Very easily soluble in acetone and alcohol. The alcoholic solution has an acid reaction, and gives a violet colour with ferric chloride. Is soluble in alkali to a yellow solution; boiling acetic acid converts it into orsellinic acid and boiling alcohol into orsellinic acid and its ethyl ester (Stenhouse, Annalen, 70, 218; Hesse, J. pr. Chem. [ii.] 58, 475; 62, 462; 63, 522; 68, 1; Zopf, Annalen, 300, 330; 313, 322; 317, 110; 338, 35; 340, 276; 346, 82).

H

HAARLEM BLUE. *Antwerp blue v.* Pigments.

HÆMATEÏN *v.* Logwood.

HÆMATIN *v.* Blood.

HÆMATITE or **HEMATITE.** A mineral consisting of ferric oxide (Fe_2O_3), crystallising in the rhombohedral system, and an important ore of iron (Fe, 70 p.c.). According to whether it is crystallised, massive, or earthy, it varies considerably in external appearance. In all cases, however, the mineral gives a characteristic brownish-red streak or powder; and it is on account of this colour (resembling that of dried blood) that the mineral receives its name hæmatite, meaning, in Greek, blood-stone. The sp.gr. of the crystals is 5·2, but of the compact and earthy varieties it may be as low as 4·2; hardness 6 (except in the soft, earthy varieties).

The crystals are iron-black with a brilliant metallic lustre, and they vary from rhombohedral to tabular in habit. This variety is distinguished as *iron-glance*, or *specular iron*; or, when the crystals are thin and scaly, as *micaceous iron-ore*. The compact varieties are distinguished as *red iron-ore* or *red hæmatite*. These sometimes exhibit a fibrous or columnar structure and a nodular surface, being then known as *kidney-iron-ore*; or, when the fibrous structure is so marked that the mineral breaks into rods, as *pencil-ore*. In these cases the material is often dark-red with a dull surface, but sometimes it may be iron-black with a sub-metallic to metallic lustre. Earthy, ochreous varieties are brighter red in colour, and are often mixed with clay and other impurities; these are known as *reddle*, *ruddle*, and *red iron-froth*.

Hæmatite occurs under a variety of conditions. The best crystals are found in connection with metamorphic silicate rocks and in mineral-veins; whilst the extensive masses of red iron-ore occur as bedded deposits in sedimentary rocks, often in association with limestone. The deposits on the east coast of the island of Elba, which have been extensively worked since the time of the Romans, consist of specular iron; whilst those of west Cumberland and north Lancashire, filling large irregular cavities in limestone, consist of red iron-ore and kidney-iron-ore.

Besides being used as an ore of iron, hæmatite, in its harder, compact varieties, is used, to a limited extent, as a gem-stone, and it was the material employed for some of the ancient Babylonian cylinder-seals. The pencil-ore of Cumberland is cut and polished for mounting on scarf-pins, &c., and for the burnishing tools used by jewellers and bookbinders. Ochreous varieties are used as a polishing material, and for making red paint and red pencils.

L. J. S.

HÆMATOGEN. A soluble iron albuminate.

HÆMATOXYLIN *v.* Logwood.

HÆMOGLOBIN *v.* Blood.

HAIDINGERITE *v.* Calcium.

HALFA. *Alfa, alva.* Arabic name for *Stipa tenacissima* (Linn.); especially applied to the Esparto grass from Algeria.

HALITE *v.* Sodium chloride.

HALLYOSITE. An uncrystallised clay-mineral with approximately the composition of kaolinite (*q.v.*) but containing rather more water (about 19 p.c.). It forms compact masses wtih a slight greasy feel and lustre, and may be white, grey, or shades of various colours; sp.gr. 2·0–2·2; H. 1–2. It occurs as beds in sedimentary rocks and as masses in mineral-veins, and has sometimes been observed as a decomposition product of granite and other rocks containing felspar. Possibly the minute amorphous granules of china-clay and some other clays may be referable to this species. (*See* H. Ries, Clays, their Occurrence, Properties, and Uses, 2nd ed., 1908.)

L. J. S.

HALOGEN. A term originally applied by Berzelius to the group of non-oxygenated electro-negative radicles, simple and compound, which combine with metals to form salts known as *haloid salts*. Usually restricted to the four elements—Fluorine, Chlorine, Bromine, and Iodine.

HALOGEN ACETIC ACIDS. Derivatives of acetic acid in which the hydrogen of the methyl group is partly or wholly replaced by a halogen.

Chloroacetic Acids.

Monochloroacetic acid $CH_2Cl{\cdot}COOH$. Prepared by passing chlorine into acetic acid alone (Hoffmann, Annalen, 102, 1), or in the presence of iodine (Müller, *ibid.* 133, 156), sulphur (Auger and Béhal, Bull. Soc. chim. [iii.] 2, 145), or red phosphorus (Russanow, J. Russ. Phys. Chem. Soc. 23, 222); by the action of chlorine on acetyl chloride in the presence of iodine (Jazukowitsch, Zeitsch. Chem. 1868, 234); by the interaction of chlorine, glacial acetic acid, and acetic anhydride at 100° (Hentschel, Ber. 1884, 17, 1286); together with acetyl chloride by the action of chlorine on acetic anhydride at 100° (Gal, Annalen, 122, 374); by the interaction of ethylene and chlorine peroxide (Fürst, *ibid.* 206, 78).

Crystallises in two modifications, α- prisms, m.p. 61·8°; β- plates, m.p. 56·01°. By evaporating an aqueous solution or by melting the solid substance, the β- modification is produced; this changes to the α- form on the addition of a crystal of the latter (Pickering, Chem. Soc. Trans. 1895, 665, 670; *cf.* Tollens, Ber. 1884, 17, 665; Tanatar, J. Russ. Phys. Chem. Soc. 24, 694); b.p. 185°–187°, 104°–105°/20 mm. (Sudborough and Lloyd, Chem. Soc. Trans. 1899, 476); sp.gr. 1·3978 at 64·5°; hydrates (Colles, *ibid.* 1906, 1252); heat of solution

(Pickering, *l.c.*; Luginin, Ann. Chim. Phys. [v.] 17, 251; Tanatar, *l.c.*); heat of combustion 171·0 Cals. (Berthelot, *ibid.* [vi.] 28, 567); electrical conductivity (Kortright, Amer. Chem. J. 18, 368); magnetic rotation (Perkin, Chem. Soc. Trans. 1896, 1236); esterification constant (Sudborough and Lloyd, *l.c.*; *cf.* Lichty, Amer. Chem. J. 1895, 17, 27; 1896, 18, 590). Readily soluble in cold water, but on heating the solution decomposes into hydrochloric and glycollic acids (Buchanan, Ber. 1871, 4, 340, 863; Thomson, Annalen, 200, 75; Bevan, Proc. Camb. Phil. Soc. 1906, 13, 269; Senter, Chem. Soc. Trans. 1907, 460). Metallic hydroxides of the type R′OH decompose it, yielding glycollic acid, whilst those of the type $R''(OH)_2$ yield diglycollic acid (Schreiber, J. pr. Chem. [ii.] 13, 346). By heating salts of chloroacetic acid with water in a sealed tube glycollic acid is produced (Kastle, Amer. Chem. J. 1892, 14, 586; Kastle and Keiser, *ibid.* 1893, 15, 471; *cf.* Euler, Ber. 1906, 39, 2726). On distilling the acid *in vacuô* with phosphorus pentoxide, the anhydride

$$(CH_2ClCOO)_2O$$

is produced, whilst by distilling the acid through a heated tube, carbon monoxide, hydrogen chloride, *sym*-dichloromethyl ether and trioxymethylene are the products (Grassi-Cristaldi, Gazz. chim. ital. 27, ii. 502). On heating with 4 parts of phosphorus pentachloride, it yields carbon tetrachloride and other products (Michael, J. pr. Chem. [ii.] 35, 96); with ammonia glycine is produced. By interaction with sodium sulphide and sulphur in alkaline solution a dithioglycollic acid is produced, which on reduction, yields thioglycollic acid (Kalle & Co. D. R. P. 180875; Chem. Soc. Abstr. 1907, i. 1008). By the electrolysis of the potassium salt acetic acid, carbon dioxide and chlorine are formed, hydrogen not being evolved until the potassium salt is completely decomposed (Lassar Cohn, Annalen, 251, 335; *cf.* Bunge, J. Russ. Phys. Chem. Soc. 24, 690). By heating the dry silver salt, silver chloride and glycollide are produced (Beckurts and Otto, Ber. 1884, 14, 576). The sodium salt or the ethyl ester react with potassium cyanide to yield the corresponding derivatives of cyanacetic acid (Phelps and Tillotson, Amer. J. Sci. 1908, [iv.] 26, 267, 275). For interaction with tertiary amines to yield betaïnes, *v.* Reitzenstein, Annalen, 1903, 326, 305; with aniline, *v.* Vallée, Bull. Soc. chim. 1905, [iii.] 33, 966; with hydroxylamine, *v.* Rivals, Compt. rend. 1896, 122, 1489; with thiocyanic acid or its salts, *v.* Nencki, J. pr. Chem. [ii.] 16, 1; Jäger, *ibid.* 17; with phenols, *v.* Saarbach, *ibid.* 21, 151; with nitrogen sulphide, *v.* Francis, Chem. Soc. Trans. 1905, 1839.

Methyl ester. Prepared by passing chlorine into methyl acetate at 110°–120° (Censi, Bull. Soc. Ind. Mulhouse, 70, 311), and as ethyl ester (*q.v.*); b.p. 115° (Censi, *l.c.*), 130° at 740 mm. (Schreiner, Annalen, 197, 8; *cf.* P. Meyer, Ber. 1875, 8, 1152); sp.gr. 1·2352 at 19·2° (Henry, J. 1885, 1329).

Ethyl ester. Prepared by the interaction of chloracetyl chloride and alcohol (Willm, Annalen, 102, 109), or by the action of alcohol on monochloroacetic acid in the presence of sulphuric acid (Conrad, *ibid.* 188, 218); b.p. 144·5°–144·9° at 754·2 mm.; sp.gr. 1·1585 at 20°/4° (Brühl, *ibid.* 203, 209). Condensation products are formed with ethyl sodiomalonate (Michael, Ber. 1905, 33, 3217); benzylamine (Mason and Winder, Chem. Soc. Trans. 1894, 628); phenylhydrazine (Reissert, Ber. 1895, 28, 1231; Busch, Schneider and Walter, *ibid.* 1903, 36, 3877; Meussdörffer, J. pr. Chem. 1907, [ii.] 75, 121); substituted ureas (Dixon, Chem. Soc. Trans. 1897, 628); magnesium ethyl bromide (Süsskind, Ber. 1906, 39, 225); magnesium phenylamine iodide (Bodroux, Compt. rend. 1905, 140, 1597).

Dichloroacetic acid $CHCl_2·COOH$. Prepared by chlorinating acetic acid (Maumene, Annalen, 133, 154; Müller, *ibid.* 159); by the interaction of chloral and potassium cyanide (Wallach, Ber. 1873, 6, 114; Annalen, 173, 295; Kötz, Chem. Soc. Abstr. 1910, i. 151); by passing chlorine into phloroglucinol (Hlaziwetz, Annalen, 155, 132; Zincke and Kegel, Ber. 1889, 22, 1476); by the interaction of perchlorethylene and sodium ethoxide at 120° (Geuther and Fischer, J. 1864, 316); of hexachlorotriketohexylene and water (Zincke and Kegel, *l.c.*); of pyrrol and sodium hypochlorite (Ciamician and Silber, Ber. 1885, 18, 1764); of trichloroacetic acid and sodium or barium hydroxides (Pinner, *ibid.* 757); by hydrolysing the ethyl ester (*q.v.*).

Colourless liquid, m.p. −10·8° (Pickering, Chem. Soc. Trans. 1895, 667); b.p. 189°–191°; sp.gr. 1·5724 at 13·5°; mag.rot. (Perkin, *ibid.* 1896, 1236); esterification constant (Sudborough and Lloyd, Chem. Soc. Trans. 1899, 476). Slowly decomposed by heating with water in a sealed tube at 100°, more rapidly with sodium or barium hydroxides (*cf.* Timoféeff, J. Russ. Phys. Chem. Soc. 1904, 36, 255). By heating with silver oxide and a small quantity of water silver chloride and glyoxylic acid are produced (Beckurts and Otto, Ber. 1881, 14, 583). On electrolysis of an aqueous solution hydrogen, carbon monoxide, carbon dioxide, and an oil containing chlorine are produced (Troeger and Ewers, J. pr. Chem. [ii.] 58, 125). The potassium salt yields potassium chloride, trichloroacetic acid, and other products on dry distillation (Friedrich, Annalen, 206, 244). Dichloroacetic acid reacts with phosphorus pentachloride (Michael, Amer. Chem. J. 9, 215); aniline and its homologues (Cech and Schwebel, Ber. 1877, 10, 179; Heller, Annalen, 1904, 332, 247; 1908, 358, 349; Ber. 1908, 41, 4264; Ostromisslensky, *ibid.* 1907, 40, 4972; 1908, 41, 3019; Heller and Aschkenasi, Annalen, 1910, 375, 261); thiourea (Dixon, Chem. Soc. Trans. 1893, 816); nitrogen sulphide (Francis, *ibid.* 1905, 1838).

Methyl ester, b.p. 142°–144° (Wallach, Annalen, 173, 299); sp.gr. 1·3808 at 19·2° (Henry, *l.c.*).

Ethyl ester. Prepared by chlorinating alcohol (Altschul and Meyer, Ber. 1893, 26, 5757); by the interaction of chloral, alcohol, and potassium cyanide (Wallach, *ibid.* 1876, 9, 1212; 1877, 10, 1526); or of dichlorinated vinyl ethers and alcohol (D. R. PP. 209268, 210502, 212592; Chem. Soc. Abstr. 1909, i. 453, 694, 873); b.p. 157·7° at 754·6 mm. (Schiff, Annalen, 220, 108); sp.gr. 1·2821 at 20°/4° (Brühl, *ibid.* 203, 22). With sodium or silver it yields maleic ester (Tanatar, Ber. 1879, 12, 1563).

Trichloroacetic acid $CCl_3·COOH$. Prepared by chlorinating acetic acid in the sunlight (Dumas, Annalen, 32, 101); by the oxidation of chloral with fuming nitric acid (Kolbe, *ibid.* 54, 183; Clermont, Ann. Chim. Phys. [vi.] 6, 135; Judson, Ber. 1870, 3, 782; Thurnlackh, Annalen, 210, 63; Tommasi and Meldola, Chem. Soc. Trans. 1874, 314), chromic acid (Clermont, Compt. rend. 76, 774), or potassium permanganate (Clermont, *ibid.* 86, 1270).

M.p. 57° (Sudborough and Lloyd, Chem. Soc. Trans. 1899, 476); sp.gr. 1·6298 at 60·6°; heat of combustion (const. press.) 92·8 Cals. (Berthelot, Ann. Chim. Phys. [vi.] 28, 569); electrical conductivity (Rivals, Compt. rend. 125, 274; Ostwald, Zeitsch. physikal. Chem. 1, 100; 3, 177; Carrara, Gazz. chim. ital. 27, i. 207); esterification constant (Sudborough and Lloyd, *l.c.*; Kailan, Monatsh. 1908, 29, 799); mag.rot. (Perkin, Chem. Soc. Trans. 1896, 1236). At 300° it decomposes into triacetyl chloride, carbon dioxide, and hydrogen chloride (Engler and Steude, Ber. 1893, 26, 1443), whilst the silver salt yields the anhydride, silver chloride, carbon monoxide, and carbon dioxide (Beckurts and Otto, Ber. 1881, 14, 576); for sodium salt, *cf.* Henry, *ibid.* 1879, 12, 1844. At 200° with iodine trichloride perchloromethane, hydrogen chloride, and carbon dioxide are produced (Krafft, *ibid.* 1876, 9, 1049). Chloroform and carbon dioxide are produced by heating the acid with water or alkalis (Dumas, *l.c.*; Otto, Ber. 1871, 14, 589; Seubert, *ibid.* 1875, 18, 3342), potassium cyanide (Bourgoin, Compt. rend. 94, 448), aniline (Goldschmidt and Braüer, Ber. 1906, 39, 109), tertiary bases (Silberstein, *ibid.* 1881, 17, 2664), antipyrine (Stollé, Ber. Deut. pharm. Ges. 1910, 20, 371), or with resorcinol or cresol, but phenol or thymol yield hydrogen chloride, carbon monoxide, and phosgene (Anselmino, *ibid.* 16, 390). Reduction with potassium amalgam or hydriodic acid gives acetic acid. The sodium or zinc salt yields on electrolysis trichloromethyl trichloroacetate (Elbs and Kratz, J. pr. Chem. [ii.] 55, 502). For compounds with aldehydes and ketones, *v.* Koboseff, J. Russ. Phys. Chem. Soc. 1903, 35, 652; Plotnikoff, *ibid.* 1904, 36, 1088; 1905, 37, 875; Ber. 1906, 39, 1794).

Methyl ester. B.p. 152·3°–152·5° at 765·3 mm. (Schiff, Zeitsch. physikal. Chem. 1, 379; *cf.* Anschutz and Haslam, Annalen, 253, 124); sp.gr. 1·4892 at 19·2° (Henry, J. 1885, 1329).

Ethyl ester. Prepared by the interaction of trichloroacetic acid and alcohol with sulphuric acid (Clermont, Compt. rend. 1901, 133, 737), or with hydrogen chloride (Spiegel, Ber. 1907, 40, 1730); b.p. 164°; sp.gr. 1·369 at 15° (Claus, Annalen, 191, 58; Brühl, *ibid.* 203, 22; Schiff, *ibid.* 220, 108). With ammonia it yields the amide; with sodium ethoxide, orthoformic ester, sodium ethyl carbonate, and sodium chloride are the products (Klein, Chem. Soc. Trans. 1877, i. 291.

Bromoacetic Acids.

Monobromoacetic acid $CH_2Br{\cdot}COOH$. Prepared by the action of bromine on acetic acid, either alone (Perkin and Duppa, Annalen, 108, 106) or in the presence of carbon disulphide (Michael, Amer. Chem. J. 5, 202), or of sulphur (Genvresse, Bull. Soc. chim. [iii.] 7, 364); by the interaction of chloroacetic and hydrobromic acids at 150° (Demole, Ber. 1876, 561); by the oxidation of ethylene dibromide with fuming sulphuric acid (Kachler, Monatsh. 2, 559), or of monobromoacetylene in alcoholic solution by air (Glöckner, Annalen, Suppl. 7, 115).

M.p. 49°–50°; b.p. 117°–118°/15 mm. (Sudborough and Lloyd, Chem. Soc. Trans. 1899, 477), 196° (Lassar-Cohn, Annalen, 251, 342). On heating an aqueous solution of the acid it is slowly decomposed into glycollic acid (Senter, Chem. Soc. Trans. 1909, 1828). Electrical conductivity (Ostwald, Zeitsch. physikal. Chem. 3, 178; Kortright, Amer. Chem. J. 18, 368). By heating the acid with silver powder at 130°, succinic acid is formed, whilst with silver nitrate silver glycollate is produced (Senter, Chem. Soc. Trans. 1910, 346). Nitrogen sulphide yields bromoacetamide and bromodiacetamide (Francis, *ibid.* 1905, 1839). The sodium salt heated *in vacuô* yields glycollide. The potassium salt gives on electrolysis acetic acid, bromine, and carbon dioxide, no hydrogen being evolved until the potassium salt is completely decomposed (Lassar-Cohn, *l.c.*). Monobromoacetic acid has been used as a reagent for detecting albumin in urine (Boymond, J. Pharm. Chim. [v.] 20, 482).

Methyl ester. Prepared by heating methyl alcohol and monobromoacetic acid in sealed tubes at 100° (Perkin and Duppa, Annalen, 108, 109); b.p. 144°.

Ethyl ester. Prepared as methyl ester, or together with other products by the interaction of sodium ethoxide and bromine (Sell and Salzmann, Ber. 1874, 7, 496); b.p. 159°. It undergoes numerous condensations: with magnesium it yields ethyl acetoacetate and ethyl γ-bromoacetoacetate (Stolle, Ber. 1908, 41, 954); with ethyl oxalylacetate, ethyl citrate (Lawrence, Chem. Soc. Trans. 1897, 458); with ethyl sodioacetoacetate, ethyl acetosuccinate (Sprankling, *ibid.* 1165); with ethyl dimethylacetoacetate, ethyl ααβ-trimethyl-β-hydroxyglutarate (Perkin and Thorpe, *ibid.* 1178).

For other esters, *v.* Clarke, *ibid.* 1910, 428; Steinlen, Bull. Acad. roy. Belg. [iii.] 34, 101; Kunckell and Scheven, Ber. 1898, 31, 172).

Dibromoacetic acid $CHBr_2{\cdot}COOH$. Prepared by the action of bromine on acetic acid alone (Perkin and Duppa, Annalen, 110, 115), or in the presence of sulphur (Genvresse, Bull. Soc. chim. [iii.] 7, 478); by the hydrolysis of the ethyl ester (*q.v.*); m.p. 48°; b.p. 232°–234°; esterification constant, *v.* Sudborough and Lloyd, Chem. Soc. Trans. 1899, 477. The silver salt, heated with water, yields silver bromide, glyoxylic acid, and dibromoacetic acid (Perkin, *ibid.* 1877, i. 91).

Ethyl ester. Prepared by the action of bromine on ethyl acetate at 160°; by passing bromine into alcohol (Schäffer, Ber. 1871, 4, 368); by the interaction of 4 parts of bromal hydrate with 1 part of alcoholic potassium cyanide (Remi, J. Russ. Phys. Chem. Soc. 7, 263); b.p. 192°.

Tribromoacetic acid $CBr_3{\cdot}COOH$. Prepared by the oxidation of bromal with fuming nitric acid (Schäffer, Ber. 1871, 4, 370; Gal, Compt. rend. 77, 786) or by heating an aqueous solution of malonic acid with bromine (Petriew, Ber. 1875, 8, 730). Monoclinic plates, m.p. 131° (Sudborough and Lloyd, Chem. Soc. Trans. 1899, 477; *cf.* Gal, Annalen, 129, 56); electrical conductivity, *v.* Swartz, Chem. Zentr. 1898, ii. 703). On heating at 245° bromine and hydrogen bromide are evolved. By heating an aqueous solution of the acid or its salts, bromoform is produced. For compounds with aldehydes and ketones, *v.* Koboseff, J. Russ. Phys. Chem. Soc. 1903, 35, 652; Plotnikoff, *ibid.* 1908, 40, 64, 1238).

Ethyl ester. Prepared by passing hydrogen chloride into a cooled alcoholic solution of tribromoacetic acid (Broche, J. pr. Chem. [ii.] 50, 98); b.p. 225°.

Chlorobromoacetic Acids.

Chlorobromoacetic acid $CHClBr{\cdot}COOH$. Prepared by heating monochloroacetic acid (1 mol.) with bromine (1 mol.) in sealed tubes at 160° (Cech and Steiner, Ber. 1875, 8, 1174). Pungent liquid, b.p. 201°; *ethyl ester,* b.p. 160°–163°; *amide,* m.p. 126°.

Monochlorodibromoacetic acid $CClBr_2{\cdot}COOH$. Prepared by heating monochlorodibromoacetaldehyde with fuming nitric acid (Neumeister, Ber. 1882, 15, 603); rhombic plates, m.p. 89°; b.p. 232°–234°, with decomposition. Potassium hydroxide converts it, on heating, into monochlorodibromomethane.

Dichloromonobromoacetic acid $CCl_2Br{\cdot}COOH$. Prepared by heating dichloromonobromoacetaldehyde with fuming nitric acid (Neumeister, *l.c.*); prisms, m.p. 64°; b.p. 215° with decomposition; readily soluble in water or alcohol. Potassium hydroxide converts it, on heating, into dichloromonobromomethane.

Iodoacetic Acids.

Mono-iodoacetic acid $CH_2I{\cdot}COOH$. Prepared by decomposing the ethyl ester (*q.v.*) with baryta water (Perkin and Duppa, Annalen, 112, 125); by heating acetic anhydride with iodine and iodic acid (Schützenberger, Zeitsch. Chem. 1868, 484). Prismatic needles, m.p. 82°; electrical conductivity (Walden, Zeitsch. physikal. Chem. 1892, 10, 647); esterification constant (Sudborough and Lloyd, Chem. Soc. Trans. 1899, 478).

Methyl ester. Prepared in the same manner as the ethyl ester (Aronstein and Kramps, Ber. 1881, 14, 604); b.p. 169°–171°.

Ethyl ester. Prepared by the interaction of ethyl chloro- or bromoacetate, potassium iodide, and alcohol (Perkin and Duppa, *l.c.*); together with other products by heating di-iodoacetylene with excess of alcoholic potassium hydroxide (Nef, Annalen, 298, 348). Colourless oil with a penetrating smell; b.p. 69°/12 mm.; 75°–78°/16 mm. (Tiemann, Ber. 1898, 31, 825).

Di-iodoacetic acid $CHI_2{\cdot}COOH$. Prepared by the interaction of 1 part of malonic acid with 1 part of iodic acid in 4 parts of water; carbon dioxide is evolved, the solution is cooled, filtered, and allowed to stand. After 2 or 3 days crystals of tri-iodoacetic acid separate; these are filtered off and, after heating the filtrate, the di-iodo compound separates on cooling; m.p. 110° (Angeli, Ber. 1893, 26, 596).

Ethyl ester. Prepared by the interaction of ethyl dibromoacetate and potassium iodide in alcoholic solution (Perkin and Duppa, Annalen, 117, 351), or of ethyl dichloroacetate and calcium iodide (Spindler, *ibid.* 231, 273). Yellow liquid, which cannot be distilled unchanged under atmospheric pressure.

Tri-iodoacetic acid $CI_3{\cdot}COOH$. For preparation, *v.* di-iodoacetic acid. Yellow plates, m.p. 150° with decomposition. By heating with acetic acid iodoform and carbon dioxide are produced.

HAMAMELIN. A preparation from the witch-hazel *Hamamelis virginiana* (Linn.), either green or brown in colour, depending upon whether the leaves or bark have been used.

HARDWICKIA RESIN *v.* Oleo-resins.

HARMALA. The seeds of the wild rue, *Peganum Harmala* (Linn.), or harmal seeds, have been employed from the earliest times in Eastern medicine as a stimulant, anthelmintic, or even as a narcotic. They are said to be the source of a red dye produced in Southern Russia, and they have been used in the manufacture of oil. Wild rue is an odoriferous herbaceous plant, 1–3 feet high, and inhabits Southern Europe, Asia Minor, Egypt, North-western India, and Southern Siberia (Flückiger, Pharm. J. [iii.] 2, 229).

Harmal seeds contain about 4 p.c. of two alkaloids (probably in combination with phosphoric acid), which are found for the most part in the outer portions of the seed. The first of these, *harmaline* $C_{13}H_{14}N_2O$ was discovered by Göbel (Annalen, 38, 363), the second, *harmine* $C_{13}H_{12}N_2O$ by Fritzsche (*ibid.* 64, 360; J. 1847–8, 639; Annalen, 68, 351; 68, 355; 72, 306; 88, 327; 88, 328; 92, 330; J. 1862, 377), who studied both alkaloids, and obtained numerous derivatives. Fritzsche extracts the seeds with water containing acetic or sulphuric acid, and saturates the solution obtained with common salt, which causes the alkaloids to precipitate in the form of hydrochlorides. The precipitate is dissolved in water, decolorised by treatment with animal charcoal, and the solution obtained is fractionally precipitated by ammonium hydroxide at 50°–60°. The first portion of the precipitate is harmine, and the last portion harmaline. The crude harmaline is best purified by recrystallisation from methyl alcohol (O. Fischer and Täuber, Ber. 18, 400). From methyl alcohol harmaline crystallises in small tables, or from ethyl alcohol in rhombic octahedra. It melts with decomposition at 238°. It is very slightly soluble in cold water or ether, but readily dissolves in hot alcohol. It forms a well-defined crystalline *hydrochloride*

$$C_{13}H_{14}N_2O,HCl,2H_2O\,;$$

hydrocyanide $C_{13}H_{14}N_2O,HCN$; *platinichloride* $(C_{13}H_{14}N_2O,HCl)_2PtCl_4$; *methiodide*

$$C_{13}H_{14}N_2O,MeI\,;$$

chromate $(C_{13}H_{14}N_2O)_2H_2CrO_4$; and *nitro derivative* $C_{13}H_{13}(NO_2)N_2O$. Both the hydrocyanide and the nitro derivative are bases, and combine with acids to form crystalline salts. Nascent hydrogen converts harmaline into a *dihydride* $C_{13}H_{16}N_2O$ (O. Fischer, Ber. 22, 638). Harmaline is shown by Fischer (*ibid.* 28, 2481) to be *dihydro- harmine*, and it can be converted into harmine by oxidation, which is best effected by potassium permanganate in dilute sulphuric acid solution. By oxidation with chromic acid in boiling acetic acid solution or by nitric acid both harmaline and harmine are converted into *harminic acid* $C_{10}H_8N_2O_4$. By the action of hydrochloric acid on harmaline, Fischer and Täuber obtained a brick-red crystalline powder *harmalol* $C_{12}H_{12}N_2O$, which melts at 212° with decomposition. This compound also occurs naturally in harmal seeds, and has been isolated from these by Fischer (Chem. Zentr. 1901, i. 957).

Harmine exists in harmal seeds in much smaller proportion than harmaline. It may, however, be prepared from the latter by simple oxidation, either by the action of heat on the dry chromate, or by heating an alcoholic solution of harmaline nitrate to which hydrochloric acid has been added. Harmine crystallises in four-sided prisms (Schabus, J. 1854, 525). It melts with decomposition at 257°–259°. It is very slightly soluble in water or alcohol, and slightly soluble in ether. The salts of harmine are crystalline and colourless, and in acid solution exhibit an indigo blue fluorescence. The more important are the *hydrochloride*

$$C_{13}H_{12}N_2O,HCl,2H_2O\ ;$$

the *platinichloride* $(C_{13}H_{12}N_2O,HCl)_2PtCl_4$; the *methiodide* $C_{13}H_{12}N_2O,MeI$ (F. and T.); and the two *sulphates* $(C_{13}H_{12}N_2O)_2,H_2SO_4,H_2O$, and $C_{13}H_{12}N_2O,H_2SO_4$. Fritszche prepared the following halogen and nitro derivatives of harmine all of which are bases and form crystalline salts: *dichloroharmine* $C_{13}H_{10}Cl_2N_2O$; *nitroharmine* $C_{13}H_{11}(NO_2)N_2O$; *chloronitroharmine* $C_{13}H_{10}Cl(NO_2)N_2O$; and *bromonitroharmine* $C_{13}H_{10}Br(NO_2)N_2O$. A *tetrabromide*

$$C_{13}H_{12}N_2OBr_4$$

has been obtained by Fischer.

When harmine is treated with concentrated hydrochloric acid at 140°, Fischer and Täuber find that it breaks up into methyl chloride and a new phenolic compound *harmol* $C_{12}H_{10}N_2O$, which crystallises in needles and melts at 321°. When harmol is fused with potash it yields a compound possessing both basic and acid properties, *harmolic acid*, $C_{12}H_{10}N_2O_5$, which melts at 247° (Fischer, Ber. 22, 637). Fischer and Täuber, by acting on harmine in acetic acid solution with chromic acid, obtained dibasic *harminic acid* $C_8H_6N_2(COOH)_2$. It forms silky needles, melting at 345°, at which point it decomposes into carbon dioxide and a crystalline basic sublimate of *apoharmine* $C_8H_8N_2$, m.p. 183°, from which Fischer obtained a well-defined gold salt. A *tetrabromide* $C_8H_8N_2Br_4$, and a *dihydride* $C_8H_8N_2H_2$, were also obtained. Other derivatives of harmine are described by Fischer and Buck (Ber. 38, 329). A. S.

HARMALIN. *Fuchsin v.* Triphenyl methane colouring matters.

HARMALINE, HARMALOL, HARMINE, HARMINIC ACID, HARMOL and **HARMOLIC ACID,** *v.* Harmala.

HARTIN *v.* Resins.

HARTITE *v.* Resins.

HAUERITE. *Manganese disulphide* MnS_2 *v.* Manganese.

HAUSMANNITE. *Trimanganic tetroxide* Mn_3O_4 (*v.* Manganese).

HAZELINE. Trade name for a fragrant essence obtained from the fresh bark of *Hamamelis virginiana* (Linn.) or witch-hazel. Is probably analogous to eucalyptol. Is a colourless oil, possessing a pleasant pungent smell and sweet astringent taste. Is used in the treatment of eczema, ulcers, burns, &c., and as a substitute for arnica.

HEAVY SPAR. Native barium sulphate *v.* Barytes and Barium.

HEBBAKHADE *v.* Gum resins.

HECLA POWDER *v.* Explosives.

HEDERIC ACID. An acid contained in ivy berries; *v. Ivy gum resin*, art. Gum resins.

HEDERINE. A poisonous glucoside $C_{64}H_{104}O_{19}$ found in ivy. Dextrorotary $[\alpha]_D = 16{\cdot}27°$. By hydrolysis yields rhamnose and *hederidine* $C_{26}H_{40}O_4$ crystallising in rhombic prisms, m.p. 324°, and subliming without decomposition. Hederine acts as a powerful cathartic (Houdas, Compt. rend. 128, 1463; Joanin, *ibid.* 128, 1476).

HEDERO-TANNIC ACID *v.* Gum resins.

HEDGE-MUSTARD OIL. An oil manufactured from the so-called hedge-mustard or bank-cresses (*Raphanus Raphanistrum* [Linn.]) cultivated in Hungary, and used as a substitute for rape-seed oil. The oil is brought to the market either by itself or mixed with rape-seed oil, and is occasionally sold under this latter name. The siliquous fruit of the plant mentioned bears little seeds which contain 30–35 p.c. oil. This can be for the most part obtained by pressing. It has a dark olive-green colour, and an odour and taste very similar to rape-seed oil; its density and faculty for saponifying with alkali is also nearly the same, so that it is difficult to recognise it in a mixture of the two oils. Valenta has tested the two oils as regards their behaviour with the usual reagents. On acting upon them with acids of different strength, such as sulphuric and nitric acids, a mixture of these, *aqua regia*, phosphoric acid, &c., as well as with oxidising mixtures, as potassium dichromate and sulphuric acid, or concentrated nitric acid saturated with nitric oxide, various colours are produced with both oils, by the shade and intensity of which they can be fairly readily distinguished. The following reaction is most characteristic for hedge-mustard oil: about 5 grams of the oil are saponified with potassium hydroxide and spirit with warming, and the soap thus obtained is filtered from the unchanged oil, which is golden-yellow, and almost odourless and tasteless. On adding a large excess of hydrochloric acid to the concentrated filtrate, it assumes a distinct green colour if a somewhat large portion of hedge-mustard oil be present (J. Soc. Chem. Ind. 11, 181).

HEDONAL *v.* Synthetic drugs.

HELCOSOL. *Bismuth pyrogallate v.* Bismuth, Organic compounds of; and Synthetic drugs.

HELIANTHIC ACID $C_{14}H_{18}O_3$. An acid found in sunflower seeds (Ludwig and Kromayer, Arch. Pharm. [ii.] 99, 1285).

HELIANTHIN *v.* Azo- colouring matters.

HELIOCHRYSIN *v.* Naphthalene colouring matters.

HELIOTROPE *v.* Azo- colouring matters.

HELIOTROPINE is a crystalline, volatile, poisonous alkaloid of bitter taste contained in *Heliotropium Europeum* (Linn.), and *H. Peruvianum* (Linn.) (Battandier, Répert de Pharm. 1876, 4, 648). The name is also applied to a perfume (*v.* Piperonal).

HELIUM. Sym. He. At. wt. 3·99 (Watson). This element is the lightest member of the group of inert gases discovered by Rayleigh and Ramsay. Its place in the periodic classification is before lithium.

History.—During the solar eclipse of 1868 Janssen observed in the spectrum of the solar chromosphere a line in the yellow, nearly coincident with the sodium lines D_1 and D_2, which was not attributable to any terrestrial substance. Lockyer and Frankland supposed it to be due to the presence in the sun of a new element to which they gave the name 'helium' (ἥλιος, the sun).

Helium was first obtained by Hillebrand, who found that the gas evolved from the mineral *uraninite* gave a fluted spectrum, by him attributed to nitrogen, but afterwards proved to be due to helium (Bull. U. S. Geol. Survey, 1889, 78, 43).

The discovery of terrestrial helium was made by Ramsay when searching for argon, &c., in the gases evolved from the mineral *cleveite*, and its presence in the atmosphere was first noticed by Kayser (Chem. News, 1895, 72, 89), who detected the helium line in the air-spectrum. For a complete bibliography and account of the earlier investigations on helium, *see* Ramsay, Ann. Chim. Phys. 1898, [vii.] 13.

Occurrence.—It is now known that helium is very widely distributed, though it occurs only in minute quantities. It is present in air in the proportion of 0·000056 p.c. by weight or 0·00040 p.c. by volume, *i.e.* about 1 volume of helium in 250,000 vols. of air (Ramsay, Proc. Roy. Soc. 1908, 80, A, 599). Helium also occurs in many minerals, of which the chief are *cleveite*, *brögerite*, *uraninite*, and *fergusonite*, and it has been detected in the gases of many mineral springs, *e.g.* Bath; in those of the Pyrenees (Bouchard, Compt. rend. 121, 392); of Wildbad (Kayser, Chem. Zeit. 19, 1549); and of Maizières, the gas from the latter containing 5·34 p.c. of helium (Moureux, Compt. rend. 121, 819).

The gas obtained from minerals usually consists principally of helium with about 10 p.c. of nitrogen and smaller amounts of argon, &c. In view of the chemical inertness of helium it is of interest to know in what state it exists in minerals. Ramsay and Travers have found that, by the action of heat alone, almost exactly half the total helium in the mineral is evolved, whilst by heating with sulphuric acid the whole is obtained. The evolution of gas is also in some cases accompanied by an evolution of heat, suggesting that the helium is present as an endothermic compound (Proc. Roy. Soc. 1898, 62, 325). Gray has investigated the conditions under which helium is liberated on grinding minerals, and finds that its evolution begins when the particles have a diameter of 10μ and attains a practical limit when the diameter is 3μ, 28 p.c. of the helium content being then liberated. He concludes that the helium is contained in a structure which is large compared with the molecular structure (Proc. Roy. Soc. 1909, 82, A, 301).

Strutt has investigated the accumulation of helium in rocks in geological time (Proc. Roy. Soc. 1908, 81, A, 272), and concludes that it is due to unknown favourable circumstances, as the rate of loss of helium from minerals under experimental conditions is much greater than the rate of production from radioactive emanations (*v.i.*) (Proc. Roy. Soc. 1909, 82, A, 166).

Helium occurs in the natural gas of Kansas in varying amounts: 1·84 p.c. was found in the gas at Dexter, Cowley Co., Kansas (Cady and McFarland, J. Amer. Chem. Soc. 1907, 29, 1523). It has also been found occluded in meteoric iron (Ramsay and Travers, Proc. Roy. Soc. 60, 442).

Preparation and *purification.*—The preparation of helium always involves its separation from a mixture with nitrogen, argon, krypton, &c. The mixed gases may be obtained by any of the following methods:—

(1) From 'atmospheric' nitrogen, by passing the gas over heated magnesium (Ramsay and Travers, Proc. Roy. Soc. 64, 183); or a heated mixture of magnesium and lime (Maquenne, Compt. rend. 121, 1147), when the nitrogen is absorbed and the inert gases can be collected.

(2) By fractional distillation of liquid air, according to the method of Ramsay and Travers (Phil. Trans. 1901, 197, 47). Claude has designed an apparatus for producing considerable quantities of the lighter constituents of the atmosphere (Compt. rend. 1908, 147, 624).

(3) From certain mineral springs (*v.s.*). (For methods of collecting the gases *see* Travers' Study of Gases, chap. iv., and Proc. Roy. Soc. 60, 442.) The gases from King's well, Bath, contain 0·12 p.c. of helium by volume, and have been used as a source of the gas by Rayleigh (Proc. Roy. Soc. 1896, 59, 198), the oxygen and nitrogen being separated as from air. It is calculated that this well produces about 1000 litres of helium annually.

(4) By heating certain minerals alone, or with dilute sulphuric acid or acid potassium sulphate. This is probably the best method of preparing helium, and may be carried out as follows:—

The mineral in fine powder is introduced into a wide tube of hard glass or iron sealed at one end and connected by a rubber joint with a manometer and a reservoir, in which the gas can be collected over mercury. The whole apparatus is completely evacuated and the tube slowly heated to redness. When, after some hours, the evolution of helium becomes very slow, the heating is stopped and the gas is pumped out of the reservoir (Travers' Gases, 111). Fusion with an equal weight of acid potassium sulphate in a hard glass tube gives a larger yield, but much frothing takes place, and a preferable method is to heat with dilute sulphuric acid in an evacuated flask (Travers, Proc. Roy. Soc. 1898, 64, 131). This is a comparatively cheap method of production as 1 gram of cleveite yields over 3·2 c.c. of helium, and a kilog. of the mineral can be obtained for £1.

From the mixture of gases thus obtained pure helium may be isolated by one of the following processes:—

Jacquerod and Perrot have found that quartz is permeable to helium at 1000°–1200°; therefore by surrounding a quartz tube with impure helium at that temperature and pumping away the gas from the interior it can be obtained free from nitrogen and other inert gases (Compt. rend. 1907, 144, 135). Watson has shown that this process is not practicable with some kinds of fused quartz (Chem. Soc. Trans. 1910, 812). Ramsay's method consists in introducing the impure gas into a vacuous tube containing charcoal at the temperature of liquid air (Proc. Roy. Soc. 1905, A, 76, 111). Under these conditions all gases except helium and neon are completely condensed, and the vapour pressure of neon is so much less than that of helium, that by systematic repetition of the process a perfectly pure product can be obtained (Watson, *l.c.*).

Properties.—Helium has so far resisted all efforts to cause it to combine with other elements. It appears, however, to be absorbed to some extent by the finely divided platinum deposited on the walls of a vacuum tube with platinum electrodes by the continued passage of an electric discharge (Travers, Proc. Roy. Soc. 60, 449). This affords a method of separating small amounts of helium and argon, as the latter is only slightly absorbed under these conditions. Cooke has found that zinc vapourised in helium has a vapour density 12 p.c. greater than when vapourised in nitrogen at the same temperature (Zeitsch. physikal. Chem. 1906, 55, 537). This indicates some tendency toward combination.

There is possibly some connection between the chemical inertness of the gas and the fact that its molecules are monatomic as shown by determinations of the ratio of the specific heats. Behn and Geiger, using a modification of Kundts' method, have found the value $C_p/C_v=1{\cdot}63$, which agrees with that required by theory and found experimentally in the case of other monatomic gases, *e.g.* mercury (Ber. deut. phys. Ges. 1907, 5, 657).

The following determinations of the density of helium have been made (0=16) :—

Ramsay and Travers (Phil. Trans. 1901, 197, 47) D=1·98
Olzewski (Ann. Physik. 1905, [iv.] 17, 997) D=2·00
Schierloh . . . . . . D=1·985
Onnes (Leyden, Comm. 1908, No. 108) D=2·02
Watson (Chem. Soc. Trans. 1910, 97, 827) D=1·997

The molecular weight is taken as 3·99, and as the gas is monatomic this is also the atomic weight.

The refractive index of helium is about 1·000035 for the whole of the visible spectrum, the dispersive power being very small (Scheel and Schmidt, Ber. deut. Phys. Ges. 1908, 6, 207; Hermann, *ibid.* 1908, 6, 211, 246). The accurate value of μ for the D lines is 1·00003500 (Burton, Proc. Roy. Soc. 1908, A, 80, 390; Cuthbertson and Metcalf, *ibid.* 411).

Helium is diamagnetic (Tänzler, Ann. Physik. 1907, [iv.] 24, 931). Its coefficient of solubility in water is less than that of hydrogen, being 0·0134 at 0° and 0·0138 at 20°, with a minimum at 10° (Antropoff, Proc. Roy. Soc. 1910, 83, A, 474). Helium resembles hydrogen also in that the product of pressure and volume increases with the pressure, and it is therefore used in thermometry at low temperatures.

Iron, platinum, palladium, and platinum-iridium are all impervious to helium at temperatures up to 1500° (Dorn, Phys. Ztg. 7, 312). The spectrum of helium is characterised by the presence of a strong line, D_3, in the yellow ($\lambda=5876$), which has been shown to be double, and a bright-green line ($\lambda=5016$). The colour of the glow given by the gas in a Plücker's tube varies with the pressure, being yellow at 7 mm. and green at 1–2 mm. pressure, according to the strength of one or other of these lines. This phenomenon led Runge and Paschen to assume that helium consists of two components (Nature, 1895, 52, 520). This idea has been disproved by subsequent experiments (Nature, 1897, 56, 380).

After many fruitless attempts helium was first liquefied by Onnes (Proc. K. Acad. Wetensch. Amsterdam, 1909, 11, 168; Compt. rend. 147, 421), who found that when cooled in solid hydrogen it gave the Joule-Kelvin effect on expansion through a small nozzle and could therefore be liquefied by the Linde process. From 200 litres of the gas he thus obtained over 60 c.c. of liquid helium in 3 hours.

It is a colourless mobile liquid of density 0·122, being thus the lightest liquid known. It boils at 4·5° absolute, and has a critical temperature about 5° absolute, with a critical pressure of 2·75 atmospheres. By the rapid evaporation of liquid helium a temperature below 2·5° absolute has been reached (−270·5°), but there was no indication of the formation of the solid (Onnes, Proc. K. Acad. Wetensch. Amsterdam, 1909, 12, 175). Liquid helium has a point of maximum density in the neighbourhood of 2° absolute (Onnes, Communication from Phys. Lab. of Leyden, No. 119).

A method has been described by Bordas (Compt. rend. 1908, 146, 628) for the detection of small amounts of helium by means of a Plücker tube connected with a Dewar tube containing charcoal (Dewar, Proc. Roy. Soc. 1904, 74, 127).

Tschermak has suggested the use of a vacuum tube containing helium as a standard in spectroscopy, and as a source of light in determining refractive indices, &c. (Chem. Soc. Abstr. 1902, ii. 189). Collie has found that the spectrum of helium is considerably modified by the presence of mercury vapour and recommends a helium-mercury tube containing a trace of hydrogen as a standard in spectroscopy (Proc. Roy. Soc. 1902, 71, 25).

Production of helium from radioactive elements. The gas evolved from a solution of radium bromide is a mixture of oxygen and hydrogen with a radioactive emanation, which can be obtained pure by condensation at a low temperature. When volatilised into a closed space the emanation phosphoresces and gives a characteristic spectrum, but in the course of about four days the radioactivity disappears and the spectrum changes to that of helium (Ramsay and Soddy, Proc. Roy. Soc. 1903, 72, 204; 1904, 73, 346). During this change the volume increases to three times that of the original emanation (Dewar and Curie, Compt. rend. 1904, 138, 190; Indrikson, Physikal. Zeitsch. 1904, 5, 214; Himstedt and Meyer, Ann. Physik. 1904, 15, 184).

It is probable that helium is the final product of the disintegration of radium. The rate of production of helium is 0·37 cub. mm. per day from 70 mgm. of radium chloride, and agrees with that calculated by Rutherford on the assumption that α-particles are helium atoms carrying two ionic charges (Dewar, Proc. Roy. Soc. 1908, 81, A, 280).

Helium is also a product of the disintegration of actinium (Giesel, Ber. 1907, 40, 3011), and of thorium radioactivity (Strutt, Proc. Roy. Soc. 1907, 80, A, 56). The rate of production in this case also supports the view that the α-

particle is identical with the helium atom (Soddy, Phil. Mag. 1908, [vi.] 16, 513; Physikal. Zeitsch. 1909, 10, 41).

HELKOMEN. Trade name for a basic bismuth dibromohydroxynaphthoate. Yellow odourless powder. Used as a substitute for iodoform.

HELLEBOREÏN, HELLEBORIN, HELLEBORESIN, HELLEBORETIN, *v.* BLACK HELLEBORE ROOT.

HELL-HOFFITE *v.* EXPLOSIVES.

HELMITOL. Trade name for a compound of hexamethylene tetramine (urotropine) and anhydromethylene citric acid (*v.* SYNTHETIC DRUGS).

HEMELLITHENOL *v.* PHENOL AND ITS HOMOLOGUES.

HEMIPINIC ACIDS $C_{10}H_{10}O_6$. *n-Hemipinic acid* (3 : 4-*dimethoxybenzene*-1 : 2-*dicarboxylic acid*) is a product of oxidation of narcotine (Wöhler, Annalen, 1844, 50, 17; Blythe, *ibid.* 43); of opianic acid (Beckett and Wright, J. 1876, 806); of berberine (Schmidt, Ber. 1883, 16, 2589); of corydaline (Dobbie and Lauder, Chem. Soc. Trans. 1894, 57; *ibid.* 1895, 18; *ibid.* 1897, 657; *ibid.* 1902, 146; Martindale, Arch. Pharm. 1898, 236, 214); and of other alkaloids. It is prepared by boiling the oxide of opianic anhydride with potassium hydroxide. The solution is then acidified and extracted with ether (Goldschmidt, Monatsh. 1888, 9, 766). It crystallises with ½ and also with 2 molecules of water.

Properties.—Both in the normal and the meta acids the m.p. varies with the rate of heating. When heated rapidly it has m.p. about 181° (Dobbie and Lauder, Chem. Soc. Trans. 1899, 678). It is sparingly soluble in cold water, readily so in alcohol; the aqueous solution gives an orange-yellow precipitate with ferric chloride, and no precipitate with silver nitrate solution. When heated with ammonia it yields an imide $C_{10}H_9NO_4$ (Kühn, Ber. 1895, 28, 809), the potassium salt of which when heated with ethyl iodide at 150° yields the characteristic *hemipinethylimide*; m.p. 92°–96° (Goldschmidt and Ostersetzer, Monatsh. 1888, 9, 762; Liebermann, Ber. 1886, 19, 2282; Freund and Heim, *ibid.* 1890, 23, 2906). When treated with phosphorus pentachloride at 140° hemipinic acid yields the anhydride, which is also obtained by the action of equal volumes of methyl alcohol and concentrated sulphuric acid on the acid (Beckett and Wright, *l.c.*; Wegscheider, Monatsh. 1897, 18, 649).

The *anhydride* $C_{10}H_8O_5$ forms brilliant needles; m.p. 166°–167°. It reacts with hydroxyquinol, forming *dihydroxydimethoxy fluorescein* (Liebermann and Wolbling, Ber. 1902, 35, 1782), and with resorcinol, forming *dimethoxy fluorescein* (Friedl, Weizmann, and Wyler, Chem. Soc. Trans. 1907, 1584).

Lagodzinski has synthesised alizarin from hemipinic acid by treating the latter with benzene in the presence of aluminium chloride. The aluminium compound so formed is decomposed with hydrochloric acid, and the resulting product $C_{15}H_{12}O_5,H_2O$ is dissolved in cold sulphuric acid and heated to 100°. The violet solution is poured on to ice and the mono-methyl ether of alizarin so obtained is decomposed with hydrogen iodide (Ber. 1895, 28, 1427).

The *methyl ester* exists in 2 modifications; m.p. 121°–122° and 138° respectively, the latter being the more stable form at ordinary temperature (Wegscheider, Monatsh. 1897, 18, 418, 589, 629).

Other esters (Wegscheider, *l.c.*; Monatsh. 1902, 23, 327, 381; Landau, Ber. 1898, 31, 2090; Cahn-Speyer, Monatsh. 1907, 28, 803); a number of metallic salts (Salzer, Ber. 1897, 30, 1102), and many other derivatives have been obtained (Goldschmidt, Monatsh. 1887, 8, 512; Mealen, Rec. trav. chim. 1896, 15, 282, 323; Claus and Predagi, J. pr. Chem. 1897, [ii.] 55, 171; Besterzycki and Fink, Ber. 1898, 31, 930; Wegscheider, *l.c.*, and Monatsh. 1903, 24, 375; Dobbie and Lauder, *l.c.*, amongst others).

On gentle nitration, hemipinic acid yields chiefly nitro derivatives, but on more energetic nitration 5 : 6-dinitro-2 : 3-dimethoxybenzoic acid is formed (Wegscheider, Monatsh. 1908, 29, 54, 557; *ibid.* 1910, 31, 709).

m-Hemipinic acid (4 : 5-dimethoxybenzene-2 : 3-dicarboxylic acid) is a product of the oxidation of papavarine (Goldschmidt, Monatsh. 1885, 6, 380); of laudanin (*ibid.* 13, 695); and of corydic acid (Dobbie and Marsden, Chem. Soc. Trans. 1897, 664). It is also obtained by the oxidation of trimethylbrazilin (Gilbody, Perkin, and Yates, Chem. Soc. Trans. 1901, 1400; *ibid.* 1902, 1045); of tetramethylhæmatoxylin (*ibid.* 1061); and of 4 : 5-dimethoxy-*o*-toluic acid (Luff, Perkin, and Robinson, *ibid.* 1910, 1136). It can be prepared according to the following method:—

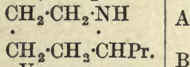
5 : 6-Dimethoxy-1-hydrindone (3 grams) is boiled with nitric acid (12 grams) and water (36 c.c.). The clear yellow solution is neutralised with sodium carbonate, mixed with hydrochloric acid until the solution turns Congo paper blue, evaporated to dryness, the residue mixed with sand and extracted in a Soxhlet apparatus with ether. The ethereal solution is dried over anhydrous sodium sulphate, evaporated, and the residue dissolved in hot water, and after digestion with animal charcoal and filtration, the solution is allowed to evaporate slowly in the air. It can also be obtained by the oxidation of *iso*-nitrosodimethoxyhydrindone with potassium permanganate, which gives an almost theoretical yield (Perkin and Robinson, Chem. Soc. Trans. 1907, 1083) and by heating aqueous dimethoxycarboxybenzoyl formic acid (Perkin, *ibid.* 1902, 1025; *see* also Perkin and Yates, *ibid.* 242).

m-Hemipinic acid crystallises with 1 and with 2 molecules of water, has m.p. about 199° (Dobbie and Lauder), and is much less soluble in water than the normal acid. Its aqueous solution gives a cinnabar orange precipitate with ferric chloride and a white precipitate with silver nitrate. On heating it forms an anhydride, m.p. 175°; when fused with potash it yields protocatechuic acid and carbon dioxide. When treated with nitric acid it gives dinitroveratrol, whilst on reduction it yields 4 : 5-dihydroxyphthalic acid (Rossin, Monatsh. 1891, 12, 488). Its *ethylimide* has m.p. 228°–230°, and unlike that from the normal acid, it is very sparingly soluble in methyl alcohol. The ethyl esters have been prepared by Rossin (*l.c.*).

HEMISINE *v.* SYNTHETIC DRUGS.

HEMLOCK. *Spotted hemlock*; *Conium. Grande ciguë*, Fr.; *Schierling*, Ger. Hemlock, *Conium maculatum* (Linn.) (Bentl. and T. 118) is an erect biennial herbaceous plant which inhabits the temperate portions of Europe and Asia as well as of North and South America. It was the essential ingredient in the poison potion administered to condemned criminals by the Greeks, and from that period to the present day it has been a well-known article of materia medica. The leaves gathered from wild British plants at the time when the fruit begins to form, and the fruits collected when fully developed, but before they have lost their green colour, are employed in medicine in this country (Brit. Pharm.; Smith, Pharm. J. [ii.] 10, 489; Harley, *ibid.* [iii.] 1, 584). The root possesses little or no activity (Lepage, J. Pharm. Chim. [v.] 6, 10). The action of hemlock on the system is that of a sedative to the motor nerves (Christison, J. Pharm. Chim. 22, 413; Hofmann, Ber. 14, 705; Kuhlmann, Arch. Pharm. [ii.] 23, 38), to which end the leaves are administered, preferably as juice or solid extract, and the fruits in the form of tincture. For further botanical and historical particulars, and the mode of detecting the accidental admixture of allied umbelliferous plants *v.* Flück. a. Hanb. 299–302.

The physiological activity of both the leaves and fruit of hemlock depends upon the presence of the strong-smelling volatile liquid alkaloid *coniine*, *conine*, *conicine*, or *circutine* $C_8H_{17}N$, together with smaller proportions of four nearly-related bases, methyl conine, conhydrine, ψ-conhydrine, γ-coniceïne (Geisecke, Brandes Arch. Pharm. 20, 97; Geiger, Berz. J. 12, 220; Planta and Kekulé, Annalen, 89, 129; Wertheim, *ibid.* 100, 328; 123, 157; Ladenburg and Adam, Ber. 24, 1161; Wolffenstein, *ibid.* 28, 302). Coniine has been prepared synthetically by Ladenburg (Ber. 19, 2579; 22, 1403) and proved to be *dextro*-(α) *propylpiperidine*



$$\begin{array}{l} CH_2\cdot CH_2\cdot NH \\ \cdot \qquad\qquad\qquad \cdot \\ CH_2\cdot CH_2\cdot CHPr. \end{array}$$

For properties and reactions *v.* VEGETO-ALKALOIDS. When hemlock leaves or fruit are triturated with an alkali a strong odour is given off, due to coniine and the other bases, with some ammonia, and by distilling such a mixture, using suitable precautions, the alkaloids are obtained. Geiger, for instance, distils the fruit with potassium carbonate or calcium hydroxide, and then by a series of operations separates the bases from the distillate. Christison distils in a similar way an alcoholic extract. Wertheim extracts with water acidulated with sulphuric acid, supersaturates the extract with lime or potash, and distils. The distillate is then neutralised with sulphuric acid, evaporated to a syrup, and treated with alcohol, which dissolves the alkaloidal sulphates, and leaves the ammonium salt, which is insoluble in that liquid. The alcohol is then removed by distillation, the residue supersaturated with potash, and extracted with ether. The ethereal solution is distilled. After the ether has come over, the distillation is conducted in a stream of hydrogen, when the first portions of the distillate contain the coniine, which may be purified by conversion into hydrochloride, recrystallisation, and regeneration by means of an alkali. Another method of isolating the alkaloids from the fruit is to extract with dilute acetic acid, evaporate the solution to a syrup in a vacuum, mix with excess of magnesia and extract with ether (Schorm, Ber. 14, 1766). V. Braun (Ber. 38, 3108) gives a method for the separation of the other bases present in the mixture of alkaloids remaining after the greater part of the conine has been removed by distillation. The percentage of alkaloids obtained varies, 0·2 p.c. of coniine being a good yield from the fruit.

Conhydrine, which is much less active physiologically than coniine, melts at 120·6°, and boils at 224·5° (719·8 mm.) (Wertheim, J. 1863, 435). Treated with phosphorus pentoxide or concentrated hydrochloric acid it loses the elements of water, and is converted into the two isomerides (α) and (β) *coniceïn* $C_8H_{15}N$ (Hofmann, Ber. 18, 7; Lellmann and Muller, *ibid.* 23, 680). γ-Coniceïne, discovered in impure conine by Wolffenstein, had been prepared previously by Hofmann (Ber. 18, 112) by treating bromconine with dilute caustic soda solution. It is a liquid, b.p. 173°, and has the same odour as conine. ψ-Conhydrine $C_8H_{17}NO$ has m.p. 100°–102°, and b.p. 229°–231°. For estimation of the alkaloids in hemlock *v.* Cripps (Pharm. J. [iii.] 18, 12 and 511) and Kremel (Ph. Post. 20, 521). Hofmann (Ber. 17, 1922) discovered *caffeïc* or *dihydoxycinnamic acid* $C_6H_3(OH)_2CH:CH\cdot COOH$ in hemlock. It contains also a *volatile oil*, said to be the product of fermentation (Landerer, Rep. Pharm. 94, 237) and the leaves yield on ignition 12·8 p.c. of *ash* (Wrightson, Pharm. J. 5, 40). A. S.

HEMLOCK SPRUCE RESIN *v.* RESINS.

HEMP. The name of various plants and of the fibres derived from them (*see* also BAST-FIBRES). The following list embraces these fibres under their commercial denominations, with the names of the plants which produce them:—

Common hemp	*Cannabis sativa* (Linn.).
African bowstring hemp	*Sansevieria guineensis* (Willd.) and others.
Bastard hemp	*Datisca cannabina* (Linn.).
Bengal or Bombay hemp	*Crotalaria juncea* (Linn.).
Bombay hemp (also)	*Hibiscus cannabinus.*
Bowstring (of India) hemp	*Sansevieria Roxburghii* and others.
Bowstring (of India) hemp (also)	*Calotropis gigantea* (Dryand.).
Brown hemp	*Crotalaria juncea* (Linn.).
Brown (Indian) hemp (also)	*Hibiscus cannabinus* (Linn.).
Florida bowstring hemp	*Sansevieria longiflora* (Sims).
Indian (in America) hemp	*Apocynum cannabinum* (Linn.).
Jubbalpore hemp	*Crotalaria juncea* (Linn.).
Madras hemp	*Crotalaria juncea* (Linn.).
Manilla hemp	*Musa textilis.*
Sisal hemp	*Agave rigida* (Mill.).
Sunn hemp	*Crotalaria juncea* (Linn.).
Virginian or Water hemp	*Acnida cannabina* (Linn.).

Of these, *Cannabis sativa*, nat. ord. *Urticaceæ*, allied to the hop plant, furnishes the true hemp. The plant is an annual, growing ordinarily to the height of 8 or 10 feet, but sometimes exceeding that limit by several feet; and it doubtless owes its origin to some part of temperate Asia. On extending its habitat, the character of the plant changed with soil and climate, giving origin to the supposed varieties *C. chinensis* and *C. indica*, the former of which is cultivated for its bast-fibres (hemp), while the latter is grown for its narcotics.

Hemp fibre examined by the microscope resembles that of flax in being round and ribbed; it has a mean diameter of 0·2 mm., and exhibits small, hairy appendages at the joints. According to Haberlandt, the breaking strain of a cord of 1 sq. mm. section is on the average 34·5 kilos. In *Manilla* hemp the fibrous bundles are oval, nearly opaque, and surrounded by a number of rectangular cells composing a dried tissue. The bundles are smooth. *Sisal* hemp forms oval fibrous bundles surrounded by cellular tissue; a few smooth ultimate fibres projecting from the bundles. It is more translucent than Manilla, and is characterised by the large quantity of spiral fibres in the bundle.

Hemp is cultivated (1) for its fibre; (2) for its resin; (3) for the oil contained in its seed; (4) for the seed itself. The tough, elastic, and durable fibre is better adapted for the manufacture of cordage and sail-cloth than any other known material. It is, moreover, employed for canvas, tarpaulin, and towelling. The finest qualities for these purposes are imported from Italy and Russia. The preparation of the fibre is similar to that of flax; the stems being bruised and 'retted' or fermented in water, after which they are again beaten out and finally 'scutched' and 'hackled' or combed (*v.* Flax). The water in which hemp has been steeped produces no evil effects on the health of a district when allowed to flow into running water, but it always destroys the fish together with certain vegetable growths (Renouard, Bied. Zentr. 1880).

The resin of hemp is employed in India as *charas*, *bhang* or *siddhi*, and *gánjá*, in which form it is used for its intoxicating and narcotic properties. *Charas* is the resin itself; *bhang* or *siddhi* consists of the dried resinous leaves and stalks; it is used for smoking, for making sweetmeats along with honey and sugar, or for forming a potable infusion. *Gánjá* is composed of the resinous fruiting heads of the female plant and is similarly employed. In 'A Report on Indian Fibres and Fibrous Substances,' Spon, 1887, it is stated that *Cannabis sativa* (var. *indica*) is chiefly, if not exclusively, cultivated on account of its narcotic principle. It has been found that the narcotic-yielding plant affords only a worthless fibre, and it is presumed that the climate of India favours the production of narcotic at the expense of the fibre. To attempt an extension of its cultivation, fiscal difficulties of a very formidable character would also have to be overcome, for the Government of India would never permit a plant of which the leaves and flowers yield so pernicious a narcotic to be widely grown. According to Hunter (The Indian Empire, and its People, History, and Products, 2nd ed. 455), excise duties are levied upon these resinous products; the hemp which furnishes them is chiefly confined to a limited area in Rájsháhí district, Bengal, and to the inner valleys of the Himalayas. The use of them is a frequent cause, not only of crime, but also of insanity. Government attempts to check consumption—first, by fixing the retail duty at the highest rate that will not encourage smuggling; and secondly, by continually raising that rate as experience allows.

The effect of hemp-resin and its compounds on the consumer is at first to exhilarate and to promote appetite. Further doses produce delirium, sleep, and sometimes catalepsy.

Hemp-resin examined by T. and H. Smith is soluble in alcohol, and has a warm, bitter, acrid taste with a slight odour. It melts between 70° and 90°, and has a pale-brown colour. It is called *cannabin*.

The oil is obtained by expression from the seed, which yields from 25 to 30 p.c. of oil, and 70–75 p.c. of residual cake used for cattle feeding, although sparingly on account of its laxative properties. This oil has a sp.gr. of 0·9307.

The essential oil of *C. sativa* was prepared by L. Valenta (Gazzetta, 10, 479–481) by distilling the fresh leaves with water and agitating the resulting milky distillate with ether. The oil dried over calcium chloride and distilled repeatedly from sodium is colourless and mobile (b.p. 256°–258°). The sp.gr. referred to water is 0·9292. The analysis agreed with the formula $C_{15}H_{24}$; the vapour density could not be determined, as it decomposes at 300°. The essential oil mixes in all proportions with alcohol, ether, or chloroform.

The seeds themselves are used as food for birds, some kinds of which are inordinately fond of them. They are roundish, ovate, of a grey colour, and contain 34 p.c. of oil and 16 p.c. of albuminoids.

HEMP SEED OIL. Hemp seed is obtained from the seeds of the hemp plant, *Cannabis sativa* (Linn.). The hemp plant is cultivated in France, Belgium, Germany, Northern Italy, Algeria, North America, India, Manchuria, and Japan. A large quantity of the seed is still grown in France, where the oil is expressed for commercial purposes. The seeds yield about 30 p.c. of oil. The colour of the freshly-expressed oil is light-green to greenish-yellow, which becomes brownish-yellow on keeping.

Hemp seed oil contains a few p.c. of solid glycerides, most likely palmitin, with a small amount of stearin or arachin. The liquid fatty acids in hemp seed oil consist of linolic acid, and smaller quantities of oleic, and linolenic (and *iso*linolenic (?)) acids.

Hemp seed oil is used as a paint oil, though less frequently in this country than on the Continent. Considerable quantities are used on the Continent for making soft soap, characterised by a dark-green colour. The lower qualities of hemp seed oil are stated to be used in the manufacture of varnishes. J. L.

HENBANE. *Hyoscyamus. Jusquiame*, Fr.; *Bilsenkraut*, Ger.

Henbane, *Hyoscyamus niger* (Linn.) (Bentl. a. Trim. 194), is one of the group of poisonous plants belonging to the natural order *Solanaceæ* and is nearly related to belladonna, stramonium, and duboisia. It has been employed in medicine since the 7th century and an allied species, having similar properties, *H. albus* (Linn.) was known to Dioscorides. There are two varieties of *H. niger*, one an annual and the other a biennial. Both are to be obtained in the market, but the leaves or green tops of second-year plants of the biennial variety are the most active and should alone be employed in medicine. The seeds possess still greater activity, but they are only used in the manufacture of alkaloid. Henbane is a coarse hairy erect herb with pale-yellow flowers marked with purple veins, and the whole plant evolves an unpleasant odour. It occurs wild throughout Britain and most parts of Europe, Asia, and Northern Africa, and has been naturalised in North and South America. Henbane is employed as a sedative, anodyne, or hypnotic, and, like belladonna and stramonium, it dilates the pupil of the eye. Its activity is destroyed by the presence of free alkali, with which it should therefore not be administered (Garrod, Pharm. J. 17, 462; 18, 174).

The active constituents of henbane are two isomeric alkaloids. The one, *hyoscyamine* $C_{17}H_{23}NO_3$, was first obtained in a pure state by Geiger and Hesse (Annalen, 7, 270) and more completely studied by Hohn and Reichardt (Annalen, 157, 98); the other, present in much smaller proportion, *hyoscine* $C_{17}H_{23}NO_3$, was discovered by Ladenburg (Annalen, 206, 282). Hyoscyamine also occurs together with atropine in belladonna and stramonium (*v.* DATURA), and 'duboisine,' the alkaloid of *Duboisia myoporoides* (R. Br.), is identical with hyoscine (Ladenburg and Petersen, Ber. 20, 1661). Both hyoscyamine and hyoscine, like atropine, are mydriatic alkaloids.

To obtain hyoscyamine from henbane seeds Höhn and Reichardt first deprive them of fixed oil by treatment with ether and then exhaust by means of alcohol acidified with sulphuric acid. The clear extract, after removal of the alcohol by distillation, is almost neutralised by soda and precipitated with tannic acid. The moist precipitate is mixed with lime and extracted with alcohol. The alcoholic solution is acidified, concentrated, and purified by washing with ether. The alkaloid is then set free by the addition of soda and isolated by extraction with ether. Other somewhat similar methods have been suggested by Rennard (Neues Rep. Pharm. 17, 91), Thorey (Pharm. J. [iii.] 12, 874), and Thibaut (Chem. Zentr. 1875, 565). Duquesnel (J. Pharm. Chim. [v.] 5, 131) extracts the seeds with hot 90 p.c. alcohol containing tartaric acid, and from the solution obtained removes the alcohol by distillation. There remains a residue of two layers, a lower syrupy and an upper oily layer, which latter is found to contain most of the alkaloid, perhaps in combination with a fatty acid. This is extracted by treating the oil with water acidified with sulphuric acid. The solution is nearly neutralised with potassium bicarbonate, concentrated to a syrup, and extracted with alcohol, which leaves potassium sulphate undissolved. The alcohol is removed from the solution by distillation, and the residue, diluted with water and treated with a slight excess of potassium bicarbonate, is extracted with chloroform. The crude hyoscyamine is removed from the chloroform solution by water acidified with sulphuric acid, is purified by treatment with animal charcoal, and the solution is then concentrated to a syrup. The alkaloid is set free by an excess of calcium carbonate, and mixed with sand, is dried over sulphuric acid. Finally, treatment with chloroform extracts the hyoscyamine and yields it on evaporation in large prismatic needles.

Hyoscyamine melts at 108·5° (Ladenburg) and dissolves more readily in water and dilute alcohol than atropine. It is lævorotatory. By the action of barium hydroxide or hydrochloric acid hyoscyamine yields, in the same manner as atropine, *tropine* $C_8H_{15}NO$ and *tropic acid* $C_9H_{10}O_3$ (Ladenburg, Ber. 13, 254 and 607), but is distinguished from that base by its metallic derivatives. *Hyoscyamine aurichloride*

$$C_{17}H_{23}NO_3,HCl,AuCl_3$$

melts at 159°, whilst the isomeric atropine aurichloride melts at 137°. The appearance and solubility of the two salts are also different (Ladenburg). Hyoscine, which is obtained from the mother liquors after crystallisation of hyoscyamine, is a syrupy liquid. It can, however, be obtained in crystals melting at about 55° (Hesse, Annalen, 271, 100). The aurichloride melts at 198°. Hyoscine is identical with scopolamine, but the commercial scopolamine is not obtained from this source (*cf.* VEGETO-ALKALOIDS).

Brandes, who analysed henbane seeds, found 24 p.c. of *fixed oil* (Berz. J. 21, 180); a substance 'hyoscypicrin,' supposed to be a glucoside, was obtained by Höhn and Reichardt; and the presence of potassium nitrate in the leaves was pointed out by Thorey and in the medicinal extract by Attfield (Pharm. J. 3, 447).

Hyoscyamus muticus (Linn.), a species of henbane occurring in certain parts of India, and used in Indian medical practice, has been examined by Dunstan and Brown (Chem. Soc. Trans. 75, 72), who find hyoscyamine to be the only alkaloid present in any notable quantity. A. S.

HENDECATOIC or UNDECATOIC ACIDS $C_{11}H_{22}O_2$.

1. *n-Undecylic acid* $CH_3[CH_2]_9COOH$ is a crystalline solid having a faint smell of caproic acid; it is obtained by the reduction of undecylenic acid or by the oxidation of methylundecylketone; m.p. 28·5°; b.p. 228° (160 mm.) (Krafft, Ber. 1879, 1664).

2. *Methyl dibutyl acetic acid*

$$[C(CH_3)_3]_2C(CH_3)COOH$$

is obtained with other products by the oxidation of *iso*tributylene. A white crystalline solid, insoluble in water, but soluble in alcohol or ether; m.p. 66°–70°; b.p. 260°.

3. *Umbellulic acid* $C_{11}H_{22}O_2$. The nuts of the Californian bay tree (*Umbellularia Californica* [Nutt.]) contain about 60 p.c. of a fat easily soluble in ether. It is a white, hard, tallowy mass m.p. 31°. By saponification with caustic potash and decomposition with hydrochloric acid, the acid is obtained as a white solid with a faint odour and very disagreeable and irritating taste; m.p. 31°–34°; b.p. 275°–280°. Its alkyl esters are colourless mobile liquids of agreeable odour (Spillman and O'Neill, Amer. Chem. J. 1882, 206). Possibly identical with *cocinic acid* found by Saint-Evre in cocoa-nut oil, and with the *undecylic acid* of Krafft (*v. supra*).

HENDECENOIC ACID $C_{11}H_{20}O_2$ an acid boiling at 258°–261° found in petroleum; known also as *petroleumic acid.* It is obtained from the petroleum distillate, b.p. 250°–270°, by adding sodium hydroxide and then to the alkaline extract, sulphuric acid. This is treated with alcohol and hydrochloric acid, and the resulting ester fractionated and hydrolysed with alcoholic potash (Hell and Medinger, Ber. 1874, 1217; 1877, 451).

HEPARADEN and **HEPARON** *v.* SYNTHETIC DRUGS.

HEPAR SICC. *v.* SYNTHETIC DRUGS.

HEPATIC CINNABAR *v.* CINNABAR.

HEPTOIC ACIDS $C_7H_{14}O_2$.

1. *n-Heptoic acid, œnanthylic acid*

$$CH_3(CH_2)_5COOH.$$

Obtained by the oxidation of œnanthol (Bussy, Annalen, 60, 248; Tilly, *ibid.* 67, 107; Krafft, Ber. 1882, 1717; Schorlemmer and Grimshaw, Annalen, 170, 141); also formed by the oxidation of castor-oil, of oleic acid, and of normal heptyl alcohol (Schorlemmer, Annalen, 161, 279; Tripier, Bull. Soc. chim. [iii.] 11, 99); from the normal hexyl cyanide (Franchimont, Annalen, 165, 237); and by the reduction of dextrose-carboxylic acid (Kiliani, Ber. 1886, 1130). An oily liquid; b.p. 222·4° (743·4 mm.), m.p. −10·5°, sp.gr. 0·9183, 20°/.

2. *isoHeptoic acid; α-methylhexoic acid*

$$CH_3[CH_2]_3CH(CH_3)COOH.$$

Obtained by boiling hexyl cyanide with alcoholic potash (Hecht, Annalen, 209, 309), or by the reduction of fructosecarboxylic acid (Kiliani, Ber. 1885, 3071). An oily rancid smelling liquid; b.p. 211·5° (745·8 mm.), sp.gr. 0·9138, 21°/. Soluble in 278 parts water.

3. *Isoœnanthylic acid* found among the products obtained by heating a mixture of sodium acetate and sodium *iso*valerate; b.p. 217°, sp.gr. 0·9260, 15°/ (Portsch, Annalen, 218, 66).

4. *isoAmyl acetic acid; δ-methylhexoic acid*

$$(CH_3)_2CH[CH_2]_3COOH.$$

Obtained by the action of sodium and *iso*amyl iodide upon ethyl acetate (Frankland and Duppa, Annalen, 138, 338), or by the distillation of *iso*amylmalonic acid (Paal and Hoffmann, Ber. 1890, 1498); b.p. 208°–210°, sp.gr. 0·9122, 13°/.

5. *Methyl diethyl acetic acid, αα-methylethylbutyric acid* $CH_3(C_2H_5)_2C\cdot COOH$. Obtained by prolonged heating of methyl diethyl carbinol cyanide with strong hydrochloric acid (Schdanow, Annalen, 185, 120); b.p. 207°–208° (753 mm.); almost insoluble in water.

6. *Methyl isopropyl propionic acid; βγ-dimethylvaleric acid*

$$CH_3(C_3H_7)CH\cdot CH_2\cdot COOH.$$

Obtained by heating sodium *iso*valerate with sodium ethoxide in a stream of carbon monoxide (Loos, Annalen, 202, 321); b.p. 220°.

7. *Ethylpropylacetic acid; α-ethylvaleric acid* $CH_3(CH_2)_2CH(C_2H_5)CO_2H$. Obtained by hydrolysing ethylpropylacetoacetic ester with alkali (Kiliani, Ber. 1886, 227); b.p. 209·2°.

8. *Active amylacetic acid; γ-methylhexoic acid* $CH_3(C_2H_5)CH\cdot CH_2\cdot CH_2\cdot COOH$. Obtained by heating active amylmalonic acid (Welt, Ann. Chim. Phys. [vii.] 6, 132); b.p. 221°; sp.gr. 0·9149, 20°/20°.

9. *Methylisobutylacetic acid; αγ-dimethylvaleric acid.* Obtained by heating methyl*iso*butylmalonic acid (Burrows and Bentley, Chem. Soc. Trans. 1895, 511); b.p. 204°–205°.

iso-**HEPTYLACETIC ACID** *v.* NONOIC ACIDS.

n-**HEPTYLSUCCINIC ACID**

$$C_7H_{15}\cdot CH(CO_2H)CH_2\cdot CO_2H.$$

Obtained by the reduction of hexylita-, -citra or -mesaconic acids with sodium amalgam (Fittig and Hoeffken, Annalen, 304, 337); m.p. 90°–91°.

HERCULES METAL *v.* ALUMINIUM.

HERCULES POWDER *v.* EXPLOSIVES.

HERMOPHENYL *v.* SYNTHETIC DRUGS.

HERNIARINE *v.* LACTONES.

HEROIN *v.* SYNTHETIC DRUGS.

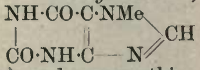
HERRING OIL is obtained from the several species of herring, *Clupea harengus* (North Sea), *C. Pallasi, C.* and *V.* (Japan). This oil is now extracted on a commercial scale in Japan, and genuine specimens of such oil have been prepared by Tsujimoto. The Japanese herring oil yields on brominating 3·82–6·5 p.c. of the octobromide of clupanodonic acid, which is a characteristic constituent of all fish oils. The herring oils produced in Europe (Norway) are not kept separate from other fish oils, and, therefore, do not represent such pure oils as those described by Tsujimoto. The iodine value of genuine herring oil lies in the neighbourhood of 130, whilst the commercial North Sea herring oil exhibits higher iodine values.

Like all other fish oils, herring oil is chiefly used in the leather industry. J. L.

HESPERIDIN *v.* GLUCOSIDES.

HESSIAN PURPLE, RED, YELLOW, *v.* AZO- COLOURING MATTERS.

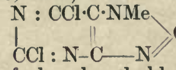
HETEROXANTHINE, *7-methylxanthine, 7-methyl-2 : 6-dioxypurine*



$$\begin{array}{l} \mathrm{NH\cdot CO\cdot C\cdot NMe} \\ \;|\qquad\qquad\;\; \| \qquad\quad \rangle \mathrm{CH} \\ \mathrm{CO\cdot NH\cdot C - N} \end{array}$$

occurs together with xanthine and paraxanthine as a constituent of normal human urine (Salomon, Ber. 1885, 18, 3406; Virchow's Archiv. 1891, 125, 554); 10,000 litres yielded 22·2 grams of the mixed bases, of which 11·36 grams was heteroxanthine (Salomon and Krüger, Zeitsch. physiol. Chem. 1898, 24, 364); it occurs also with xanthine in the urine of the dog (Salomon, *ibid.* 1887, 11, 410). Heteroxanthine appears to be a product of the metabolism of theobromine and caffeine, for when rabbits, dogs, or men are dosed with these alkaloids, heteroxanthine appears in the urine (Bondzynski and Gottlieb, Ber. 1895, 28, 1113). According to Albanese (Gazz. chim. ital. 1895, 25, ii. 298) heteroxanthine is an intermediate product in the transformation that caffeine undergoes in the organism, the methyl groups being removed one by one until xanthine is obtained, and this is converted into urea and ammonia. Heteroxanthine acts as a powerful diuretic on dogs and rabbits when hypodermically injected in small doses; larger doses are toxic, an injection of 1 gram killed a dog weighing 8 kilos. in 10 days (Albanese, *l.c.*). (*Cp.* also Krüger and Salomon, Zeitsch. physiol. Chem. 1895, 21, 169; Schmiedeberg, Ber. 1901, 34, 2556.)

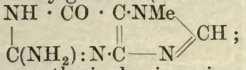
The synthesis of heteroxanthine from theobromine has been effected by Fischer (Ber. 1897, 30, 2400). When 2 : 6-dichloro-7-methylpurine



$$\begin{array}{l} \mathrm{N : CCl\cdot C\cdot NMe} \\ \;|\qquad\qquad\; \| \qquad\quad \rangle \mathrm{CH} \\ \mathrm{CCl : N{-}C - N} \end{array}$$

, obtained by the action of phosphoryl chloride on theobromine, is heated at 120°–125° with hydrochloric acid (sp.gr. 1·19), it is converted into the hydrochloride of 7-methylxanthine or heteroxanthine. Krüger and Salomon (Zeitsch. physiol. Chem. 1898, 26,

389) also obtained it by the action of nitrous acid on *epiguanine*, 7-methylguanine (2-amino-6-oxy-7-methylpurine) ; and as Fischer (*l.c.*) has synthesised epiguanine, this method of preparation is also synthetical.



Heteroxanthine is a crystalline powder; when heated gradually it melts and decomposes at 341°–342°, when heated rapidly it darkens at 360°, and melts and decomposes at 380°. It dissolves in 142 parts of boiling water (Fischer, *l.c.*), or in 7575 parts of alcohol at 17°, or in 2250 parts at the boiling temperature (Bondzynski and Gottlieb, Ber. 1895, 28, 1113). Heteroxanthine possesses both acidic and basic properties, the basic dissociation constant k_b being 3·754K; and the acidic dissociation constant k_a being 1276K, where K is the dissociation constant of water (Wood, Chem. Soc. Trans. 1906, 1840).

Heteroxanthine forms salts with acids that are readily dissociated in water, the *hydrochloride* crystallises in tufts of transparent crystals, and yields a microcrystalline platinichloride; the *sulphate* $C_6H_6O_2N_4{\cdot}H_2SO_4$ is decomposed by water. Heteroxanthine forms a characteristic *sodium* derivative $NaC_6H_5O_2N_4,5H_2O$, crystallising in plates or prisms, melting at about 300°, readily soluble in water, sparingly so in sodium hydroxide; the *potassium* derivative has similar properties and a higher melting-point (Salomon, Ber. 1885, 18, 3406; Virchow's Archiv. 1891, 125, 554). Heteroxanthine yields a crystalline precipitate with mercuric chloride, and forms a crystalline derivative with silver nitrate. It is also precipitated by copper acetate, phosphotungstic acid or lead acetate in the presence of ammonia (Salomon, *l.c.*). It is differentiated from hypoxanthine, xanthine, and guanine by the sparing solubility of its sodium derivative in sodium hydroxide; it differs from paraxanthine in being amorphous and sparingly soluble, and in not yielding a precipitate with picric acid in the presence of hydrochloric acid.

When a solution of heteroxanthine containing chlorine water and nitric acid is evaporated, the residue develops a red colour with ammonia, becoming blue on the addition of sodium hydroxide. On oxidation with potassium permanganate in concentrated sulphuric acid heteroxanthine yields three of its four nitrogen atoms as ammonia or carbamide, and the fourth as methylamine (Jolles, Ber. 1900, 33, 2126, 2120).

By electrolytic reduction in sulphuric acid solution, heteroxanthine yields 7-methyl-2-oxy-1:6-dihydropurine (Tafel and Weinschenck, Ber. 1900, 33, 3374). M. A. W.

HETOCRESOL, HETOFORM, HETOL CAFFEIN, HETRALIN *v.* SYNTHETIC DRUGS.

HEXADECYLENEDICARBOXYLIC ACID, *Tetradecylsuccinic acid* $C_{18}H_{34}O_4$. Prepared by heating hexadecylenedibromide, potassium cyanide, and alcohol at 160°–190°, and decomposing the nitrile thus formed with alcoholic potash (Krafft and Grosjean, Ber. 1890, 2355); m.p. 121°. The anhydride melts at 89°.

HEXAHYDROXYBENZENE *v.* PHENOL AND ITS HOMOLOGUES.

cyclo-**HEXANONE** *v.* KETONES.

HEXOIC ACIDS *v.* CAPROIC ACIDS.

HEXOSEPHOSPHORIC ACID *v.* FERMENTATION.

HEXOSES *v.* CARBOHYDRATES.

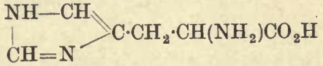
HIDDENITE. A transparent, emerald-green variety of the mineral spodumene $LiAlSi_2O_6$ (*q.v.*), used as a gem-stone. It is found with emerald in North Carolina, and has been popularly, but erroneously, known as 'lithia-emerald.' L. J. S.

HIGHGATE RESINS *v.* RESINS.

HING *v.* GUM RESINS.

HIPPURIC ACID, *Benzamino-acetic acid benzoylglycine* $NH(C_7H_5O)CH_2{\cdot}CO_2H$, an acid found in the urine of horses and cows and other herbivora and in human urine when benzoic acid is taken internally. The crude acid obtained from urine is strongly coloured; it may be purified by passing chlorine into the hot aqueous solution, filtering while hot, and rapidly cooling the filtrate. May be prepared by action of benzoic anhydride on glycocoll (Curtius, Ber. 1884, 1663). Crystallises in large trimetric prisms, soluble in water and alcohol; m.p. 187·5°. Has a slightly bitter taste and reddens litmus. Decomposes on heating, forming benzonitrile and benzoic acid (Limpricht and Uslar, Annalen, 88, 133). Its aqueous solution boiled with mineral acids yields glycocoll (glycine) and benzoic acid. Oxidation with potassium permanganate in acid solution yields carbamide (Jolles, Ber. 1900, 2834). Hippuric acid may be detected in urine by treating a few c.c. with sodium hypobromite, just sufficient being taken to decompose the carbamide and impart a permanent yellow colour to the solution. If hippuric acid is present, a characteristic orange- or brownish-red precipitate is formed (Dehn, J. Amer. Chem. Soc. 1908, 1508). For quantitative estimation in urine *v.* Henriques and Sörensen (Chem. Zentr. 1909, ii. 2043; 1910, i. 870).

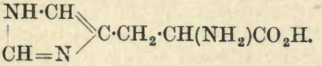
HISTIDINE, *glyoxaline-4-alanine, l-α-amino-β-glyoxaline-*4 (or 5)*-propionic acid, β-iminazole-α-aminopropionic acid*



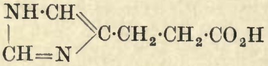
was discovered by Albrecht and Kossel (Zeitsch. physiol. Chem. 1896, 22, 176) among the hydrolytic products of the protamine sturine, which contain 12·9 p.c. histidine, 12 p.c. lysine, and 58·2 p.c. arginine (Kossel, *ibid.* 1900, 31, 207). Hedin (*ibid.* 1896, 22, 191) isolated it from the bases precipitated by silver nitrate from the decomposition products of other proteins. Kutscher (*ibid.* 1898, 25, 195) found it present in antipeptone obtained by the pancreatic digestion of fibrin. Lawroff (*ibid.* 1899, 28, 388) and Abderhalden and Rona (*ibid.* 1904, 41, 278) prepared it from thymus histon; and Koch (J. Biol. Chem. 1911, 9, 121) established its presence among the hydrolytic products of the globulin from pigs' thyroids. Histidine occurs also with arginine and lysine among the hydrolytic products of vegetable proteins, notably in the seeds and seedlings of *Picea excelsa* (Link.), *Pinus sylvestris* (Linn.), *Cucubita Pepo* (Linn.), *Lupinus luteus* (Linn.), and *Pisum sativum* (Linn.); in the case of conifer seeds 300 grams of the dry proteid yield 3 grams histidine hydrochloride, 19 grams arginine nitrate, and 3 grams lysine picrate (Schulze and

Winterstein, Zeitsch. physiol. Chem. 1899, 28, 459; 465; 1901, 33, 547).

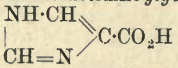
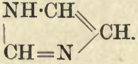
The constitution of histidine as *α-amino-β-glyoxaline-*4 (or 5)*-propionic acid,* has been established by the work of Fränkel, Pauly, Knoop and Windaus, and Pyman. Fränkel (Monatsh. 1903, 24, 229) showed that histidine contains a *carboxyl* group, since it displaces carbon dioxide from silver and copper carbonates, and an *amino* group because on treatment with hypobromite or nitrous acid one nitrogen atom is removed and a hydroxyl group introduced. Frankel, therefore, represented histidine by the partially expanded formula $NH_2{\cdot}C_5H_6N_2{\cdot}CO_2H$, and gave the name *histine* to the complex —$C_5H_6N_2$—, and *hydroxydeaminohistidine* or *hydroxyhistinecarboxylic acid* to the compound $OH{\cdot}C_5H_6N_2{\cdot}CO_2H$ obtained from histidine by the action of nitrous acid. Pauly (Zeitsch. physiol. Chem. 1904, 42, 508) confirmed the presence of the carboxyl group in histidine by preparing the methyl ester, and proved that the *histine* complex —$C_5H_6N_2$— contains an *imino*-group, because histidine yields a *dinaphthalene-β-sulphone* derivative, and forms a red dye with diazobenzenesulphonic chloride. These considerations, and the stability of the compound towards oxidising agents led Pauly to conclude that the complex *histine* contains an iminazole or glyoxaline ring, and that histidine is *α-amino-β-glyoxaline-*4 (or 5)*-propionic acid*



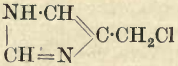
This conclusion has been confirmed by Knoop and Windaus (Beitr. Chem. Physiol. Path. 1905, 7, 144), who obtained *glyoxaline-*4 (or 5)*-propionic acid*



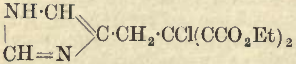
by reducing Fränkel's hydroxydeaminohistidine, and showed that it is identical with the synthetic product prepared by the action of formaldehyde and ammonia on Wolff's glyoxylpropionic acid (Annalen, 1890, 260, 79).

Knoop (Beitr. Chem. Physiol. Path. 1907, 10, 111) also showed that, by the successive oxidation of hydroxydeaminohistidine *glyoxaline-*4 (or 5)*-carboxylic acid*  is obtained, which, when heated at 286°, loses carbon dioxide and yields glyoxaline .

The complete synthesis of histidine from 4 (or 5)-chloromethylglyoxaline is described by Pyman (Chem. Soc. Trans. 1911, 1386). 4 (or 5)-Chloromethylglyoxaline (I), obtained from diaminoacetone (*ibid.* 668), condenses with ethyl sodiochloromalonate to form *ethyl* 4 (or 5)*-glyoxalinemethylchloromalonate* (II)

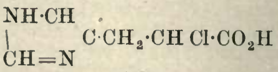


I.

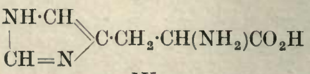


II.

This ester on hydrolysis is converted into *r-α-chloro-β-glyoxaline-*4 (or 5)*-propionic acid* (III), which reacts with ammonia to form *r-α-amino-β-glyoxaline-*4 (or 5)*-propionic acid* (IV), that is *r*-histidine



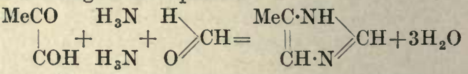
III.



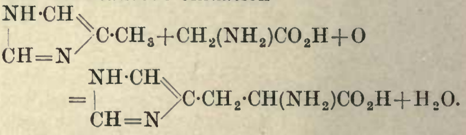
IV.

r-Histidine can be resolved by the fractional crystallisation of the salts it forms with *d*-tartaric acid into the *d*- and *l*- isomerides, and the *l*-histidine thus obtained is identical with the naturally occurring compound.

A possible explanation of the formation of histidine in the plant economy is afforded by the work of Knoop and Windaus (Beitr. Chem. Physiol. Path. 1905, 6, 392; Ber. 1906, 39, 3886; 1907, 40, 799) on the synthetic formation of iminazole derivatives from sugars and ammonia. These authors find that when a solution of glucose containing zinc hydroxide dissolved in ammonia is exposed to the sunlight at the ordinary temperature for some weeks, it is converted to the extent of 10 p.c. into 4- or 5-*methyliminazole.* It is probable that glyoxal and formaldehyde are produced as intermediate products and then react with the ammonia according to the equation



d-Mannose, *d*-fructose, *d*-sorbose, *l*-arabinose, or *l*-xylose also yield methyliminazole when similarly treated. The authors suggest that histidine may be formed naturally by the condensation of methyliminazole with glycocoll and simultaneous oxidation



Histidine crystallises from water in needles or tables, m.p. 287° (corr.); the aqueous solution has a sweet taste (Frankel, Monatsh. 1903, 24, 229; Pyman, Chem. Soc. Trans. 1911, 1397), is feebly alkaline (Hedin, Zeitsch. physiol. Chem. 1896, 22, 191), and is optically active $[\alpha]_D -39{\cdot}74°$ (Kossel and Kutscher, *ibid.* 28, 382); $[\alpha]_D -36{\cdot}7°$ (Pyman, *l.c.*).

r-Histidine crystallises in quadrilateral plates, and decomposes at 283° (corr.); *d-histidine* crystallises in monoclinic plates forming elongated hexagons; it decomposes at 287–288° (corr.). and has $[\alpha]_D + 39{\cdot}3°$ (Pyman, *l.c.*).

When histidine is administered as a food, or by intravenous injection very little (0·4 gram out of 10 grams) is recoverable as such in the urine; the urea and ammonia in the urine are largely increased, but the increase of allantoin is very slight (Abderhalden, Einbeck and Schmid, Zeitsch. physiol. Chem. 1909, 62, 322; 1910, 68, 395; Kowalewsky, Biochem. Zeitsch. 1909, 23, 1).

Salts. *l*-Histidine forms stable salts with acids and their solutions are dextrorotatory.

Monohydrochloride $C_6H_9O_2N_3{\cdot}HCl,H_2O$ forms large colourless rhombic crystals

$$a:b:c=0{\cdot}7665:1:1{\cdot}71104,$$

has $[\alpha]_D+1{\cdot}74°$, m.p. 80°, and loses H_2O at 140° (Albrecht and Kossel, Zeitsch. physiol. Chem. 1896, 22, 176; Hedin, *ibid.* 191; Kossel and Kutscher, *ibid.* 1899, 28, 382; Fränkel, Monatsh. 1903, 24, 229); the *di-hydrochloride* $C_6H_9O_2N_3{\cdot}2HCl$ is isomorphous with the mono-compound $[a:b:c=0{\cdot}76537:1:1{\cdot}77516]$, it has $[\alpha]_D+5{\cdot}3°$ to $6{\cdot}4°$ (Kossel and Kutscher, *l.c.*; Schwartze, Zeitsch. physiol. Chem. 1900, 29, 493). *Histidine cadmium chloride*

$$C_6H_9O_2N_3{\cdot}HCl,CdCl_2$$

melts and decomposes at 270°–275° (Schenck, *ibid.* 1904, 43, 72). *Histidine monopicrolonate* $C_6H_9O_2N_3{\cdot}C_{10}H_8O_5N_4$ is yellow. The *dipicrolonate* $C_6H_9O_3N_2{\cdot}2C_{10}H_8O_5N_4$ is orange (Steudel, Zeitsch. physiol. Chem. 1905, 44, 157; Brigl, *ibid.* 1910, 64, 337); the *dipicrate*

$$C_{18}H_{15}O_{16}N_9,2H_2O$$

has m.p. 86° (corr.), (Pyman, Trans. Chem. Soc. 1911. 343).

l-Histidine-d-hydrogen tartrate

$$C_6H_9O_2N_3,C_4H_6O_6$$

is easily soluble in water, crystallises in large well-defined prisms, and decomposes at 172°–173° (corr.); and has $[\alpha]_D+16{\cdot}3°$. *l-Histidine-l-hydrogen tartrate* is sparingly soluble in cold water, crystallises in clusters of prisms and decomposes at 234° (corr.), and has $[\alpha]_D-12{\cdot}1°$ (Pyman, *ibid.* 1397, 1400).

d-Histidine-d-hydrogen tartrate is sparingly soluble, decomposes at 234° (corr.), and has $[\alpha]_D+13{\cdot}3°$ (Pyman, *l.c.*).

r-Histidine mono-hydrochloride

$$C_6H_9O_2N_3{\cdot}HCl,2H_2O$$

has m.p. 117°–119° (corr.); *sesquihydrochloride*

$$(C_6H_9O_2N_3)_2{\cdot}3HCl,H_2O$$

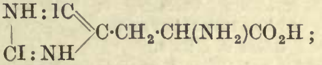
has m.p. 168°–170° (corr.); the *dihydrochloride* has m.p. 235°–236° (corr); *r-histidine monopicrate* $C_{12}H_{12}O_9N_6,H_2O$ decomposes at 180°–181° (corr.); the *dipicrate* $C_{18}H_{15}O_{16}N_9,2H_2O$ decomposes at 190° (corr.), (Pyman, *ibid*, 339).

Derivatives. *Histidine methyl ester hydrochloride* $C_5H_8N_3{\cdot}CO_2Me{\cdot}2HCl$ forms flat rhombic prisms, m.p. 196° (decomp.), the free ester is an oil (Pauly, Zeitsch. physiol. Chem. 1904, 42, 508). *Chlorohistinecarboxylic acid* (*α-chloro-β-glyoxaline-* 4 (or 5)*-propionic acid*) forms thick prisms, m.p. 191° (decomp.), the corresponding *racemic* compound decomposes at 201° (corr.) (Pyman, *ibid.* 1394), the *oxalate* of the *ester* has m.p. 161° (Windaus and Vogt, Beitr. chem. Physiol. Path. 1908, 11, 406). *Histidine anhydride* $C_{12}H_{14}O_2N_6$ forms glittering prisms, m.p. 340° (Fischer and Suzuki, Sitzungsber. K. Akad. Wiss. Berlin, 1904, 1333); the *l*-anhydride has m.p. 328° in a closed evacuated tube, crystallises with $2\frac{1}{2}H_2O$, and has $[\alpha]_D^{20°}-66{\cdot}24°$ in normal hydrochloric acid solution; the *dl-anhydride* also has m.p. 328°, and is obtained by heating the ethyl ester of histidine at 160° (Pauly, Zeitsch. physiol. Chem. 1910, 64, 75); the *picrate* decomposes at 255° (corr.); the *hydrochloride* at 320°. The *tetraiodo* derivative has m.p. 240°, and is amphoteric and forms a *silver* salt (Pauly, Ber. 1910, 43, 2243). *Histidylhistidine* $C_{12}H_{16}O_3N_6$ forms a yellow *picrate*, m.p. 165°–175° (Fischer and Suzuki, *l.c.*).

Of the *acyl* derivatives of histidine the *benzoyl* has m.p. 249° (decomp.) (Pauly, *l.c.*; Fränkel, *l.c.*); the *dinaphthalene β-sulphone*

$$C_6H_7O_2N_3(SO_2{\cdot}C_{10}H_7)_2$$

melts at 149°–150° (Pauly); *p-Nitrobenzoyl* $C_6H_8N_3O_2{\cdot}CO{\cdot}C_6H_4{\cdot}NO_2$ m.p. 251°–252° (Pauly). *Benzoyldiiodohistidine*, m.p. 161°–164°, in an evacuated tube; and *p-nitrobenzoyldiiodohistidine*, m.p. 172° (decomp.) are derivatives of the unknown diiodohistidine



they give orange-red colourations with diazobenzenesulphonic acid and sodium carbonate, and form silver salts (Pauly, Ber. 1910, 43, 2243). *d-α-Bromoisohexoyl-l-histidine methyl ester*

$$C_4H_9{\cdot}CHBr{\cdot}CO{\cdot}NH{\cdot}CH(C_4H_5N_2)CO_2Me$$

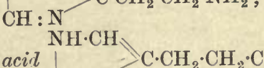
has m.p. 175° (corr.); *d-α-bromoisohexoyl-l-histidine* $C_{12}H_{18}O_3N_3Br$ has m.p. 118° (corr.); *l-leucyl-l-histidine*

$$C_4H_9{\cdot}CH(NH_2){\cdot}CO{\cdot}NH{\cdot}CH(C_4H_5N_2)CO_2H$$

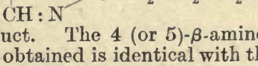
crystallises in plates or prisms, containing H_2O, which it loses at 100°/15–20 mm., and has m.p. 178° (corr.) (decomp.), the *copper* salt forms deep violet crystals; *formyl-l-histidine* has m.p. 203° (corr.) (Fischer and Cone, Annalen, 1908, 363, 107).

Colour reactions. Histidine gives the *biuret* reaction (Herzog, Zeitsch. physiol. Chem. 1903, 37, 248). It also gives the Weidel pyrimidine reaction under the following conditions: a solution of histidine hydrochloride and a little potassium chlorate is evaporated to dryness, hydrochloric acid containing one drop of nitric acid added and the solution again evaporated; on exposing the residue to ammonia fumes an intense red colour is produced, becoming reddish-violet on the addition of sodium hydroxide (Frankel, *l.c.*). With diazobenzenesulphonic chloride in the presence of sodium carbonate histidine gives a dark cherry-red colouration, becoming orange on the addition of an acid. This is an extremely delicate test for histidine, and with the exception of tyrosine no other product of protein hydrolysis gives a similar reaction (Pauly, Zeitsch. physiol. Chem. 1904, 42, 508). Histidine develops a yellow colour with bromine water; this disappears on warming, but after a time a pink colour appears, which afterwards deepens to a wine red. The reaction is sensitive with solutions of 1 : 1000, but is destroyed by too large excess of bromine water (Knoop, Beitr. Chem. Physiol. Path. 1908, 11, 356).

Decomposition. When histidine undergoes anærobic bacterial cleavage by the action of putrefying pancreas, it is converted almost quantitatively by the loss of carbon dioxide into 4 (or 5)-*β-aminoethylglyoxaline* (*β-iminazolylethylamine*)



; *iminazolylpropionic acid*



being the other product. The 4 (or 5)-*β*-aminoethylglyoxaline thus obtained is identical with the base prepared synthetically by Windaus and Vogt (Ber. 1907, 40, 3691) from ethyl iminazolylpropionate; or by Pyman (Chem. Soc. Trans. 1911, 668) from diaminoacetone, and is also identical with one of the *ergot* bases isolated by Barger and Dale (Phil. Trans. 1910, 2592), and which is also present in Popielski's *vaso-dilatin* (Barger and Dale, J. Physiol. 1911, 41, 499). It has a direct stimulating action on plain muscle; cardiac muscle is mildly stimulated, and skeletal muscle is not affected. The drug produces narcosis, and is a mild stimulant to the salivary glands and pancreas. M. A. W.

HOANG-NAN *v.* Nux vomica.

HOFMANN'S VIOLET *v.* Triphenyl methane colouring matters.

HOG GUM *v.* Gums.

HOLLANDITE. A manganese ore of essentially the same composition as psilomelane, but occurring in a crystallised condition, usually as fibrous masses and sometimes as crystals. It is a manganate with the general formula

$$mR_2''MnO_5+nR_4'''(MnO_5)_3,$$

where R″ is Mn, Ba, K_2, H_2, (Fe, Ca, Mg, Na, Co, Ni, Cu), and R‴ is Mn, Fe_2(Al). It contains about 70–75 p.c. of manganese dioxide. The colour is greyish-black, and the lustre submetallic; sp.gr. 4·70–4·95; H. 4–6. The mineral occurs abundantly in the manganese ore deposits at several places in Central India, and is largely exported from the mines at Sitapár and Bálághát. (L. L. Fermor, The Manganese Ore Deposits of India, Mem. Geol. Survey India, 38.) L. J. S.

HOLOCAINE *v.* Synthetic drugs.

HOMBERG'S PHOSPHORUS *v.* Calcium.

HOMOANTHRANILIC ACID *v.* Amino acids (aromatic).

HOMOCATECHOL *v.* *Homopyrocatechol*, Phenol and its homologues.

HOMOGENTISIC ACID *v.* Phenylacetic acid.

HOMORENON *v.* Synthetic drugs.

HOMOTERPENYLIC ACID *v.* Lactones.

HONEY. Honey is the substance secreted by the working-bee (*Apis mellifica*) from the nectar of flowers, and deposited by the insect in the wax-cells forming the honeycomb. Its essential constituents are varying quantities of the sugars, dextrose, lævulose, and sometimes cane-sugar, together with a small quantity of water. It also contains very small quantities of wax, colouring matters, aromatic substances, phosphoric acid, nitrogenous compounds, and occasionally mannitol.

The relative proportions in which the three above-named sugars occur is very variable. Thus Hehner (Analyst, 9, 164) obtained the following results from the analysis of 25 different varieties:

	Maximum	Minimum	Mean
Water . .	23·26	12·43	19·3
Glucose . .	75·34	61·42	67·2
Other constituents	16·51	8·48	13·5

In 8 cases the amount of glucose was unaltered by inversion, in 7 increased, and in the remainder slightly diminished.

Sieben (Bied. Zentr. 1885, 134) analysed 60 specimens of honey, and states that the quantity of cane-sugar may amount to as much as 4 or even 8 p.c., and that the ratio of dextrose to lævulose varies considerably, the total amount of these two sugars being 68–78 p.c. The average composition of the 60 specimens was as follows:—

Dextrose	34·71 p.c.
Lævulose . . .	39·24 „
Sucrose . . .	1·08 „
Water . . .	19·98 „
Non-saccharine matter .	5·02 „

Turning now from average results to the composition of the several varieties, we find the following table of the analysis of 9 specimens of honey from different localities (J. C. Brown, Analyst, 1878, 257).

—	England	Wales	Normandy	Germany	Greece	Lisbon	Jamaica	California	Mexico
Water expelled at 100° .	19·10	16·40	15·50	19·11	19·80	18·80	19·46	17·90	18·47
Water expelled at a high temperature and loss	7·60	6·56	4·95	11·00	7·80	6·66	7·58	8·13	10·03
Lævulose . . .	36·60	37·20	36·88	33·14	40·00	37·26	33·19	37·85	35·96
Dextrose . . .	36·55	39·70	42·50	36·58	32·20	34·94	35·21	36·01	35·47
Sucrose . . .	?	—	—	—	—	1·20	2·20	—	?
Wax, pollen, and insoluble matter . .	trace	trace	trace	trace	0·05	1·00	2·10	trace	trace
Mineral matter . .	0·15	0·14	0·17	0·17	0·15	0·14	0·26	0·11	0·07

The characteristic composition of ordinary honey can be judged from the analysis of 10 samples of genuine honey by Hoitsema (Zeitsch. anal. Chem. 1899, 439) which gave the following results:—

Specific gravity . .	1·102–1·140
Water . . .	8·3–17·8 p.c.
Rotation . . .	−9·1° to −3·0°
Ash . . .	0·12–0·34 p.c.
Pollen and wax . .	0·02–0·46 „
Reducing sugars .	71·2–74·4 „
Sucrose . . .	0·2–6·4 „

The amount of water present in honey varies with the dryness of the season and the conditions of storage, evaporation being much lessened when all the cells of the comb are closed (Graftian, Analyst, 1895, 251).

Erlenmeyer and v. Plata (Rep. Pharm. 23, 610) found that in 6 samples of good honey the amount of water varied from 17·5 to 19·5 p.c., whilst a liquid honey from Senegal contained as much as 25·6 p.c. The amount of phosphoric acid present (calculated on the dried substance) varied from 0·0123 to 0·883 p.c.

Sumatra honey, formed by *Apis indica*, contains water, dextrose, lævulose, a little wax and pollen, and 0·23 p.c. ash, but no cane-sugar or dextrin (Franchimont, Rec. trav. chim. 1, 223). An Ethiopian honey, made in hollows without wax by a kind of mosquito, gave the following result on analysis (Compt. rend. 88, 292):—

Water	25·5
Lævulose and dextrose $(\frac{1}{6})$.	32·0
Mannitol	3·0
Dextrin	27·9
Ash	2·5
Other constituents . . .	9·1

It has also been shown (Vogel, Ber. 15, 2271) that all honey contains a small quantity of formic acid, derived from the stings of the bees, and that to this is due the fact that honey keeps so well. It amounts only to 0·0011–0·0024 p.c., therefore most of the acidity of honey must be due to some other acid, possibly malic acid (Farnsteiner, Zeitsch. Nahr. Genussm. 1908, 15, 598).

The formic acid may be estimated by conversion into sodium formate, heating with conc. sulphuric acid, and measuring the volume of carbon monoxide evolved. As lactic acid also gives this gas it must be oxidised with potassium permanganate and estimated as oxalate and a correction applied (Merl, Zeitsch. Nahr. Genussm. 1908, 16, 385).

If bees be fed on dextrose only, the honey formed contains that sugar alone. Heather-fed honey, on the other hand, contains invert sugar only, whilst Cuban honey contains dextrose in larger quantity than lævulose (Röders, Chem. Zentr. 1864, 1002).

Eucalyptus honey is produced in Australia by a black bee which builds large hives on the *Eucalypti* containing as much as 5000 kilogs. of honey. The honey is a thick syrup, having a strong aromatic odour (Maquenne, Ann. Chim. Phys. [vi.] 17, 495).

Marck has given the following figures for the composition of East Indian honeys (Analyst, 1890, 196):—

Glucose, about 30 p.c. ; lævulose, 23–37 p.c. ; ash, 0·12–0·54 p.c. ; sp.gr. 1·3099–1·3586 ; rotation +13° to −2° 54′.

In the honey of *Polybia apicipennis* large crystals of cane-sugar are frequently found (J. pr. Chem. [i.] 71, 314). The honey of the Mexican honey-ant is almost a pure solution of lævulose, and when dried *in vacuô*, has the composition $C_6H_{12}O_6,H_2O$. It contains traces of a volatile acid which reduces silver salts (J. pr. Chem. [i.] 58, 430).

To obtain honey the syrup is first simply allowed to flow from the comb at the ordinary temperature, the portion thus collected being known as 'virgin-honey.' As soon as the flow ceases, the residual comb is heated and pressed, by which means a darker and less pure variety is obtained. According to Zwilling (Bied. Zentr. 1885, 67) it is best to gather the honey when it has thickened and the cells are sealed, as then sufficient sugar and formic acid are present.

The honey-syrup remains clear for a long time if kept in the dark, but on exposure to light dextrose gradually separates, and such varieties as contain that sugar in the largest quantity become sufficiently solid to be cut with a knife into pieces which are not hygroscopic. As, however, the composition of honey is so variable, the consistency and colour likewise differ considerably in the different samples. Thus Narbonne honey has a light yellow colour, and forms an almost solid mass, whereas Cuban honey is a clear and almost colourless syrup.

Honey has a sp.gr. of from 1·439 to 1·448. When diluted with water it gives a somewhat cloudy, faintly acid solution, the cloudiness being due to small quantities of proteid matter. Its specific rotatory power varies from −5·5 to +2, but dextrorotatory honey is exceptional.

Frühling has shown (Zeitsch. öffentl. Chem. 4, 410) that freshly prepared solutions of honey in cold water show an abnormal rotation, which, after some hours, becomes normal. This behaviour, which is due to 'bi-rotation,' may lead to erroneous observations unless care is taken to dissolve the honey in boiling water and to add about 0·1 p.c. of ammonia.

A pure solution of honey does not readily undergo alteration in the air, but when impure, both acid and alcoholic fermentation speedily take place. An alcoholic liquor known as 'mead' (Ger. *Meth*; Fr. *Hydromel*) has long been prepared from honey by fermentation. The process is, however, frequently unsuccessful, owing to the fact that honey does not usually contain sufficient nitrogenous food for the sustenance of the ferment. If a suitable food be added, the fermentation proceeds smoothly and with certainty (Gastine, Compt. rend. 109, 479). According to Boussingault (Ann. Chim. Phys. [iv.] 26, 362) the quantity of carbon dioxide formed during fermentation is greater, and the quantity of alcohol less, than would be expected from the amount of sugar fermented. Thus, instead of the calculated quantities of 193·6 parts of alcohol and 170 parts of carbon dioxide, he obtained 177·6 parts of alcohol, and 190 parts of carbon dioxide.

For medicinal purposes honey is purified by warming on the water-bath, and straining it through flannel which has been previously moistened with hot water. The purified compound is known as *Mel depuratum.* Dietrich (Chem. Zentr. 1877, 318) brought a filtered solution of 1 part of honey in 3 parts of water on to a dialyser, and found that 50 p.c. of the honey passed through. The solution of the crystalloids gave on evaporation a honey having an unusually pleasant aromatic taste. The colloidal liquid, in which gummy flocculæ remained suspended, gave on evaporation a syrup possessing a purely sweet, insipid, non-aromatic taste.

In order to purify honey Riecker (J. 1873, 1066) adds a little precipitated aluminium hydroxide, which carries down any foreign substances present. If ordinary honey be shaken with absolute alcohol, dextrose remains behind. Ether precipitates lævulose from the alcoholic solution, and the ethereal solution when shaken with lime loses tannic acid, whilst wax remains in solution.

Honey is frequently adulterated with starch-sugar, invert-sugar, molasses, water, &c., and owing to the wide variations in the composition of genuine honey such adulteration is frequently difficult to detect (Racine, Zeitsch. öffentl. Chem. 1902, 281).

Dextrorotatory honey was formerly regarded with suspicion (Haenle, Zeitsch. anal. Chem. 1894, 99), but it has been shown that pine-honey, and honey made by bees using honey-dew, contain a dextrin which can be isolated by precipitation with alcohol, and is strongly dextrorotatory (König and Karsch, Zeitsch. anal. Chem. 1895, 1; Raumer, *ibid.* 1896, 397; Hilger, Zeitsch. Nahr. Genussm. 1904, 189). For a detailed account of the 'honey-dextrins' of pine-honey, *see* Haenle and Scholz (Zeitsch. Nahr. Genussm. 1903, 1027).

Several methods have been recommended for distinguishing between genuine and adulterated honey. Brautigam states that genuine honey contains an albumin by the reactions of which it can be distinguished (Pharm. Zeit. 47, 109). Methods for the microscopic examination of honey have been described by Dietrich (Analyst, 1896, 255). Langer has found in natural honey an inverting ferment which can be precipitated by alcohol and tested on cane-sugar (Zeitsch. angew. Chem. 1902, 1041).

Adulteration with starch-syrup, which usually contains erythro-dextrin and amylo-dextrin can usually be detected by adding methyl alcohol to the conc. aqueous solution, when the dextrins are precipitated. The addition of molasses is best detected by testing for raffinose with basic lead acetate (Beckmann, Zeitsch. anal. Chem. 1896, 263).

Ley's reagent, an ammoniacal solution of silver oxide, when warmed with a strong solution of pure honey gives a greenish colouration, but if the honey is adulterated the liquid becomes dark-brown or black (Utz, Zeitsch. angew. Chem. 1907, 993).

If 1 gram of honey be rubbed down with ether in a mortar, the ether filtered off and evaporated, and the residue treated with a drop of a solution of 1 gram resorcinol in 100 c.c. of hydrochloric acid of sp.gr. 1·19, only a momentary pink colour will be obtained with pure honey, whilst adulterated or artificial honey will give an orange-red colour changing through cherry-red to a strong brown-red (Fiehe, Zeitsch. Nahr. Genussm. 1908, 75; Keiser, Analyst, 1909, 399).

Adulteration with cane-sugar may be detected by determining the reducing power of the honey for Fehling's solution, both before and after inversion. This, however, is not very reliable, as in cases where the bees feed on sucrose considerable quantities are found in the honey, though the larger proportion undergoes inversion in the insect's stomach (Raumer, Zeitsch. anal. Chem. 1902, 333; *see* also Lipmann Analyst, 1889, 20).

Sugar in honey is estimated by diluting with twice its volume of water, and ascertaining the sp.gr. This varies between 1·101 and 1·115. The first number corresponds to 24 p.c., and the latter to 27 p.c. of sugar in the solutions, or to 72 p.c. and 82 p.c. in the original honey (Flückiger, Pharmaceut. Chemie, [ii.] 267).

Wiley has described a process for the estimation of lævulose in honey, &c., based on the fact that its optical rotation is much diminished with rise of temperature. The observation tube of the polarimeter is jacketed, and can be cooled to zero or heated to 88° at which temperature a mixture of molecular proportions of dextrose and lævulose becomes optically inactive (J. Amer. Chem. Soc. 1896, 81).

HONTHIN *v.* SYNTHETIC DRUGS.

HOPEÏNE is a crystalline alkaloid said to be contained in wild American hops. It melts below 100° and partially sublimes below 160°. It is doubtful, however, whether it really exists (Ladenburg, Ber. 1886, 19, 783; J. Pharm. Chim. [v.] 12, 460; Williamson, Chem. Zeit. 1886, 10, 20, 38, 207, 238, 491).

HOPS *v.* BREWING.

HORDEIC ACID *v.* DODECATOIC ACID.

HORDEIN *v.* *Barley*, art. BREWING.

HORDENINE (p-*Hydroxyphenylethyldimethylamine*) $C_{10}H_{15}NO$ was discovered by Léger (Compt. rend. 1906, 142, 108) in malt culms from which it is extracted by Stas' method. The ethereal solution of the alkaloid thus obtained is evaporated to dryness and the hordenine residue is purified by repeated recrystallisation from alcohol. Its constitution was determined by Léger (Compt. rend. 1906, 143, 234, 916) and by Gaebel (Arch. Pharm. 1906, 244, 435).

Hordenine has also been synthesised from phenyl ethyl alcohol (Barger, Chem. Soc. Trans. 1909, 2194; Léger, Bull. Soc. chim. 1910, [iv.] 7, 172), and by the methylation of β-*p*-methoxyphenylethylamine hydrochloride with alcoholic potash and methyl iodide at 100° (Rosenmund, Ber. 1910, 43, 306).

Properties.—Hordenine forms colourless, almost tasteless anhydrous orthorhombic prisms, m.p. 117·8° and subliming like camphor at 140°–150°. It is readily soluble in alcohol, ether, or chloroform, but sparingly so in benzene, xylene, or toluene. It is a strong base, is alkaline towards litmus and phenolphthalein, liberates ammonia from its salts, reduces acid solutions of potassium permanganate in the cold and ammoniacal solutions of silver nitrate and iodic acid on warming. It is not attacked by concentrated sulphuric acid or by potash, but readily forms soluble salts with acids. When boiled with nitric acid it yields picric acid, and when methylated and oxidised with alkaline permanganate it gives anisic acid (Léger, J. Pharm. Chim. 1907, 25, 5; Compt. rend. 1907, 144, 488).

Hordenine sulphate crystallises in needles and has a slightly bitter taste. It forms brown crystals with iodine, but gives no precipitate with the tannins of vegetable infusions. In small doses it has a tonic action on the heart, but in toxic doses (1–2 grams per kilo) it produces the reverse effect.

It has been employed as a remedy in cases of typhoid, dysentery, enteritis, &c. It is not so energetic as digitalis, sparteine, or strophanthus, but is less toxic than any of these (Sabrazès and Guéreve, Compt. rend. 1908, 147, 1076; *see* also Camus, *ibid.* 1906, 142, 110, 237).

Hordenine methiodide, which probably possesses a similar physiological action to that of adrenaline, has been synthesised from *p*-methoxyphenylethylamine by treatment with methyl iodide, an almost quantitative yield being obtained. It crystallises in colourless prisms, m.p. 229°–230° (Rosenmund, *l.c.*). Other organic and inorganic compounds of hordenine have also been obtained (Léger, *l.c.*, and Compt. rend. 1907, 144, 208).

Detection.—A few drops of hordenine are dissolved in a few c.c. of acetic acid and boiled with a few drops of formaldehyde; 3 c.c. of sulphuric acid is now added when a green colouration is produced (Denigés, Bull. Soc. chim. 1908, [iv.] 3, 786).

1 c.c. of 1 p.c. hordenine sulphate solution is boiled with an equal volume of urotropine solution of the same strength, and 2 c.c. of strong

sulphuric acid, a fine emerald green colour is produced even with 0·0001 gram of hordenine sulphate (Labat, J. Pharm. Chim. 1909, 29, 433).

HOREHOUND *v.* Marrubium.

HORN LEAD *v.* Lead.

HORN QUICKSILVER. *Calomel v.* Mercury.

HORNSILVER. Native silver chloride *v.* Cerargyrite, Silver.

HORSE-CHESTNUT. *Hippocastanum. Marronier d'Inde*, Fr.; *Rosscastanien*, Ger. The well-known horse-chestnut tree, *Æsculus hippocastanum* (Linn.), is a native of Persia and Northern India. It was introduced into Europe in the 16th century, and is now largely cultivated for ornament throughout the temperate regions of the world. It is unimportant in medicine; but it is interesting chemically as the source of several glucosides and allied compounds.

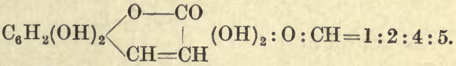
Besides tannin (Rochleder, Zeitsch. Chem. 1867, 76), fat, and constituents common to plants, horse-chestnut bark contains the glucoside *æsculin* $C_{15}H_{16}O_9$ (Minor, Berz. J., 12, 274; Jonas, Annalen, 15, 266) and in smaller proportion *æsculetin* $C_9H_6O_4$ (Rochleder, J. 1863, 589) which is also a product of the action of dilute acids or emulsin on æsculin (Rochleder and Schwartz, Annalen, 88, 356). *Fraxin* or *paviin* $C_{16}H_{18}O_{10}$ a glucoside occurring in the bark of the common ash, *Fraxinus excelsior* (Linn.), is another constituent of horse-chestnut bark (Stokes, Chem. Soc. Trans. 11, 17; 12, 126) accompanied by *fraxetin* $C_{10}H_8O_5$ (Rochleder, Chem. Zentr. 1864, 415), also produced when fraxin is boiled with dilute acids.

To obtain *æsculin*, Rochleder extracts the bark with hot water, precipitates the solution with alum and a slight excess of ammonia, filters, and evaporates the filtrate to dryness at 100°. The residue yields æsculin to hot alcohol, when it may be purified by successive crystallisations. Another method (Fairthorne, Chem. News, 26, 4) consists in exhausting the bark with dilute ammonia, evaporating to dryness, mixing the residue with alumina, and extracting with 95 p.c. alcohol. The alcoholic solution yields crystals of æsculin which are purified by washing with water, ether, and benzene. Æsculin forms colourless prisms which lose water of crystallisation at 120°–130°, and melt with decomposition at 160° (Zwenger, Annalen, 90, 65). It is soluble in glacial acetic acid, acetic ester, and in hot alcohol; very slightly soluble in cold water and nearly insoluble in ether. The aqueous solution has a blue fluorescence. Emulsin or dilute acids convert it into *æsculetin* and *glucose* (Rochleder and Schwartz). Heated with baryta water it yields *æsculetic acid* and *glucose* (Rochleder, J. 1856, 678). Sodium amalgam reacts forming *hydræsculin* (Rochleder, Zeitsch. Chem. 1868, 727). A characteristic colour reaction is obtained by agitating æsculin with nitric acid, when a yellow solution results which on the addition of ammonia turns deep red (Sonnenschein, Ber. 9, 1182). Concentrated sulphuric acid followed by solution of sodium hypochlorite strikes a violet colour (Raby, J. Pharm. Chim. [v.] 9, 402).

Æsculetin is usually prepared by the action of dilute acid on æsculin (Zwenger, Annalen, 90, 63). It crystallises in shining needles or scales containing a molecule of water. It melts with decomposition above 270°. It is soluble in hot but only slightly soluble in cold water and alcohol, and nearly insoluble in ether. The aqueous solution has a slight blue fluorescence.

By reduction with sodium amalgam, æsculetin yields *hydroæsculetin* $C_{18}H_{14}O_8$ and *æsculetin dihydride* $C_9H_8O_4$. Hydroæsculetin appears to be identical with the *æscorcin* of Rochleder (J. 1867, 751). It is converted by gaseous ammonia into *dehydroæscorcein* $C_{18}H_{13}O_7N_3$, a deep violet coloured mass. Æsculetin dihydride, similarly, when treated with ammonia, exhibits a striking series of colour reactions. Æsculetin unites with sodium hydrogen sulphite forming *sodium dihydroæsculetinsulphonate*. This compound is not decomposed by dilute acids; by the action of gaseous ammonia it is converted into the deep violet coloured compound described by Rochleder as *æscorceïn* $C_9H_7O_5N$, but which is in reality *sodium æscorceïnsulphonate* $C_{18}H_{12}O_{16}N_2S_2Na_6$ (Liebermann and Wiedermann, Ber. 34, 2608; Liebermann and Lindenbaum, *ibid.* 35, 2919).

The diacetyl derivative of æsculetin has been prepared by Gattermann and Köbner (Ber. 32, 287) by the action of sodium acetate and acetic anhydride on 2:4:5-trihydroxybenzaldehyde. Æsculetin is thus shown to have the constitution



$$C_6H_2(OH)_2\left\langle\begin{matrix}O\text{—}CO\\ \quad\ \ |\\ CH{=}CH\end{matrix}\right.(OH)_2:O:CH=1:2:4:5.$$

Fraxin crystallises in colourless needles containing half a molecule of water of crystallisation. By the action of dilute acids it is converted into *fraxetin* and *glucose* (Salm, J. 1859, 576). Fraxetin consists of tables (from alcohol) very slightly soluble in water, but soluble in ether and hydrochloric acid.

Horse-chestnut cotyledons were found by Rochleder (J. pr. Chem. [i.] 87, 1; [i.] 101, 415) to contain three compounds. *Argyræscin* $C_{27}H_{42}O_{12}$ a crystalline glucoside converted by dilute acids into *glucose* and *argyræscetin* $C_{21}H_{30}O_6$, and by potash into *propionic acid* and *æscinic acid* $C_{24}H_{40}O_2$, a compound found ready formed in the cotyledons. The third constituent of the cotyledons is the glucoside *aphrodæscin* $C_{52}H_{82}O_{23}$, which, acted on by potash, also yields *æscinic acid*, the second product being in this case *butyric acid*, or when heated with dilute acids *glucose*, and *telæscin* $C_{18}H_{30}O_7$. Telæscin acted on by hydrochloric acid gas gives up another molecule of *glucose* and forms *æscigenin* $C_{12}H_{20}O_2$ (Rochleder, J. 1862, 491; 1867, 751).

The leaves of the horse-chestnut contain the glucoside *quercitrin* $C_{36}H_{38}O_{20}$ and the flowers *quercetin* $C_{24}H_{16}O_{11}$ (Rochleder, J. 1859, 522). *Quercitrin* is usually prepared from black oak bark, *Quercus discolor* (Ait.) (Liebermann and Hamburger, Ber. 12, 1179) and from this compound by treatment with dilute acids *quercetin* together with *isodulcite* is obtained.

For other reactions and the constitution of these compounds *v.* Glucosides.

For examination of horse-chestnuts *see* Laves (Chem. Zentr. 1903, ii. 1133). The oil present in them was at one time used in medicine; it has been investigated by Stillesen (Chem. Zentr. 33, 497). A. S.

HORSE-RADISH. The root of *Cochlearia Armoracia* (Linn.), used as a condiment. Its pungent flavour is due to the presence of *iso*butyl *iso*thiocyanate, $C_4H_9\cdot NCS$. The root contains—

Water	Nitrogenous substances	Fat	*N*-free extract	Crude fibre	Ash	Organic sulphur
76·7	2·7	0·3	15·9	2·8	1·5	0·08

The following is an analysis of the ash of horse-radish:—

Per cent. of ash in the dry subst.	K_2O	Na_2O	CaO	MgO	Fe_2O_3	P_2O_5	SO_3	SiO_2	Cl
7·1	30·8	4·0	8·2	2·9	1·9	7·8	30·8	12·7	0·9

H. I.

HUMIC ACID. The substance produced by the decay of vegetable matter and found in the soil. Various humic acids have been described; an octobasic acid $C_{60}H_{54}O_{27}$ (Detmer, J. 1873, 844); an acid $C_{24}H_{10}O_{10}$ (Thenard, J. 1873, 844); an acid $C_{26}H_{22}O_{10}$, from brown coal (Hoppe, Zeitsch. physiol. Chem. 13, 108); and an acid $C_{46}H_{46}O_{25}$ from coal (John, Zeit. Kryst. Min. 23, 289). According to Robertson, Irvine, and Dobson (Bio-Chem. J. 1907, 2, 458), the natural humic acid from peat varies greatly in composition, according to the method of preparation. The artificial acid from sugar, according to them, has the composition $C_{39}H_{32}O_{14}$, but Berthelot and André (Compt. rend. 112, 916) state that this acid is tribasic and has the composition $C_{18}H_{16}O_7$. Humic acid is capable of absorbing ammonia, which is then removed by the acid of sprouting seeds, humic acid being regenerated (Borntraeger, Chem. Zentr. 1900, ii. 1202). Gautreau, Charbonnier, and Serrant (Eng. Pat. 22028; J. Soc. Chem. Ind. 1895, 977) treat peat or vegetable refuse with dilute sulphuric acid, to produce humic acid. The mass after the removal of the liquid matter is treated with excess of lime, potassium sulphate is added and the resulting substance sold as a manure.

HUNGARIAN TURPENTINE *v.* OLEO-RESINS.

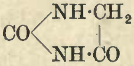
HUNGARY BLUE. *Cobalt blue v.* PIGMENTS.

HUNGARY GREEN. *Malachite green v.* PIGMENTS.

HYACINTH *v.* ZIRCON and ZIRCONIUM.

HYÆNASIC ACID $C_{24}H_{49}\cdot COOH$, m.p. 77·5°, is found as a glyceride in the anal glandular pouches of the striped hyaena (Carius, Annalen, 129, 168).

HYALINE CORUNDUM *v.* ALUMINIUM.

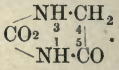
HYDANTOIN, *glycolylcarbamide*  $\mathrm{CO}\left<\begin{array}{l}\mathrm{NH\cdot CH_2}\\ \quad\;|\\ \mathrm{NH\cdot CO}\end{array}\right.$ was found together with allantoin in the leaf buds of *Platanus orientalis* (Linn.) (Schulze and Barbieri, Ber. 1881, 14, 1834); and also in beet juice (v. Lippmann, Ber. 1896, 29, 2652). It is prepared (1) by reducing allantoin or alloxanic acid with concentrated hydrogen iodide at 100° (Baeyer, Annalen, 1864, 130, 158); (2) by the action of excess of alcoholic ammonia on bromacetylurea at 100° (Baeyer, Ber. 1875, 8, 612); (3) by the condensation of sodium dihydroxytartrate and carbamide in the presence of hydrochloric acid at 50°–60° (Anschütz, Annalen, 1889, 254, 258); (4) by the condensation of glyoxal and carbamide in the presence of hydrochloric acid (Siemonsen, Annalen, 1904, 333, 101); (5) from ethyl hydantoate by heating at 135° for 7 hours, or by warming with 25 p.c. hydrochloric acid (Harries and Weiss, Ber. 1900, 33, 3418), or by heating with alcoholic ammonia at 100° (Harries, Annalen, 1908, 361, 69); the ethyl hydantoate is prepared by the condensation of the hydrochloride of the ethyl ester of glycine with potassium cyanate (Harries and Weis, *l.c.*) or by the interaction of glycollic ester and ethyl sodiocarbonate (Diels and Heintzel, Ber. 1905, 38, 305).

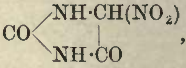
Hydantoin crystallises in colourless needles, m.p. 216° (Schulze and Barbieri, Anschütz, *l.c.*); 217°–220° (Harries and Weiss, *l.c.*); its heat of combustion at constant volume is +312·4Cal., and heat of formation +109Cal. (Matignon, Ann. Chim. Phys. 1893, [vi.] 28, 70). Its dissociation constant *Ka* is $7{\cdot}59\times10^{-10}$ (Wood, Phil. Trans. 1906, 1833). It is sparingly soluble in cold, readily so in hot water, and the solution has a sweetish taste. Hydantoin is not attacked by ammonia, hydrochloric, or dilute nitric acid; when boiled with baryta water it is converted into the barium salt of *hydantoic acid*

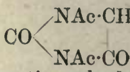
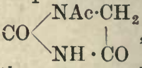
$$NH_2\cdot CO\cdot NH\cdot CH_2\cdot CO_2H,$$

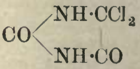
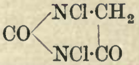
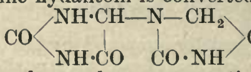
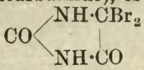
the heat of combustion of which is 308·9Cal. and heat of formation +181·6Cal. (Matignon, *l.c.*).

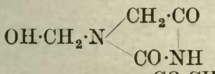
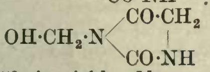
The *silver derivative* $C_3H_3O_2N_2Ag,H_2O$ is precipitated by silver nitrate from an ammoniacal solution of hydantoin.

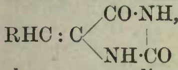
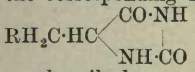
Substituted derivatives of hydantoin are referred to the ring  $\overset{2}{\mathrm{CO}}\left<\begin{array}{l}\mathrm{NH\cdot CH_2}\\ \;\,{}^{3}\;\;{}^{4}|\\ \;\,{}_{1}\;\;{}_{5}|\\ \mathrm{NH\cdot CO}\end{array}\right.$.

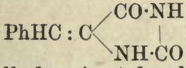
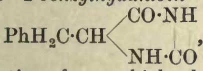
Nitrohydantoin  $\mathrm{CO}\left<\begin{array}{l}\mathrm{NH\cdot CH(NO_2)}\\ \quad\;\;|\\ \mathrm{NH\cdot CO}\end{array}\right.$, prepared by the action of nitric acid on hydantoin, forms shining crystals, melting and decomposing at 170° (Franchimont and Klobbie, Rec. trav. chim. 1888, 7, 12).

1 : 3-Diacetylhydantoin  $\mathrm{CO}\left<\begin{array}{l}\mathrm{NAc\cdot CH_2}\\ \mathrm{NAc\cdot CO}\end{array}\right.$, obtained by the action of acetic anhydride on hydantoin, has m.p. 104°–105°, and yields 3-*acetylhydantoin*  $\mathrm{CO}\left<\begin{array}{l}\mathrm{NAc\cdot CH_2}\\ \quad\;\;|\\ \mathrm{NH\cdot CO}\end{array}\right.$, m.p. 143°–144°, when boiled with water, and this forms a sparingly soluble *lead salt* (Harries and Weiss, Annalen, 1903, 327, 355; Siemonsen, Annalen, 1904, 333, 101).

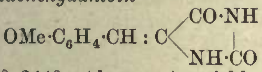
Dichlorohydantoin  $\mathrm{CO}\left<\begin{array}{l}\mathrm{NH\cdot CCl_2}\\ \mathrm{NH\cdot CO}\end{array}\right.$ or  $\mathrm{CO}\left<\begin{array}{l}\mathrm{NCl\cdot CH_2}\\ \quad\;\;|\\ \mathrm{NCl\cdot CO}\end{array}\right.$ obtained in the form of lustrous crystalline leaves, m.p. 120°–121° by the action of chlorine on an aqueous solution of hydantoin (Harries and Weiss, Annalen, 1903, 327, 355; Siemonsen, Annalen, 1904, 333, 101; Biltz and Behrens, Ber. 1910, 43, 1984). Attempts to prepare bromine derivatives of hydantoin have been unsuccessful; by the action of ½ molecule of bromine hydantoin is converted into iso*allituric acid*  $\mathrm{CO}\left<\begin{array}{l}\mathrm{NH\cdot CH{-}N{-}CH_2}\\ \qquad\;\;|\quad\;\;|\\ \mathrm{NH\cdot CO\quad CO\cdot NH}\end{array}\right>\mathrm{CO}$, m.p. 258°–260°, when a larger proportion of bromine is employed, parabanic acid (oxalylcarbamide), is formed, the bromo derivative  $\mathrm{CO}\Big\langle\begin{array}{l}\mathrm{NH{\cdot}CBr_2}\\ \mathrm{NH{\cdot}CO}\end{array}$ being probably first produced.

Condensation with aldehydes. Hydantoin condenses with formaldehyde (1–3 mols.) in aqueous solution to form *hydroxymethylhydantoin*  $\mathrm{OH{\cdot}CH_2{\cdot}N}\Big\langle\begin{array}{l}\mathrm{CH_2{\cdot}CO}\\ \mathrm{CO{\cdot}NH}\end{array}$ or  $\mathrm{OH{\cdot}CH_2{\cdot}N}\Big\langle\begin{array}{l}\mathrm{CO{\cdot}CH_2}\\ \mathrm{CO{\cdot}NH}\end{array}$ m.p. 125°–135°, it yields *chloromethylhydantoin* $C_4H_5O_2N_2Cl$, m.p. 150°–157°, when treated with phosphorus pentachloride or concentrated hydrochloric acid. When hydantoin is warmed with formaldehyde in the presence of acids more complex products are obtained (Behrend and Niemeyer, Annalen, 1909, 365, 38).

Hydantoin condenses with aromatic aldehydes in the presence of glacial acetic acid and sodium acetate to form compounds of the type  $\mathrm{RHC:C}\Big\langle\begin{array}{l}\mathrm{CO{\cdot}NH,}\\ \mathrm{NH{\cdot}CO}\end{array}$ which, on reduction, yield the corresponding 4-*aryl*-substituted hydantoin  $\mathrm{RH_2C{\cdot}HC}\Big\langle\begin{array}{l}\mathrm{CO{\cdot}NH}\\ \mathrm{NH{\cdot}CO}\end{array}$. The following compounds are described:—

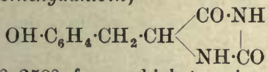
Benzylidenehydantoin  $\mathrm{PhHC:C}\Big\langle\begin{array}{l}\mathrm{CO{\cdot}NH}\\ \mathrm{NH{\cdot}CO}\end{array}$ m.p. 220°, yields 4-*benzylhydantoin* (*phenylalaninehydantoin*)  $\mathrm{PhH_2C{\cdot}CH}\Big\langle\begin{array}{l}\mathrm{CO{\cdot}NH}\\ \mathrm{NH{\cdot}CO}\end{array}$, m.p. 188°–190° on reduction, from which phenylalanine is obtained by boiling with baryta water (Ruhemann and Stapleton, Phil. Trans. 1900, 246).

Anisylidenehydantoin



$$\mathrm{OMe{\cdot}C_6H_4{\cdot}CH:C}\Big\langle\begin{array}{l}\mathrm{CO{\cdot}NH}\\ \mathrm{NH{\cdot}CO}\end{array}$$

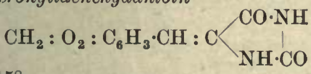
m.p. 243°–244° (decomp.) yields a *bromo* derivative, m.p. 247°; and on reduction with hydrogen iodide forms 4-*p*-*hydroxybenzylhydantoin* (*tyrosinehydantoin*)



$$\mathrm{OH{\cdot}C_6H_4{\cdot}CH_2{\cdot}CH}\Big\langle\begin{array}{l}\mathrm{CO{\cdot}NH}\\ \mathrm{NH{\cdot}CO}\end{array}$$

m.p. 257°–258°, from which *tyrosine* is obtained by prolonged boiling with hydrogen iodide. The tyrosinehydantoin, m.p. 275°–280°, described by Blendermann (Bied. Zentr. 1883, 209) is probably the optically active isomeride of this compound.

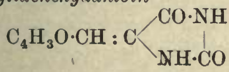
Piperonylidenehydantoin



$$\mathrm{CH_2:O_2:C_6H_3{\cdot}CH:C}\Big\langle\begin{array}{l}\mathrm{CO{\cdot}NH}\\ \mathrm{NH{\cdot}CO}\end{array}$$

m.p. 245°.

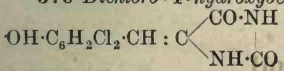
Furfurylidenehydantoin



$$\mathrm{C_4H_3O{\cdot}CH:C}\Big\langle\begin{array}{l}\mathrm{CO{\cdot}NH}\\ \mathrm{NH{\cdot}CO}\end{array}$$

m.p. 232°.

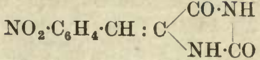
3 : 5-*Dichloro*-4-*hydroxybenzylidenehydantoin*



$$\mathrm{OH{\cdot}C_6H_2Cl_2{\cdot}CH:C}\Big\langle\begin{array}{l}\mathrm{CO{\cdot}NH}\\ \mathrm{NH{\cdot}CO}\end{array}$$

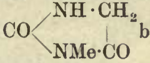
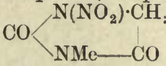
m.p. 300°.

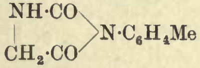
p-Nitrobenzylidenehydantoin



$$\mathrm{NO_2{\cdot}C_6H_4{\cdot}CH:C}\Big\langle\begin{array}{l}\mathrm{CO{\cdot}NH}\\ \mathrm{NH{\cdot}CO}\end{array}$$

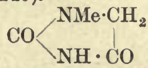
m.p. 254° (Wheeler and Hoffmann, Amer. Chem. J. 1911, 45, 368).

Alkyl and aryl substituted derivatives. 1-*Methylhydantoin*  $\mathrm{CO}\Big\langle\begin{array}{l}\mathrm{NH{\cdot}CH_2}\\ \mathrm{NMe{\cdot}CO}\end{array}$ by methylating hydantoin by means of methyl iodide, potassium hydroxide, and methyl alcohol at 100° (Franchimont and Klobbie, Rec. trav. chim. 1889, 8, 289); from methylcarbamide and glycine (Guareschi, Chem. Zentr. 1892, i. 140); crystallises in prisms, m.p. 182°. The *nitro* derivative  $\mathrm{CO}\Big\langle\begin{array}{l}\mathrm{N(NO_2){\cdot}CH_2}\\ \mathrm{NMe\text{——}CO}\end{array}$ has m.p. 168° (Franchimont and Klobbie, *l.c.*). 1-*p-tolylhydantoin*



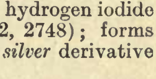
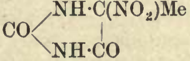
$$\begin{array}{l}\mathrm{NH{\cdot}CO}\\ \mathrm{CH_2{\cdot}CO}\end{array}\Big\rangle\mathrm{N{\cdot}C_6H_4Me}$$

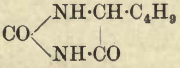
from *p*-tolylcarbamide and glycine (Quenda, Chem. Zentr. 1892, i. 140).

3-*Methylhydantoin*  $\mathrm{CO}\Big\langle\begin{array}{l}\mathrm{NMe{\cdot}CH_2}\\ \mathrm{NH{\cdot}CO}\end{array}$ prepared (1) by fusing sarcosine and urea (Huppert, Ber. 1873, 6, 1278; Horbaczewski, Monatsh. 1887, 8, 586); (2) by passing cyanogen chloride through fused sarcosine (Traube, Ber. 1882, 15, 2111); (3) by heating caffuric acid with baryta water (Fischer, Annalen, 1882, 215, 286); or (4) by reducing 3-methylallantoin with hydrogen iodide (Fischer and Ach, Ber. 1899, 32, 2748); forms soluble prisms, m.p. 156°; the *silver* derivative $AgC_4H_5N_2O_2$ is crystalline.

3-*Phenylhydantoin* from phenylglycine and urea has m.p. 191°; 3-*tolylhydantoin* has m.p. 210° (Schwebel, Ber. 1877, 10, 2045; 11, 1128).

Homologues of hydantoin containing the substituent in position 4- are most numerous; and are prepared by the following general methods: (1) by interaction between the cyanohydrin of an aldehyde and carbamide (Pinner, Ber. 1887, 20, 2351; 21, 2320; 22, 685); (2) by the action of dilute hydrochloric acid on the hydantoic acid obtained by evaporating to dryness a solution of an *α*-amino acid and potassium cyanate (Dakin, Amer. Chem. J. 1910, 44, 48); or by the interaction of carbamide, the *α*-amino acid and baryta water (Lippich, Ber. 1908, 41, 2953); (3) by reducing the compound obtained by the condensation of hydantoin and an aromatic aldehyde (Wheeler and Hoffmann, *l.c.*).

4-*Methylhydantoin* (*lactylurea*)  $\mathrm{CO}\Big\langle\begin{array}{l}\mathrm{NH{\cdot}CHMe}\\ \mathrm{NH{\cdot}CO}\end{array}$ (Heintz, Annalen, 1873, 169, 125; Urech, Ber. 1873, 6, 1113), m.p. 140° or 145°. The *nitro*-derivative  $\mathrm{CO}\Big\langle\begin{array}{l}\mathrm{NH{\cdot}C(NO_2)Me}\\ \mathrm{NH{\cdot}CO}\end{array}$ m.p. 148° (Franchimont and Klobbie, Rec. trav. chim. 1888, 7, 13). 4-*isoButylhydantoin*

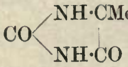
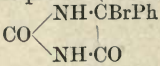
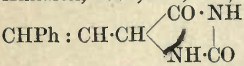
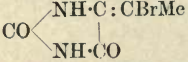
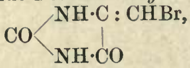


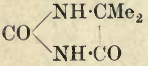
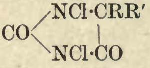
$$\mathrm{CO}\Big\langle\begin{array}{l}\mathrm{NH{\cdot}CH{\cdot}C_4H_9}\\ \mathrm{NH{\cdot}CO}\end{array}$$

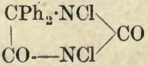
has m.p. 209°–210° (Pinner and Lifschütz, Ber

1887, 20, 2351), 212° (Lippich, *ibid.* 1908, 41, 2953). *l*-4-*iso Butylhydantoin* has m.p. 212°, $[\alpha]_D^{20°}-68{\cdot}2°$ in normal sodium hydroxide solution, becoming zero in 30 hours owing to the enol-keto desmotropy of the group

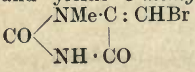
$$CH{\cdot}CO \rightleftarrows C:C{\cdot}OH.$$

-4:4-*Methylethylhydantoin*  $CO\!<\!\begin{array}{l} NH{\cdot}CMeEt \\ \qquad | \\ NH{\cdot}CO \end{array}$ has m.p. 172°–173°, and $[\alpha]_D^{20}+32°$, and this is constant in normal sodium hydroxide solution (Dakin, *l.c.*). 4-*Phenylhydantoin*, m.p. 178°; the *acetyl* derivative has m.p. 145° (Pinner, *l.c.*); the *bromo* derivative  $CO\!<\!\begin{array}{l} NH{\cdot}CBrPh \\ \qquad | \\ NH{\cdot}CO \end{array}$ melts above 200°, and is decomposed by hot water yielding 4-*hydroxy*-4-*phenylhydantoin* (Gabriel, Annalen, 1906, 350, 118). 4-*Cinnamylhydantoin*  $CHPh:CH{\cdot}CH\!<\!\begin{array}{l} CO{\cdot}NH \\ \qquad | \\ NH{\cdot}CO \end{array}$ m.p. 171°–172° (Pinner and Spilker, Ber. 1889, 22, 685). 4-*Ethylhydantoin*, m.p. 117°–118°, yields 4-*bromoethylidenehydantoin*  $CO\!<\!\begin{array}{l} NH{\cdot}C:CBrMe \\ \qquad | \\ NH{\cdot}CO \end{array}$ m.p. 230°–236°, on bromination; the corresponding methyl compound yields 4-*bromomethylenehydantoin*  $CO\!<\!\begin{array}{l} NH{\cdot}C:CHBr, \\ \qquad | \\ NH{\cdot}CO \end{array}$ m.p. 241°–242° (Gabriel, Annalen, 1906, 348, 50).

4:4-*Dimethylhydantoin* (acetonylcarbamide)  $CO\!<\!\begin{array}{l} NH{\cdot}CMe_2 \\ \qquad | \\ NH{\cdot}CO \end{array}$ formed by the action of hydrocyanic acid, and cyanic acid on acetone has m.p. 175°; the *nitro* derivative has m.p. 161°–162° (Urech, Annalen, 1872, 164, 264; Errera, Gazz. chim. ital. 1896, 26, 1, 210); 4:4-*diethylhydantoin* has m.p. 165°, and 4:4-*dipropylhydantoin*, m.p. 199° (Errera, *l.c.*). By the action of sodium hypochlorite and free hypochlorous acid on 4:4-disubstituted hydantoins, the corresponding 1:3-*dichloro* compounds  $CO\!<\!\begin{array}{l} NCl{\cdot}CRR' \\ \qquad | \\ NCl{\cdot}CO \end{array}$ are obtained. These compounds can be crystallised from chloroform, but are decomposed by water, alcohol, or hydrogen iodide, regenerating the original hydantoin (Biltz and Behrens, Ber. 1910, 43, 1984).

1:3-*Dichloro*-4:4-*diphenylhydantoin*  $\begin{array}{l} CPh_2{\cdot}NCl \\ | \\ CO{-\!\!-}NCl \end{array}\!\!>\!CO$ has m.p. 164° with decomposition, it yields 4:4-*diphenyl*-1:3-*dimethylhydantoin* when treated with methyl sulphate.

1-*Methyl*-4-*phenylhydantoin* has m.p. 161°–162° (Pinner, Ber. 1888, 21, 2320). 4-*Methyl*-3-*ethylhydantoin* forms volatile plates (Duvillier, Bull. Soc. chim. 1895, [iii.] 13, 487).

3:4-*Dimethylhydantoin* has m.p. 120°–121°, and yields 3-*methyl*-4-*bromomethylenehydantoin*  $CO\!<\!\begin{array}{l} NMe{\cdot}C:CHBr \\ \qquad | \\ NH{\cdot}CO \end{array}$ m.p. 143°–144°, by the action of bromine (Gabriel, Annalen, 1906, 348, 50).

M. A. W.

HYDNO-CARPIC ACID, HYPOGALIC ACID, *v.* OILS, FIXED, and FATS.

HYDRACRYLIC ACID *v.* LACTIC ACID.

HYDRÆSCULIN *v.* HORSE-CHESTNUT.

HYDRARGOL, HYDRARGOTIN, HYDRARGYROSEPTOL, *v.* SYNTHETIC DRUGS.

HYDRASTINE $C_{21}H_{21}NO_6$ occurs, together with berberine and canadine, in the roots of the golden seal (*Hydrastis canadensis* [Linn.]), a plant belonging to the *Ranunculaceæ* and indigenous to North America (Durand, Amer. J. Pharm. 23, 13; Perrins, Pharm. J. May, 1862; Power, Jahrb. 1884, 1396; Freund and Will, Ber. 1886, 19, 2798; Linde, Arch. Pharm. 1898, 236, 696, 698; Schmidt, *ibid.* 232, 136). It was first isolated by Durand in 1850, but was obtained pure for the first time by Perrins in 1862.

Preparation.—The aqueous or alcoholic extract of the root is treated with dilute sulphuric acid to precipitate the berberine, and after filtration, the filtrate (if alcohol has been used for extracting) is treated with ammonia water until nearly neutral, the ammonium sulphate is filtered off and the liquid after concentration is mixed with cold water to precipitate resinous and oily matter. The filtrate is then treated with excess of ammonia water and the hydrastine thus precipitated, is recrystallised from alcohol or ethyl acetate (*see* also Freund and Will, *l.c.*; Ough, Chemist and Druggist, 1901, 59, 152).

Properties.—Hydrastine is closely related to narcotine, of which it is probably a methoxyl derivative. Our knowledge of its structure is mainly due to the work of Schmidt and of Freund (Annalen, 1892, 271, 311; Fritsch, *ibid.* 1895, 286, 18; Rabe and McMillan, *ibid.* 1910, 377, 223). It forms colourless, almost odourless and tasteless 4-sided prisms, which melt at 132°, to a light amber coloured liquid. It is almost insoluble in water but is readily soluble in ether, alcohol, chloroform, and benzene. It is lævorotatory. When oxidised with potassium permanganate opianic acid is formed (Labat, Bull. Soc. chim. 1909, [iv.] 5, 743), and when heated with nitric acid at 50°–60°, it yields opianic acid and *hydrastinine* (Freund and Will, Ber. 1887, 20, 94), whilst when oxidised in alkaline solution, it yields hemipinic and nicotinic acids.

When fused with potash, it yields protocatechuic and formic acids. Hydrastine forms a faint yellow solution in sulphuric acid, which turns reddish purple on warming and which decolorises potassium permanganate. With platinum chloride hydrastine gives an orange-yellow precipitate; with gold chloride, a yellow-red; with picric acid, a yellow; and with potassium dichromate, a yellow precipitate, which turns red on addition of sulphuric acid. In contact with a potassium iodide solution containing free iodine it yields a brown hexaiodide, or a hydriodide pentiodide $C_{21}H_{21}NO_6HI{\cdot}I_5$ (Prescott and Gordin, J. Amer. Chem. Soc. 1899, 21, 732).

Hydrastine combines readily with ketones, forming condensation products with elimination of water (Liebermann and Kropf, Ber. 1904, 37, 211). It also forms similar condensation products with most compounds containing methylene groups between carbonyl groups and also with such compounds as hydroquinone, phloroglucinol, and pyrogallol (Liebermann and Glawe, *ibid.* 2738). When heated with carbamide it forms meconin (Beckurts and Frerichs, Arch. Pharm. 1903, 241, 259). When 0·1 c.c. of a hydrastine solution in alcohol is added to 2 c.c. of pure sulphuric acid (sp.gr. 1·84), and 0·1 c.c. of a phenolic substance is added, the mixture, on warming, develops beautiful colourations. Thus with gallic acid the colour is emerald green, which gradually becomes blue. With guaiacol or catechol, a red colour is produced which turns violet, and with morphine the mixture becomes violet (Labat, Bull. Soc. chim. 1909, [iv.] 5, 742).

Hydrastine may be distinguished from most other alkaloids by the fact that when a few drops of Nessler's reagent are added to a solution of its hydrochloride, a precipitate which instantly blackens is produced. Only morphine, apomorphine, and picrotoxin precipitate mercury more or less quickly from the reagent (Jorissen, Ann. Chim. anal. 1903, 8, 127). When chlorine is added to the hydrochloride, a blue fluorescence appears.

For the estimation of hydrastine in extract and tincture of hydrastis, *see* Gordin and Prescott, *l.c.*; Maben, Chem. and Druggist, 1901, 59, 234; Matthes and Rammstedt, Arch. Pharm. 1907, 245, 112; Packner, Chem. Zentr. 1908, ii. 266; Roeder, J. Soc. Chem. Ind. 1908, 1037; Rupp, *ibid.* 1910, 449.

Hydrastine and its salts, which form hygroscopic crystalline powders of bitter taste, are used in medicine chiefly for external use in the treatment of subacute and of chronic inflammatory conditions of the mucous membrane; also in uterine catarrh and more rarely, internally for gastro-intestinal catarrh and catarrhal jaundice (Falk, Virchow's Arch. 1895, 142, 360; Bunge, Chem. Zentr. 1895, i. 1173; Phillips and Pembrey, Proc. Physiol. Soc. 1896–7, 4).

For the salts and derivatives of hydrastine, *see* Merck, Chem. Zeit. Rep. 1893, 17, 30; Freund, *l.c.*; Ber. 1889, 22, 456; *ibid.* 1890, 23, 404, 416, 2897, 2907; *ibid.* 1893, 26, 2488; Norton and Newman, J. Amer. Chem. Soc. 1897, 19, 838; Schmidt, Arch. Pharm. 1898, 236, 334; D. R. P. 58394; Rabe and McMillan, *l.c.*

Hydrastinine $C_{11}H_{13}O_3N$, which is formed by the oxidation of hydrastine with dilute nitric acid, can also be prepared by the dry distillation of a mixture of hydrastine and soda lime in an atmosphere of hydrogen (Schmidt, Arch. Pharm. 231, 541). It forms needle shaped crystals, m.p. 116°–117°, and is readily soluble in alcohol, ether, and chloroform, more sparingly in hot water. When reduced with zinc and hydrochloric acid, or when boiled with potash, or electrolysed in dilute sulphuric acid, it forms *hydrohydrastinine*, m.p. 171° (Freund; Bandow and Wolfenstein, Ber. 1898, 31, 1578). Oxidised with nitric acid, it yields apophyllic acid. By the continued oxidation of hydrastinine with potassium permanganate, *hydrastinic acid* $C_{11}H_9NO_6$, m.p. 164° (decomp.), is obtained in fine white needles. Hydrastinic acid when boiled with nitric acid, yields a crystalline substance, $C_{10}H_7NO_4$, m.p. 233°, which, on boiling with potash, yields *hydrastic acid*, m.p. 175°. a dibasic acid which readily forms an anhydride (Freund, Ber. 1889, 22, 1156, 2322, 2329; Annalen, 1892, 271, 375; Perkin, Chem. Soc. Trans. 1890, 1095; Perkin and Robinson, *ibid.* 1907, 1086).

Hydrastinine hydrochloride, m.p. 212° (decomp.), forms a light yellow granular or crystalline deliquescent powder. It is odourless, has a bitter saline taste, is very soluble in cold and hot water and alcohol, and is said to be an efficient oxytoxic. It has also been recommended in the treatment of uterine hæmorrhage (Merck, J. Soc. Chem. Ind. 1892, 545).

HYDRAULIC CEMENTS *v.* CEMENTS.

HYDRAULIC LIME *v.* CEMENTS.

HYDRAZINES. The name 'hydrazine' was applied by Emil Fischer to the then unknown diamide $H_2N{\cdot}NH_2$, which he regarded as the parent substance of the hydrazines, a large and important class of bases which had been prepared by him and the reactions of which showed them to possess a structural formula derived from diamide by the replacement of one or two hydrogen atoms by hydrocarbon radicles. The name was intended to indicate the connection of these compounds with the azo and diazo compounds and particularly with hydrazobenzene, $C_6H_5{\cdot}NH{\cdot}NH{\cdot}C_6H_5$, the oldest known member of this class, which itself may be regarded as a symmetrically disubstituted hydrazine.

It is apparent that there are five different ways in which the four hydrogen atoms of diamide may be replaced by hydrocarbon radicles, thus: (1) $RNH{\cdot}NH_2$, (2) $RRN{\cdot}NH_2$, (3) $RHN{\cdot}NHR$, (4) $RRN{\cdot}NHR$, (5) $RRN{\cdot}NRR$, but the name hydrazine was formerly only applied to those derivatives of diamide which had the hydrocarbon radicle or radicles asymmetrically attached to the molecule, that is to say, those which are constituted in accordance with formulæ (1) and (2).

This was mainly owing to the fact that the compounds constituted as in formula (3) had already been named, as for example, hydrazobenzene, $C_6H_5NH{\cdot}NH{\cdot}C_6H_5$, and that no substances of the formulæ 4 and 5 had as yet been prepared. At the present time compounds of all five classes are known, and therefore the name hydrazine is applied to all derivatives of diamide.

The hydrocarbon radicles forming the hydrazines may belong either to the aliphatic or aromatic series, although the most important members of the group belong to the aromatic series. Like the amines, they are divided into primary and secondary hydrazines, according as one or two hydrocarbon radicles are contained in them; that is to say, the primary hydrazines are constituted as in formula (1), the secondary hydrazines as in formula (2). The secondary hydrazines may be symmetrical or asymmetrical as in formula (2) or (3): compounds constituted as in formula (4) are tertiary hydrazines, whilst quarternary hydrazines have a structure represented by formula (5).

General methods of preparation.—The primary and secondary hydrazines can be considered as being derived from the primary and secondary amines respectively by the replacement of one of the hydrogen atoms attached to the nitrogen by the primary amino group—

$$RNHH \longrightarrow RNH{\cdot}NH_2, \quad RRNH \longrightarrow RRN{\cdot}NH_2$$

These compounds are therefore prepared from the primary and secondary amines through the agency of nitrous acid.

Since the primary aromatic amines yield diazonium salts when treated with nitrous acid, these salts are always intermediate products in the formation of the primary aromatic hydrazines and are converted into them by the action of reducing agents. For general purposes this reduction may be effected in one of two ways—

(1) By the reduction of the solution of the diazonium salt by stannous chloride (V. Meyer and Lecco, Ber. 1883, 16, 2976)—

$$C_6H_5\cdot N_2Cl+4H=C_6H_5\cdot NH\cdot NH_2,HCl.$$

(2) By treating the diazonium salt with alkali sulphite, in order to prepare the alkali salt of the sulphonic acid, and then by reducing this with zinc dust and acetic acid to form the alkali salt of the hydrazine sulphonic acid thus—

$$C_6H_5\cdot N_2SO_3K+2H=C_6H_5\cdot NH\cdot NH\cdot SO_3K.$$

Finally, by boiling this salt with hydrochloric acid to convert it into the hydrochloride of the hydrazine and potassium hydrogen sulphate (E. Fischer, Annalen, 1877, 190, 71; Reychler, 1887, 20, 2463).

$$C_6H_5\cdot NH\cdot NH\cdot SO_3K+H_2O+HCl$$
$$=C_6H_5\cdot NH\cdot NH_2,HCl+KHSO_4.$$

These reactions can only be applied to the aromatic amines because those of the aliphatic series do not form diazonium salts.

Primary aliphatic hydrazines have, however, been prepared by E. Fischer (Ber. 1884, 2841; Annalen, 1877, 199, 281) from the symmetrical dialkyl ureas by transforming them into their nitroso derivatives by the aid of nitrous acid and then by converting the hydrazinureas, formed from these on reduction, into the primary hydrazines by the action of fuming hydrochloric acid.

$$RHN\cdot CO\cdot NHR+NOOH=RHN\cdot CO\cdot N(NO)R$$
$$RHN\cdot CO\cdot N(NO)R+4H$$
$$=RHN\cdot CO\cdot N(NH_2)R+H_2O$$
$$RHN\cdot CO\cdot N(NH_2)R+H_2O$$
$$=CO_2+(NH_2)NH\cdot R+NH_2\cdot R.$$

Primary hydrazines of the aromatic series are also formed when certain diazoamino compounds are reduced in alcoholic solution with zinc dust and acetic acid. Thus diazoaminobenzene passes in this manner into phenylhydrazine (E. Fischer, Annalen, 1887, 90, 77).

$$C_6H_5\cdot N_2\cdot NH(C_6H_5)+4H$$
$$=C_6H_5\cdot NH\cdot NH_2+C_6H_5NH_2.$$

The secondary hydrazines both of the aromatic and aliphatic series are prepared from the corresponding secondary amines. The amines are converted into their nitroso derivatives, by the aid of nitrous acid, which are then transformed into the hydrazines by reduction.

$$R_2NH+NOOH=R_2N\cdot NO+H_2O$$
$$R_2N\cdot NO+4H=R_2N\cdot NH+H_2O.$$

Phenylhydrazine $C_6H_5\cdot NH\cdot NH_2$, the most important member of the hydrazine group, can be prepared by either of the methods mentioned above.

(1) *From aniline by the aid of stannous chloride.* Ten grams of aniline are dissolved in 100 grams of concentrated hydrochloric acid and the semi-solid mass of aniline hydrochloride is then cooled, externally, by means of ice. A solution of 10 grams of sodium nitrite dissolved in 50 c.c. of water is then gradually added until a test portion diluted with water shows, by means of starch and potassium iodide paper, the presence of excess of nitrous acid. The solution of benzene-diazonium chloride formed in this manner is then treated with a solution of 60 grams of stannous chloride dissolved in 50 c.c. of concentrated hydrochloric acid, the reducing agent being cooled by means of ice and added gradually with constant stirring to the solution of the diazonium salt. After standing for one hour, the phenylhydrazine hydrochloride is filtered at the pump, dissolved in water and converted into the free base by the addition of excess of aqueous caustic potash. The liberated base is extracted with ether, dried by potassium carbonate and purified by distillation under diminished pressure.

(2) *From aniline by the aid of sodium sulphite.* A solution of 50 grams of aniline in 2½ molecules of hydrochloric acid and 300 c.c. of water is diazotised by the addition of the calculated quantity of sodium nitrite solution, and is then mixed with a cold concentrated aqueous solution of 2½ molecules of sodium sulphite. The whole is then gently warmed on the water bath and treated with zinc dust and a little acetic acid until colourless, when it is heated to the boiling-point and filtered, whilst hot, from the unchanged zinc. One-third of its volume of concentrated hydrochloric acid is then added to the hot solution and the phenylhydrazine hydrochloride, which separates on cooling, is removed by filtration and treated in the same manner as in the previous preparation.

For the preparation of phenylhydrazine and its derivatives from urea and substituted ureas by the action of alkaline hypobromites, *cp.* Schestakow, D. R. P. 164755; Patentol. 26, 1869.

Tertiary aromatic hydrazines of the general formula $RNH\cdot NR_2$ may be prepared by the interaction of β-arylhydroxylamine and magnesium halogen aryl (Busch and Hobein, Ber. 1907, 40, 2099). Thus triphenylhydrazine $C_6H_5NH\cdot N(C_6H_5)_2$ is formed when phenylmagnesium bromide reacts with β-phenylhydroxylamine. The corresponding quaternary hydrazine tetraphenylhydrazine

$$(C_6H_5)_2N\cdot N(C_6H_5)_2$$

has been prepared by Chattaway and Ingle (Trans. 1895, 67, 1090) by the action of iodine on the sodium compound of diphenylamine, and by Weland and Gambarjan (Ber. 1906, 39, 1501) by the oxidation of diphenylamine.

Certain compounds belonging to the group of the dihydrazines have been prepared by V. Braun (Ber. 1908, 41, 2169; *ibid.* 2604; 1910, 1495), and are recommended as reagents for compounds containing carbonyl oxygen. Thus diphenylmethandimethyldihydrazine

$$[NH_2\cdot N(CH_3)C_6H_4]_2CH_2$$

is prepared by condensing methylaniline with formaldehyde to give *p*-dimethyldiaminodiphenylmethane $[HN(CH_3)C_6H_4]_2CH_2$, the nitroso compound of which gives the dihydrazine on reduction with zinc and acetic acid.

Properties and reactions of the hydrazines. The primary aromatic hydrazines are mono-acid bases which form well-defined, stable salts with both mineral and organic acids. Unlike the corresponding aliphatic primary hydrazines they do not form salts containing two equivalents of a mono-basic acid. The secondary aromatic hydrazines are also mono-acid bases but their salts are partially decomposed by water. The primary aromatic hydrazines, for example phenylhydrazine, react with metallic sodium forming a sodium compound from which alkyl derivatives can be prepared by the action of alkyl iodides—

$$C_6H_5\cdot NNa\cdot NH_2+RI=C_6H_5\cdot NR\cdot NH_2+NaI$$

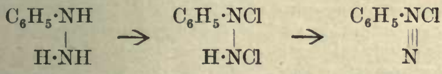
(*cp.* Michaelis, Ber. 1886, 19, 2448; 1887, 20, 43; also Annalen, 1889, 252, 267). The pure sodium compound can be prepared by acting on sodamide with a dilute benzene solution of phenylhydrazine (Titherley, Chem. Soc. Trans. 1897, 71, 461)—

$$NaNH_2+C_6H_5\cdot NH\cdot NH_2=C_6H_5\cdot NNa\cdot NH_2+NH_3$$

The corresponding potassium salt may be obtained as large colourless rhombic crystals when phenylhydrazine is treated with a saturated alcoholic solution of potassium hydroxide in the absence of air (Chattaway, Chem. Soc. Trans. 1907, 91, 1326).

The primary hydrazines are readily affected by oxidising agents and are consequently strong reducing agents. Phenylhydrazine reduces Fehling's solution in the cold, even in very dilute solution, a reaction which distinguishes this compound from the secondary base, diphenylhydrazine, which reduces Fehling's solution only on warming. (For the behaviour of phenylhydrazine on oxidation, *cp.* Fischer, Annalen, 1878, 190, 67; 1879, 199, 281; Fischer and Ehrhard, Annalen, 1879, 199, 333; Haller, Ber. 1885, 18, 90; Zincke, *ibid.* 1885, 18, 786; Strache, Monatsh. 1891, 12, 523; 1892, 13, 316; Murster, Ber. 1887, 20, 2633.)

The original statement by Fischer that the oxidation of phenylhydrazine by mercuric oxide leads to a partial production of the diazonium salt has been modified by Chattaway (Chem. Soc. Trans. 1908, 93, 270), who finds that diazonium salts are not produced when the action is carried out in alkaline solution but only in the presence of a large excess of strong acid. Azoimides are formed when alkali is absent and the hydrazines are present in excess. The quantitative conversion of phenylhydrazine into benzenediazonium chloride may be effected by dissolving the hydrazine in glacial acetic acid, cooling the solution to about −15° by the addition of crushed ice and either by passing in a rapid stream of chlorine or (if the diazonium bromide is desired) adding the calculated quantity of bromine dissolved in acetic acid and similarly cooled by ice. The reaction evidently proceeds in accordance with the scheme



$$\begin{array}{c} C_6H_5\cdot NH \\ | \\ H\cdot NH \end{array} \rightarrow \begin{array}{c} C_6H_5\cdot NCl \\ | \\ H\cdot NCl \end{array} \rightarrow \begin{array}{c} C_6H_5\cdot NCl \\ ||| \\ N \end{array}$$

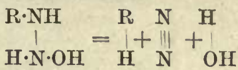
(Chattaway, Chem. Soc. Trans. 1908, 93, 853).

The mechanism of the reaction involved in the oxidation of phenylhydrazine either by oxygen or an oxidising agent, is explained in the following way (Chattaway, Trans. 1908, 93, 270):—

In the first instance, one of the hydrogen atoms of the hydrazino group is attacked and a hydroxyhydrazine is produced

$$RNH\cdot NH_2+O=RNH\cdot NH(OH).$$

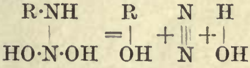
This substance, however, not being stable in the presence of alkali, undergoes disruption in accordance with the scheme



$$\begin{array}{c} R\cdot NH \\ | \\ H\cdot N\cdot OH \end{array} = \begin{array}{c} R \\ | \\ H \end{array} + \begin{array}{c} N \\ ||| \\ N \end{array} + \begin{array}{c} H \\ | \\ OH \end{array}$$

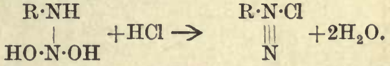
the splitting off of the hydrocarbon and water occurring in either one or two stages.

If, however, a very energetic oxidising agent is used, a certain number of molecules may, before breaking down, undergo a further oxidation thus:—



$$\begin{array}{c} R\cdot NH \\ | \\ HO\cdot N\cdot OH \end{array} = \begin{array}{c} R \\ | \\ OH \end{array} + \begin{array}{c} N \\ ||| \\ N \end{array} + \begin{array}{c} H \\ | \\ OH \end{array}$$

yielding a phenol and free nitrogen. In the absence of alkali, which acts as a catalytic agent and much accelerates the decomposition of these hydroxyhydrazines, the introduction of the second hydroxyl group takes place to a much greater extent and in the presence of strong acid and at a low temperature a diazonium salt is formed thus—



$$\begin{array}{c} R\cdot NH \\ | \\ HO\cdot N\cdot OH \end{array} +HCl \rightarrow \begin{array}{c} R\cdot N\cdot Cl \\ ||| \\ N \end{array} +2H_2O.$$

The oxidation of phenylhydrazine by basic metallic oxides leads to the formation of the free metal. The following process is recommended for producing a film of metallic copper on glass vessels (Chattaway, Chem. Soc. Trans. 1908, 93, 275; *see* also Proc. Roy. Soc. 1908, A, 80, 88). One part of freshly distilled phenylhydrazine and 2 parts of water are heated until a clear solution is obtained, when it is mixed with about half its bulk of a warm saturated solution of cupric hydroxide in strong ammonia. Nitrogen is freely evolved during the addition, and the cupric hydroxide is reduced to cuprous hydroxide, which remains dissolved in the ammoniacal liquid and does not undergo any immediate further reduction. A hot 10 p.c. solution of potassium hydroxide is then added until a slight permanent precipitate of cuprous hydroxide is produced and the clear liquid is then cautiously heated in contact with a perfectly clean glass surface. Metallic copper is deposited on it in the form of a thin reflecting coherent lamina. To obtain a film of sufficient thickness, it is best not to pour off the warm reducing fluid but to allow it to remain in contact with the glass until cold. When the liquid is poured off, the film of copper should be well washed with water and afterwards with alcohol and ether. It should then be protected by one or two coats of quickly drying varnish.

When phenylhydrazine is oxidised with copper sulphate or ferric chloride, the parent hydrocarbon is formed and the whole of the nitrogen is eliminated in the free state (Haller, Ber. 1885, 18, 90; Zincke, *ibid.* 786)—

$$C_6H_5\cdot NH\cdot NH_2+CuSO_4+H_2O$$
$$=C_6H_6+Cu_2O+N_2+2H_2SO_4.$$

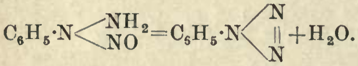
This reaction can be used as a means of estimating phenylhydrazine by measuring the amount of nitrogen evolved (Gallinek and V. v. Richter, Ber. 1885, 18, 3177; Strache, Monatsh.

1891, 12, 524; Strache and Kitt, *ibid.* 1892, 13, 316). (For other methods of estimating hydrazines, *cp.* Denigès, Ann. Chim. Phys. 1895, [vii.] 6, 381; Causse, Compt. rend. 1897, 125, 712, and Forster, Chem. Soc. Trans. 1898, 74, 792.)

Phenylhydrazine also reacts with hydrogen peroxide, yielding benzene together with some diazobenzeneimide; it moreover acts as a strong reducing agent towards nitro compounds, reducing them to the corresponding amino derivatives (Barr, Ber. 1887, 20, 1498). (For the reduction of nitro compounds, *cp.* also Walter, J. pr. Chem. 1896, [ii.] 53, 433. Reduction of 1:5-dinitroanthraquinone, Schmidt and Gattermann, Ber. 1896, 29, 2941. Reduction of nitro derivatives of phenanthraquinone, Schmidt and Kampf, Ber. 1902, 35, 3124. Reduction of hydroxyazo compounds, Oddo and Puxeddo, Ber. 1905, 38, 2752. Reduction of 5-nitrosalicylic acid, Puxeddo, Gazz. chim. ital. 1906, 36, ii. 87.) The hydrazines resist the action of reducing agents but pass on protracted treatment with zinc dust and hydrochloric acid into aniline and ammonia (E. Fischer, Annalen, 1887, 239, 248)

$$C_6H_5{\cdot}NH{\cdot}NH_2+2H=C_6H_5{\cdot}NH_2+NH_3.$$

Primary hydrazines yield with nascent nitrous acid in ice cold solution unstable nitroso derivatives which pass into diazo-imides and water, when warmed with alkali—



$$C_6H_5{\cdot}N\left<\begin{matrix}NH_2\\NO\end{matrix}\right.=C_6H_5{\cdot}N\left<\begin{matrix}N\\ \|\\ N\end{matrix}\right.+H_2O.$$

The diazoimide is formed directly if the above reaction is carried out at a higher temperature (E. Fischer, Annalen, 1877, 190, 89, 158, 181). Phenylhydrazine yields *iso*diazobenzene salts with amyl nitrite in the presence of sodium or potassium ethoxide (Stolle, Ber. 1908, 41, 2811). The primary aliphatic hydrazines are hygroscopic liquids readily soluble in water and which possess a smell resembling that of ammonia. The aromatic primary hydrazines are usually solids at the ordinary temperature. They possess a faint aromatic smell and are only sparingly soluble in water.

Phenylhydrazine $C_6H_5{\cdot}NH{\cdot}NH_2$ when freshly distilled is a practically colourless, highly refracting oil which distils under diminished pressure without decomposition, or at 240°–241° (780 mm.) with slight evolution of ammonia. When cooled it sets to a mass of tabular monoclinic crystals which melt at 17·5°. According to E. Fischer (Ber. 1908, 41, 73), the melting point of phenylhydrazine is 19·6°, after the substance has been purified first by fractional distillation at 15–20 mm., then by solidification and removal of the liquid portion, an operation repeated four times, then by recrystallisation from anhydrous ether, and finally by distillation under a pressure of 0·5 mm. For ordinary purposes it is sufficient to crystallise the base once or twice from its own volume of pure ether and then distil under a pressure of 10–20 mm. The base should be coloured pale yellow and should dissolve in 10 times its volume of a mixture of 50 p.c. acetic acid (1 part) and water (9 parts). Phenylhydrazine is rather less volatile with steam than aniline and rapidly becomes brown when exposed to the air. It has a sp.gr. of 1·097 at 23°. The base is sparingly soluble in water but forms a hydrate of the formula $2(C_6H_5{\cdot}NH{\cdot}NH_2),H_2O$ which melts at 24·1°. It is almost insoluble in concentrated aqueous caustic alkali, but is very readily soluble in certain alkaline salts, such as the alkali salts of the sulphinic and sulphonic acids, soaps, &c. (Otto, Ber. 1894, 27, 2131). For some time it has been prepared on the large scale from diazotised aniline by the sulphite method, and is used commercially for the production of antipyrine, &c., and in the form of its sulphonic acid for the production of the so-called tartrazine colouring matters. Phenylhydrazine is a valuable reagent in organic chemistry, owing to the ease with which it forms crystalline compounds with substances containing carbonyl oxygen. These compounds, which belong to the class of the hydrazones and osazones, are dealt with elsewhere (*see* HYDRAZONES).

When taken internally phenylhydrazine acts as a violent poison, and when brought in contact with the skin causes painful inflammation. Chemists who work much with this substance usually suffer from ill health, of which the most prominent feature is a kind of eczema. It seems to form a definite green compound with the blood to which the name *hæmoverdin* has been given (*cp.* Lewin, Compt. rend. 1901, 133, 599; Zeit. Biol. 1901, 42, 107).

Of the salts of phenylhydrazine, the *hydrochloride* $C_6H_5{\cdot}NH{\cdot}NH_2,HCl$ is the most important. It crystallises as colourless glistening leaflets which dissolve readily in hot water but separate from the solution on cooling. It can be recrystallised from alcohol and by careful heating can be sublimed unchanged. Other aromatic hydrazines of importance are—

Diphenylhydrazine $(C_6H_5)_2N{\cdot}NH_2$. This compound is produced by the reduction of nitrosodiphenylamine $(C_6H_5)_2N{\cdot}NO$, which is obtained from diphenylamine $(C_6H_5)_2NH$ by the action of nitrous acid (E. Fischer, Annalen, 1877, 190, 174; Stahel, *ibid.* 1890, 258, 242; Overton, Ber. 1893, 26, 19). It forms colourless plates which melt at 34·5° and is partially decomposed on distillation under diminished pressure. The hydrazine yields well-defined crystalline compounds with sugars and can be used for the quantitative estimation of arabinose (Neuberg and Wohlgemuth, Ber. 1894, 27, 3106).

Methylphenylhydrazine $C_6H_5(CH_3)N{\cdot}NH_2$ may be prepared either by the reduction of the nitroso compound $C_6H_5(CH_3)N{\cdot}NO$ (E. Fischer, Annalen, 1877, 190, 150), or by the alkylation of sodium phenylhydrazine by means of methyl iodide (A. Michaelis, Ber. 1886, 19, 2450; Phillips, *ibid.* 1887, 20, 2485). It is a colourless liquid, boiling with slight decomposition and evolution of ammonia at 227° (745 mm.); under a pressure of 75 mm. it boils without decomposition at 131°. Methylphenylhydrazine is a valuable reagent for the isolation of certain ketones (Neuberg, Ber. 1902, 35, 959).

Phenylbenzylhydrazine

$$C_6H_5(CH_2{\cdot}C_6H_5)N{\cdot}NH_2$$

(Ofner, Monatsh. 1904, 25, 593) is prepared by the direct action of benzyl chloride on phenylhydrazine and is a colourless liquid boiling at 216°–218° at 38 mm. It is a useful reagent for the isolation of the sugars, as the hydrazones formed from it are less soluble and more easily produced than those from simpler hydrazines (*cp.* Ruff and Ollendorf, Ber. 1899, 32, 3255; Lobry de Bruyn, Rec. trav. chim. 15, 97, 227).

p-**Bromophenylhydrazine** $H_2N{\cdot}NH{\cdot}C_6H_4Br$ may be prepared by brominating phenylhydrazine hydrochloride in the presence of a large excess of strong hydrochloric acid (Neufeld, Annalen, 1888, 248, 94; L. Michaelis, Ber. 1893, 26, 2191). It crystallises from hot water as long needles which melt at 107° and is a useful reagent for the characterisation of sugars. It has been used for the preparation of hydrazones from certain naturally occurring ketones, as for example camphor (Tiemann and Kruger, Ber. 1895, 28, 1756; Tiemann, *ibid.* 2191).

Phenylhydrazine-*p*-sulphonic acid

$C_6H_4(SO_3H)NH{\cdot}NH_2$

is of historical interest as being the first derivative of hydrazine to be prepared, and was obtained from diazotised *p*-amidobenzenesulphonic acid by reduction with sodium hydrogen sulphite (Strecker and Römer, Ber. 1871, 4, 784; Römer, Zeitsch. Chem. 1871, 482). It may be prepared by the direct sulphonation of phenylhydrazine and when pure crystallises as glistening needles containing ½ a molecule of water of crystallisation. It is prepared on the large scale from *p*-sulphanilic acid by diazotisation and reduction with sodium sulphite, and is used for the production of the tartrazine colouring matters (*q.v.*).

p-**Nitrophenylhydrazine** $C_6H_4(NO_2)NH{\cdot}NH_2$. This substance is recommended by Bamberger (Ber. 1899, 32, 1806) for the investigation of aldehydes and ketones as being more stable than *p*-bromophenylhydrazine. It is prepared from the sodium salt of *p*-nitrophenylhydrazinesulphonic acid by the action of concentrated hydrochloric acid (Purgotti, Ber. 1892, 25, 119; Bamberger and Sternitzki, *ibid.* 26, 1306), and also by boiling the potassium salt of *p*-nitrophenylhydrazinedisulphonic acid with dilute hydrochloric acid (Hantzsch and Borghaus, Ber. 1897, 30, 91). It may also be prepared from *p*-nitraniline by diazotisation and reduction. The base forms orange red leaflets and needles from hot alcohol, which melt with decomposition at 157°. (For the use of this base in the preparation of hydrazones of the aldehydes and ketones, *cp.* Bamberger, Ber. 1899, 32, 1806; Hyde, *ibid.* 1810.)

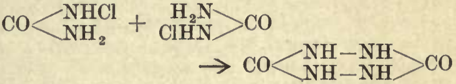
The naphthylhydrazines. Both the α- and β-naphthylhydrazines can be used for the preparation of hydrazones from compounds containing carbonyl oxygen, but the β- compound is especially recommended by Hilger and Rothenfusser (Ber. 1902, 35, 2627) for the isolation of numerous sugars. The two bases are prepared in a similar manner from the corresponding diazonaphthalenes on reduction with stannous chloride, or by heating the naphthol with hydrazine hydrate at 160° (Hoffmann, Ber. 1898, 31, 2909). α-Naphthylhydrazine forms leaflets from water which melt at 116°–117° and boil almost without decomposition at 203° (20 mm.) (Knorr, Ber. 1884, 17, 551). β-Naphthylhydrazine forms glistening leaflets from water which melt at 124°–125° (*cp.* also Franzen, Ber. 1905, 38, 266).

HYDRAZINE AND SOME OF ITS DERIVATIVES USED AS REAGENTS FOR THE ISOLATION OF ALDEHYDES AND KETONES.

Hydrazine $H_2N{\cdot}NH_2$. This substance was first prepared by Curtius by the action of hot dilute acids on triazoacetic acid (Ber. 1887, 20, 1632). It has since been obtained by other methods of which the more important are (1) from aminoguanidine $H_2N{\cdot}C(NH)NH{\cdot}NH_2$ on treatment with caustic alkali (Thiele, Annalen, 270, 1). (2) From sodium hypochlorite and ammonia (Raschig, D. R. PP. 192783, 198307; Chem. Zentr. 1908, i. 427, 1957). (3) From dichlorocarbamide (Chattaway, Chem. Soc. Trans. 1909, 95, 237). The last-named preparation is carried out in the following way:—

Dichlorocarbamide $NHCl{\cdot}CO{\cdot}NHCl$ (Chattaway, Chem. Soc. Trans. 1909, 95, 465). Six grams of carbamide are dissolved in 50 c.c. of distilled water and 10 grams of finely divided zinc oxide are added. The mixture is cooled to about −5° in a freezing mixture and a rapid stream of chlorine passed through the liquid. If the operation is carried out in a small flask, and this is well shaken in the freezing mixture during the passage of the gas, the temperature does not rise above zero. The zinc oxide quickly dissolves and a clear liquid results, from which in a short time crystals of dichlorocarbamide begin to separate. When the liquid has become a thick pulp from the separated solid and crystals no longer appear to separate, the dichlorocarbamide is rapidly collected at the pump, washed twice with 5 c.c. of ice-cold distilled water and then several times with chloroform. The yield is 77·5 p.c. of the theory.

p-**Urazine.** This substance is formed by the elimination of hydrogen chloride from two molecules of monochlorocarbamide, which may be regarded as the initial product formed by the action of ammonia on dichlorocarbamide—



$$CO{<}\begin{matrix}NHCl\\NH_2\end{matrix} + \begin{matrix}H_2N\\ClHN\end{matrix}{>}CO \rightarrow CO{<}\begin{matrix}NH-NH\\NH-NH\end{matrix}{>}CO$$

p-Urazine.

the condensation is therefore effected by the action of ammonia (Chattaway, Chem. Soc. Trans. 1909, 95, 237). Crude dichlorocarbamide free from all adhering mother-liquor is dissolved in from 10 to 20 times its weight of water and rapidly added to excess of strong ammonia, the mixture being thoroughly stirred. A vigorous evolution of nitrogen takes place and a white crystalline powder separates; a little more crystallises out on keeping and a still further small quantity on evaporating the mother-liquor after neutralising with hydrochloric acid.

Hydrazine sulphate. When *p*-urazine is mixed with about 5 times its weight of concentrated sulphuric acid and warmed to about 80°, it dissolves apparently without change; on heating the solution to about 95°–100°, hydrolysis slowly takes place with evolution of carbon dioxide. On raising the temperature still higher, the rate of evolution of carbon dioxide increases, until, at about 120°–130°, it is very rapidly liberated; at this temperature, hydrolysis is soon complete and a clear colourless liquid is obtained which deposits crystals of hydrazine sulphate on cooling. It is best, however, to add to the cooled liquor its own bulk of water, when pure hydrazine sulphate at once separates as a white crystalline powder.

Free hydrazine has been prepared by Lobry de Bruyn (Ber. 1895, 27, 3085) by the action of sodium methoxide in methyl alcohol on hydrazine hydrochloride, and also by heating the hydrate N_2H_4,H_2O with barium oxide at 100°. It is a very stable liquid which boils without decomposition at 113·5° (761 mm.), and at 56° (71 mm.). It solidifies when cooled below 0°, and then melts at 1·4°. It has a sp.gr. of 1·003 at 23° (*cp.* Raschig, Ber. 1910, 43, 1927).

Hydrazine hydrate N_2H_4,H_2O is the form in which hydrazine is liberated from its salts by the action of aqueous alkalis. It is a strongly refracting, almost odourless liquid, which boils without decomposition at 118·5° (739·5 mm.) and solidifies when placed in a mixture of solid carbon dioxide and ether, but melts again below −40°. It is advisable when preparing this substance to employ a silver retort and to avoid the use of rubber connections, as the hydrate, when hot, attacks glass strongly and quickly destroys cork and rubber.

Semicarbazide $H_2N{\cdot}CO{\cdot}NH{\cdot}NH_2$. This substance was first used for the preparation of derivatives of ketones by Baeyer acting on the suggestion of Thiele (Ber. 1894, 27, 1918), the compound having been prepared earlier in the year by Thiele and Strange (Ber. 1894, 27, 31; Annalen, 1894, 283, 19), who obtained it by the action of potassium cyanate on hydrazine sulphate, and by Curtius and Heidenreich (Ber. 1894, 27, 56), who prepared it by the interaction of hydrazine hydrate and urea. Semicarbazide may be conveniently prepared in the following way: 225 grams of nitrourea in 1700 c.c. of concentrated hydrochloric acid are mixed at 0° with excess of zinc dust and are then left for a short time after all action has subsided. The filtered solution, after being saturated with sodium chloride, is treated with 200 grams of sodium acetate and 100 grams of acetone. The acetonesemicarbazone zinc chloride, which separates after some time, is washed with salt solution and decomposed by strong ammonia (350 c.c. to 200 grams of the compound) (Thiele and Heuser, Annalen, 1895, 288, 312).

Semicarbazide crystallises from absolute alcohol as prisms which melt at 96°. It readily reacts with substances containing carbonyl oxygen, in accordance with the scheme

$$H_2N{\cdot}CO{\cdot}NH{\cdot}NH_2+OCR_2 \\ =H_2N{\cdot}CO{\cdot}NH{\cdot}N:CR_2+H_2O$$

forming semicarbazones which possesses the advantage of being readily decomposed into their components on treatment with dilute acids. The method recommended by Baeyer (Ber. 1894, 27, 1918) for the preparation of a carbazone is as follows:—

Semicarbazide hydrochloride is dissolved in a little water and the requisite amount of alcoholic potassium acetate together with the ketone are added, as well as sufficient alcohol and water to effect complete solution. The length of time required for the reaction depends on the nature of the ketone and varies from a few minutes to 4–5 days; it is finished when the addition of water precipitates a crystalline solid. Semicarbazide is usually met with in the form of its hydrochloride. The free base slowly alters on keeping.

Thiosemicarbazide $NH_2{\cdot}CS{\cdot}NH{\cdot}NH_2$. This substance, like semicarbazide, reacts with compounds containing carbonyl oxygen in accordance with the equation—

$$H_2N{\cdot}CS{\cdot}NH{\cdot}NH_2+OCR_2 \\ =H_2N{\cdot}CS{\cdot}NH{\cdot}N:CR_2+H_2O$$

forming thiosemicarbazones, which possess the property of forming insoluble salts with the heavy metals from which the ketone or aldehyde can be readily regenerated (Neuberg and Neimann, Ber. 1902, 2049).

The base can be prepared from hydrazine sulphate in the following manner (Freund and Schander, Ber. 1896, 29, 2501; Freund and Imgart, *ibid.* 1895, 28, 948). 50 grams of hydrazine sulphate and 27 grams of anhydrous potassium carbonate are dissolved in 200 c.c. of water and mixed with 40 grams potassium thiocyanate. The mixture is boiled for some minutes and is then treated with 200–300 c.c. of hot alcohol and filtered. The filtrate is freed from alcohol by vigorously boiling and, when cooled, deposits long needles of the base which melt at 181°.

Semioxamazide $H_2N{\cdot}CO{\cdot}CO{\cdot}NH{\cdot}NH_2$ (Kerp and Unger, Ber. 1897, 30, 586). This substance may be prepared by gently heating oxamethane with an alcoholic solution of hydrazine for a short time on the water bath. It crystallises in slender lustrous leaflets which melt and decompose at 220–221°. Semioxamazones are produced in quantitative yield from aldehydes, but the ketones react in a less general manner and seem to require special conditions for their formation.

Aminoguanidine $H_2N{\cdot}C(NH)NH{\cdot}NH_2$ is prepared from nitroguanidine on reduction (Thiele, Annalen, 270, 23; D. R. P. 59241; Frdl. iii. 16), and from cyanamide, hydrazine hydrochloride and alcohol (Pellizari and Cuneo, Gazz. chim. ital. 1894, 24, 453). The hydrochloride forms long prisms from dilute alcohol which melt at 163°.

The base is recommended by Baeyer (Ber. 1894, 27, 1919) for the preparation of derivatives of ketones, the following method being used.

Aminoguanidine hydrochloride is dissolved in a little water containing a trace of hydrochloric acid and is then mixed with the ketone together with sufficient alcohol to effect solution. The reaction is finished after warming for a short time on the water bath, when water and caustic potash solution are added and the base is extracted by ether. The oil which remains after evaporating the ether is suspended in hot water and heated with an aqueous solution of picric acid. The picrate separates as a crystalline precipitate which is recrystallised either from dilute or absolute alcohol, according to its solubility.

J. F. T.

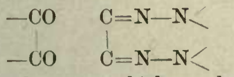
HYDRAZONES. Substances containing the complex $>N{\cdot}NH_2$ react with those compounds which have in their molecule an oxygen atom doubly bound to carbon, forming condensation products in accordance with the general equation

$$>C:O+H_2N{\cdot}N< \;\rightarrow\; >C:N{\cdot}N<+H_2O.$$

Such condensation products are termed hydrazones. Only the carbonyl compounds which belong to the groups of the aldehydes and ketones react, however, in this manner; the carboxylic acids containing the group COOH do not react as if they contained carbonyl oxygen, but give hydrazides in accordance with the scheme

$$R{\cdot}COOH+H_2N{\cdot}N{<}\longrightarrow R{\cdot}CO{\cdot}NH{\cdot}N{<}+H_2O.$$

One or more carbonyl-groups present in the compound may enter into combination with the hydrazine residue, forming—for example, in the case of the dicarbonyl derivatives—dihydrazones, thus:



$$\begin{array}{ll}-CO & C=N-N{<}\\ & |\\ -CO & C=N-N{<}\end{array}$$

Those dihydrazones, which are derived from dicarbonyl compounds having the two carbonyl-groups on contiguous carbon atoms, are termed osazones. Thus in the case of the two compounds formed from glyoxal CHO·CHO and phenylhydrazine

$$\begin{array}{l}CHO\\ |\\ CH:N{\cdot}NHC_6H_5\end{array}$$ is glyoxalphenylhydrazone;

$$\begin{array}{l}CH:N{\cdot}NHC_6H_5\\ |\\ CH:N{\cdot}NHC_6H_5\end{array}$$ is glyoxalphenylosazone

(Fischer, Ber. 1888, 21, 985).

Phenylhydrazine $C_6H_5{\cdot}NH{\cdot}NH_2$ was the first member of the class of the hydrazines to be applied to the characterisation and isolation of the carbonyl compounds (comp. E. Fischer, Ber. 1884, 17, 572), but since that time the reaction has been shown to be a general one for all derivatives of hydrazine having a primary amino group intact.

Hydrazine $H_2N{\cdot}NH_2$ itself reacts with aldehydes and ketones, as Curtius has shown, forming either hydrazones of the type

$$R{\cdot}CH:N{\cdot}NH_2$$

(or $RRC:N{\cdot}NH_2$), in which one molecule of the carbonyl compound reacts, or azines of the formula $R{\cdot}CH:N{\cdot}N:CHR$) or

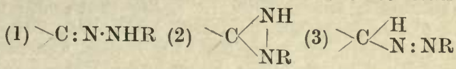
$$RRC:N{\cdot}N{\cdot}CRR)$$

in which two molecules of the carbonyl derivative take part. The azines from the aldehydes are known as aldazines, those from the ketones as ketazines. In the aliphatic series, the aldehydes pass directly into the aldazines when treated with hydrazine, whilst the hydrazones, $RRC:N{\cdot}NH_2$, which can be isolated from the product of the interaction of ketones and hydrazine, readily pass into the ketazine and hydrazine in accordance with the equation

$$2(R_2C:N{\cdot}NH_2)\longrightarrow R_2C:N{\cdot}N{\cdot}R_2+H_2N{\cdot}NH_2.$$

It is apparent that azine formation in the manner described above cannot occur with the substituted derivatives of hydrazine of the general formulæ $RNH{\cdot}NH_2$ and $R_2N{\cdot}NH_2$, and it is therefore compounds of this type which are of such great importance as reagents for the preparation of the hydrazones, osazones, and semicarbazones.

Constitution of the hydrazones. The constitution of the hydrazones formed from carbonyl compounds by the action of secondary asymmetric hydrazines $R_2N{\cdot}NH_2$, admits of only one formula, namely, $R_2N{\cdot}N:CR_2$; but the hydrazones formed from the primary hydrazines may conceivably be constituted in accordance with one or other of the three forms



$$(1)\ {>}C:N{\cdot}NHR\quad (2)\ {>}C{<}\begin{array}{l}NH\\ \,|\\ NR\end{array}\quad (3)\ {>}C{<}\begin{array}{l}H\\ N:NR\end{array}$$

Of these, formula (2) may be discarded, because the same compound is formed by the interaction of benzaldehyde and phenylethylhydrazine

$$C_6H_5{\cdot}CHO+H_2N{\cdot}N(C_2H_5)C_6H_5 =C_6H_5{\cdot}CH:N{\cdot}N(C_2H_5)C_6H_5$$

as by the ethylation, by means of sodium ethoxide and ethyl iodide, of the hydrazone formed by the condensation of benzaldehyde and phenylhydrazine

$$C_6H_5{\cdot}CHO+H_2N{\cdot}NH{\cdot}C_6H_5 =C_6H_5{\cdot}CH:N{\cdot}NH{\cdot}C_6H_5$$

$$C_6H_5{\cdot}CH:N{\cdot}NH{\cdot}C_6H_5+NaO{\cdot}C_2H_5 =C_6H_5{\cdot}CH:N{\cdot}NNa{\cdot}C_6H_5+HO{\cdot}C_2H_5$$

$$C_6H_5{\cdot}CH:N{\cdot}NNa{\cdot}C_6H_5+C_2H_5I = C_6H_5{\cdot}CH:N{\cdot}N(C_2H_5)C_6H_5+NaI.$$

The azo formula (3) would appear, at first sight, to be untenable, because the hydrazone prepared from phenylhydrazine and acetaldehyde is different from ethaneazobenzene

$$CH_3{\cdot}CH_2{\cdot}N:N{\cdot}C_6H_5$$

which is prepared by the oxidation of ethanehydrazobenzene. It has been shown, however, that there is an intimate connection between these two substances, and that the change

$$C_6H_5{\cdot}N:N{\cdot}C_2H_5\longrightarrow C_6H_5{\cdot}NH{\cdot}N:CHCH_3$$

is readily effected by mineral acids (Fischer, Annalen, 1879, 199, 328; Ber. 1896, 29, 703), or by sodium ethoxide (Bamberger, Ber. 1903, 36, 56); whereas the reverse change

$$C_6H_5{\cdot}NH{\cdot}N:CHCH_3\longrightarrow C_6H_5{\cdot}N:N{\cdot}CH_2CH_3$$

is effected by the action of light (Chattaway, Chem. Soc. Trans. 1906, 89, 462). The question as to the azo or hydrazone structure of these compounds has given rise to a great deal of controversy, and is even at the present time not definitely settled. The discussion may be said to have arisen owing to the discovery made by Japp and Klingemann (Ber. 1887, 20, 3284, 3398), that the hydrazone of pyruvic acid

$$C_6H_5NH{\cdot}N:C(CH_3)CO_2H$$

was identical with benzene-α-azopropionic acid $C_6H_5N:N{\cdot}CH(CH_3)CO_2H$. R. Meyer (Ber. 1888, 21, 118) also showed that the dicarboxylic acid obtained by the hydrolysis of the ethyl salt which is formed by the interaction of benzenediazonium chloride and ethyl malonate, thus:

$$C_6H_5{\cdot}N_2Cl+CH_2(CO_2R)_2 =C_6H_5{\cdot}N:N{\cdot}CH(CO_2R)_2+HCl$$

$$C_6H_5{\cdot}N:N{\cdot}CH(CO_2R)_2+2H_2O =C_6H_5{\cdot}N:N{\cdot}CH(CO_2H)_2+2R{\cdot}OH$$

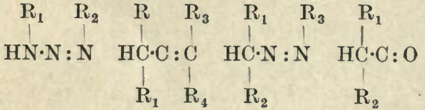
was identical with the compound prepared by the condensation of mesoxalic acid and phenylhydrazine, thus:

$$C_6H_5{\cdot}NH{\cdot}NH_2+CO(CO_2H)_2 =C_6H_5{\cdot}NH{\cdot}N:C(CO_2H)_2+H_2O.$$

That is to say, the question arose as to whether these compounds were true hydrazones having the structure $R{\cdot}NH{\cdot}N:C{<}$ or whether they were azo compounds having the structure $R{\cdot}N:N{\cdot}CH{<}$.

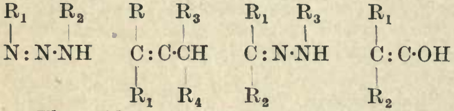
Since that time many other instances of the same kind as that recorded by these chemists have been investigated, and repeated attempts have been made to establish either one or other of these constitutional formulæ for the hydrazones (R. Meyer, Ber. 1891, 24, 1241; Japp and Klingemann, Annalen, 1888, 247, 190; V. Meyer, Ber. 1888, 21, 11; Haller, Compt. rend. 1888, 106, 1173; Beyer and Claisen, Ber. 1892, 25, 746; v. Pechmann, Ber. 1892, 25, 3190; Bamberger and Wheelwright, *ibid.* 1892, 25, 3201; Bamberger, *ibid.* 1894, 27, 2591).

Much of the evidence falls under the head of the constitution of the azo compounds, and the article under this heading should be consulted for further information; but it is evident that much still remains to be learnt regarding the conditions controlling the tendency of a hydrogen atom attached to the terminal atom of any system such as



$$\mathrm{H}\overset{R_1}{\mathrm{N}}\cdot\mathrm{N}:\overset{R_2}{\mathrm{N}}\qquad \mathrm{H}\underset{R_1}{\overset{R}{\mathrm{C}}}\cdot\mathrm{C}:\underset{R_4}{\overset{R_3}{\mathrm{C}}}\qquad \mathrm{H}\underset{R_2}{\overset{R_1}{\mathrm{C}}}\cdot\mathrm{N}:\overset{R_3}{\mathrm{N}}\qquad \mathrm{H}\underset{R_2}{\overset{R_1}{\mathrm{C}}}\cdot\mathrm{C}:\mathrm{O}$$

to pass to the other terminal atom with a consequent shifting of the double bond, thus:



$$\overset{R_1}{\mathrm{N}}:\overset{R_2}{\mathrm{N}}\cdot\mathrm{NH}\qquad \underset{R_1}{\overset{R}{\mathrm{C}}}:\mathrm{C}\cdot\underset{R_4}{\overset{R_3}{\mathrm{CH}}}\qquad \underset{R_2}{\overset{R_1}{\mathrm{C}}}:\mathrm{N}\cdot\overset{R_3}{\mathrm{NH}}\qquad \underset{R_2}{\overset{R_1}{\mathrm{C}}}:\mathrm{C}\cdot\mathrm{OH}$$

The evidence at present available seems to show that the hydrogen atom in compounds of this type may assume either one or other of these positions, in which case definite compounds are formed, having, as in the case under discussion, either the azo or hydrazone form: on the other hand, there may be tautomerism between the two forms, in which case the hydrogen atom acts as if it vibrated between the two terminal atoms of the system (*cf.* Bulow and Hopfner, Ber. 1901, 34, 71; Bulow and Hailer, *ibid.* 1902, 35, 915). There is, however, little doubt that in the majority of cases the compounds formed from benzenediazonium chloride and substances of the type of ethyl malonate as well as those produced by the action of phenylhydrazine on carbonyl compounds have the hydrazone structure.

The formation of phenylhydrazones. As a rule, phenylhydrazine readily reacts with ketones and aldehydes, yielding phenylhydrazones, which are crystalline and of definite melting-point. The following method generally gives the phenylhydrazone in a pure condition. Phenylhydrazine is dissolved in 50 p.c. aqueous acetic acid and diluted with three times its volume of water. The carbonyl compound diluted when necessary by a suitable solvent is then added and the whole is warmed. The phenylhydrazone then separates either in the crystalline condition or as an oil which usually crystallises when scratched with a glass rod.

Derivatives of phenylhydrazine, such as phenylhydrazine-*p*-sulphonic acid

$$C_6H_4(SO_3H)NH\cdot NH_2,$$

p-nitrophenylhydrazine $C_6H_4(NO_2)NH\cdot NH_2$ or *p*-bromophenylhydrazine

$$C_6H_4(Br)NH\cdot NH_2,$$

may be used for the production of hydrazones; moreover other hydrazines, such as β-naphthylhydrazine $C_{10}H_7\cdot NH\cdot NH_2$, methylphenylhydrazine $C_6H_5(CH_3)N\cdot NH_2$, *asym*-diphenylhydrazine $(C_6H_5)_2N\cdot NH_2$, and benzylphenylhydrazine $C_6H_5\cdot CH_2(C_6H_5)N\cdot NH_2$ are often used for this purpose (*cp.* HYDRAZINES).

Reaction of the hydrazones. When warmed with mineral acids, the hydrazones are more or less readily hydrolysed into the carbonyl compound and the hydrazine. This reaction proceeds, however, much more readily when the hydrazone is warmed with an aqueous solution of pyruvic acid, when the following reaction often occurs (Fischer and Ach, Annalen, 1889, 253, 57):—

$$R_2C:N\cdot NH\cdot C_6H_5+CH_3\cdot CO\cdot CO_2H$$
$$=R_2CO+CH_3\cdot C(:N\cdot NH\cdot C_6H_5)CO_2H.$$

The hydrazones of the aliphatic aldehydes and ketones form addition products with hydrocyanic acid, yielding nitriles in accordance with the equation

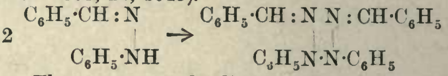
$$C_6H_5\cdot NH\cdot N:CR_2+HCN$$
$$=C_6H_5\cdot NH\cdot NH\cdot C(CN)\cdot R_2$$

(*cp.* V. Miller and Plöchl, Ber. 1892, 25, 2023).

Hydrazones when reduced break at the point of union of the two nitrogen atoms and pass into amines. This method has been made use of by Tafel (Ber. 1886, 19, 1924; 1889, 22, 1854) for the formation of primary amines from aldehydes and ketones. Thus the hydrazone of acetaldehyde yields in this manner a mixture of aniline and ethylamine

$$CH_3\cdot CH:N\cdot NH\cdot C_6H_5+4H$$
$$=CH_3\cdot CH_2NH_2+C_6H_5NH_2.$$

When oxidised by amyl nitrite, hydrazones are converted into hydrotetrazines (V. Pechmann, Ber. 1893, 26, 1045).

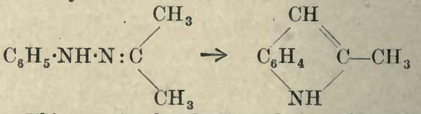


$$2\begin{array}{l}C_6H_5\cdot CH:N\\ \qquad\quad\ |\\ \quad C_6H_5\cdot NH\end{array}\rightarrow\begin{array}{c}C_6H_5\cdot CH:N\ \ N:CH\cdot C_6H_5\\ |\qquad |\\ C_6H_5N\cdot N\cdot C_6H_5\end{array}$$

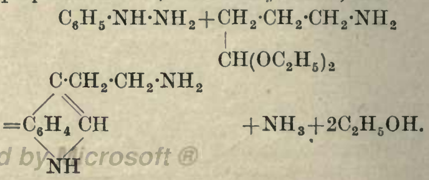
These compounds dissolve in concentrated sulphuric acid, forming intensely coloured solutions. It is probable that Bulow's reaction for hydrazides and hydrazones, which depends on the formation of a coloured solution, when the hydrazone, dissolved in concentrated sulphuric acid, is treated with a drop of ferric chloride solution, is due to the production of the hydrotetrazine.

The action of zinc chloride on hydrazones causes the elimination of ammonia and leads to the formation of derivatives of indole (E. Fischer and Hess, Ber. 1884, 17, 559; E. Fischer, *ibid.* 1886, 19, 1563; Annalen, 1886, 236, 116; Brunner, Monatsh. 1895, 16, 183, 849).

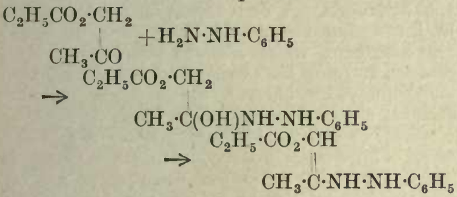
The reaction may be expressed by the following general equation but is difficult to follow by means of structural formulæ:—



This reaction has been made use of by Ewins (Chem. Soc. Trans. 1911, 99, 270) for the preparation of 3-β-aminoethylindole, thus—

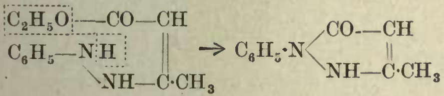


This compound was found to be identical with the base obtained by the action of putrefactive bacteria on tryptophan. It will be noticed that, owing to the unstable character of the aldehyde, it could not be used in the free state for the production of the hydrazone and that the acetal derivative was used in its place. Hydrazones which are formed from β-ketonic ethyl salts pass, when heated, into alcohol and a derivative of pyrazolone. Thus the phenylhydrazone of ethyl acetoacetate, which is a colourless crystalline substance and is therefore probably ethyl benzenehydrazocrotonate formed in accordance with the equation



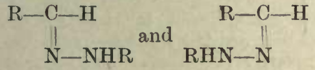
$$\begin{array}{l} C_2H_5CO_2\cdot CH_2 \\ \quad\; | \qquad\quad + H_2N\cdot NH\cdot C_6H_5 \\ CH_3\cdot CO \end{array} \rightarrow \begin{array}{l} C_2H_5CO_2\cdot CH_2 \\ \qquad\quad | \\ CH_3\cdot C(OH)NH\cdot NH\cdot C_6H_5 \end{array} \rightarrow \begin{array}{l} C_2H_5\cdot CO_2\cdot CH \\ \qquad\quad \| \\ CH_3\cdot C\cdot NH\cdot NH\cdot C_6H_5 \end{array}$$

passes when heated at 200° under diminished pressure into phenylmethylpyrazolone



In many cases the formation of the pyrazolone derivative takes place immediately without the intermediate formation of the hydrazone.

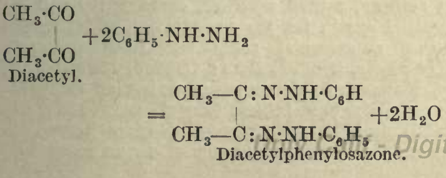
Stereoisomerism, in accordance with the Hantzsch-Werner hypothesis, has been observed among the hydrazones, and in certain instances the two forms



$$\begin{array}{c} R—C—H \\ | \\ N—NHR \end{array} \quad \text{and} \quad \begin{array}{c} R—C—H \\ \| \\ RHN—N \end{array}$$

have been isolated (*cp.* E. Fischer, Ber. 1884, 17, 575; Biltz, *ibid.* 1894, 2288; Hantzsch and Hornbostel, *ibid.* 1897, 30, 3003; Bamberger and Schmidt, *ibid.* 1901, 34, 2001).

As already mentioned, the name 'osazone' denotes a compound containing in its molecule two hydrazine residues, R—NH—N=, attached to two contiguous carbon atoms. E. Fischer (Ber. 1884, 17, 579) obtained from carbohydrates a series of characteristic compounds formed by the introduction of two phenylhydrazone groups into the molecule of a carbohydrate. The compound from dextrose was termed 'phenylglucosazone'; that from galactose 'phenylgalactosazone,' and so on. Later, when it was found that in these compounds the two phenylhydrazine residues were in contiguous positions, the name 'osazone' was applied to all compounds containing this particular grouping (E. Fischer, Ber. 1888, 21, 985). Osazones are formed by the action of two molecules of phenylhydrazine on α-dicarbonyl compounds, namely, such as contain the group CO·CO;



$$\begin{array}{l} CH_3\cdot CO \\ \quad | \qquad + 2C_6H_5\cdot NH\cdot NH_2 \\ CH_3\cdot CO \end{array} = \begin{array}{l} CH_3—C:N\cdot NH\cdot C_6H \\ \qquad | \\ CH_3—C:N\cdot NH\cdot C_6H_5 \end{array} + 2H_2O$$

Diacetyl. Diacetylphenylosazone.

The yellow colouring matters known as 'tartrazines' are derived from osazones, formed in this way from dihydroxytartaric acid.

Osazones are also formed by the action of phenylhydrazine on compounds containing the group —CH(OH)·CO—, thus on α-keto-alcohols and α-aldehydo-alcohols; and it is the members of the carbohydrate family belonging to these classes which yield osazones. In the cold, unless on long standing, only the carbonyl group reacts with phenylhydrazine, and a hydrazone containing the group

$$—CH(OH)C(N_2H\cdot C_6H_5)—$$

is formed; but this compound, on heating with excess of phenylhydrazine, is converted into an osazone, the alcohol group also taking part in the reaction. The molecule of hydrogen which is removed in this process reduces a molecule of phenylhydrazine to aniline and ammonia. Thus with dextrose—

$$CH_2OH[CHOH]_4CHO+3C_6H_5NH\cdot NH_2$$
$$\rightarrow CH_2OH[CHOH]_3C(N_2H\cdot C_6H_5)CH(N_2HC_6H_5)$$
Phenylglucosazone.
$$+NH_2C_6H_5+NH_3+2H_2O.$$

These osazones have proved of great use in identifying various sugars. Sometimes, however, two distinct sugars yield the same osazone: thus lævulose, like dextrose, gives phenylglucosazone:—

$$CH_2OH[CHOH]_3CO\cdot CH_2OH+3C_6H_5NH\cdot NH_2$$
Lævulose.
$$\rightarrow CH_2OH[CHOH]_3C(N_2H\cdot C_6H_5)CH(N_2H\cdot C_6H_5)$$
Phenylglucosazone.
$$+NH_2C_6H_5)+NH_3+2H_2O$$

the α-aldehyde alcohol and the α-keto alcohol-yielding the same osazone.

The osazones are crystalline compounds, of a yellow colour, and generally have a definite melting point, by means of which they may be identified. Concentrated sulphuric acid dissolves the various osazones, giving characteristic colourations, and the solution generally exhibits some particular colour change on standing (Japp and Klingemann, Ber. 1888, 21, 549). Fuming hydrochloric acid hydrolyses the osazones in the cold into phenylhydrazine and the α-dicarbonyl compound from which they are derived (E. Fischer, *ibid.* 1888, 21, 2631).

J. F. T.

HYDRAZONE COLOURING MATTERS *v.* PYRAZOLONE COLOURING MATTERS.

HYDRINDENE *v.* KETONES and INDENE.

HYDRINDONE *v.* INDENE.

HYDRIODIC ACID *v.* IODINE.

HYDROBROMIC ACID *v.* BROMINE.

HYDROCARBOSTYRIL *v.* QUINOLINE.

HYDROCHLORIC ACID *v.* CHLORINE.

HYDROCURCUMIN *v.* TURMERIC.

HYDROCYANIC ACID *v.* CYANIDES.

HYDROFLUORIC ACID *v.* FLUORINE.

HYDROFLUOSILICIC ACID *v.* FLUORINE.

HYDROGELS *v.* COLLOIDS.

HYDROGEN. At.wt. 1·008. Symbol H. The existence of this gas was recognised in the 16th century; its combustible property was discovered in the following century by Turquet de Mayerne, and in 1700 Lemery observed the detonating property of a mixture of air and hydrogen.

Cavendish, in 1766, showed that when the gas was produced from dilute acid and one of the metals, iron, zinc, or tin, it was obtained in amount varying with the metal used.

Hydrogen was for a time confounded with other combustible gases, such as marsh-gas, carbon monoxide, and vapour of ether; all were supposed to contain the same inflammable principle, *phlogiston*, modified by variable amounts of other substances.

Macquer and De la Metherie first observed, in 1766, that water was produced by burning hydrogen, but it was then thought that other products than water were produced at the same time, and Lavoisier made many experiments with the object of detecting the presence of an acid which he imagined should be among the products of combustion, as was the case in the combustion of such bodies as sulphur, carbon, phosphorus, &c. Cavendish, however, in 1781, proved conclusively that water was the only product of combustion when hydrogen burns in air or oxygen, and that if a mixture of hydrogen and oxygen in the proportion of two volumes of the former to one of the latter were burnt, the whole of the gases were converted into water.

Sources. Hydrogen occurs free in nature in the gaseous mixtures evolved from certain volcanos (Bunsen, Ann. Chim. Phys. 1853, [iii.] 38, 215; Deville, Compt. rend. 1862, 55, 75). The gases evolved from Mte. Pelée in Martinique during the eruptions of 1902 contained 22·3 p.c. of hydrogen by volume (Moissan, Compt. rend. 1902, 135, 1085). It also occurs in the jets of steam, known as *fumerolles*, which occur in Tuscany and other places. The gases issuing from the salt beds of Stassfurt (Reichardt, Arch. Pharm. 1860, [ii.] 103, 347; Precht, Ber. 1880, 13, 2326), and Wieliczka (Rose, Pogg. Ann. 48, 353) contain hydrogen, and it also occurs in the gases given off by the oil-wells of Pennsylvania (Engler, Ber. 1888, 21, 1816). Hydrogen has been found occluded in certain meteorites (Graham, Proc. Roy. Soc. 1867, 15, 502; Mallet, *ibid.* 1872, 20, 365), and in a large number of minerals (Ramsay and Travers, Proc. Roy. Soc. 1897, 60, 442; Tilden, *ibid.* 1897, 60, 453). To a very slight extent, hydrogen occurs free in the atmosphere (Gautier, Ann. Chim. Phys. 1901, [vii.] 22, 5; Liveing and Dewar, *ibid.* 1901, 22, 482; Rayleigh, Phil. Mag. 1902, [vi.] 3, 416; Leduc, Compt. rend. 1902, 135, 860, 1332). According to Claude (Compt. rend. 1909, 148, 1454), there is less than 1 part of hydrogen in one million parts of air. Hydrogen is also produced in the decay of various organic bodies, being found in the intestinal gases of many animals (Tappeiner, Ber. 1881, 14, 2375).

Spectroscopic observations have shown that hydrogen completely surrounds the sun, forming an envelope which has received the name of the *chromosphere*. Hydrogen also occurs in certain stars and nebulæ.

In a state of combination, hydrogen forms one-ninth the weight of water and one-fourth the weight of marsh-gas. It also occurs in smaller quantities in combination with phosphorus, sulphur, iodine, bromine, carbon, and nitrogen. It is an essential constituent of all acids; most animal and vegetable substances contain it, and it is a constituent of many minerals. It exists in the air in small quantities in combination with nitrogen as ammonia; and in certain mineral and volcanic springs it is found in combination with sulphur and chlorine as sulphuretted hydrogen and hydrochloric acid respectively.

Preparation. (1) *Electrolysis of certain aqueous solutions.*—Pure hydrogen is readily prepared by the electrolysis of a mixture of 1 part of sulphuric acid and 10 parts of water, between platinum electrodes. The potential difference between the terminals must exceed 1·7 volts. The hydrogen is evolved at the cathode, and suitable provision must be made to prevent oxygen from the anode diffusing into the hydrogen. A convenient method consists in immersing the anode in a mass of liquid zinc-amalgam, which absorbs the oxygen completely, forming zinc oxide and eventually zinc sulphate. The current from three or four Bunsen elements is sufficient to work such an electrolytic cell for laboratory use. A suitable piece of apparatus is described in Amer. Chem. J. 1897, 19, 810. A 30 p.c. solution of sodium hydroxide may also be employed; plate nickel electrodes are most convenient, and a useful piece of apparatus for this purpose is described by Vèzes and Labatut (Zeitsch. anorg. Chem. 1902, 32, 464). Hydrogen prepared from sodium hydroxide solution always contains a little organic matter, owing to the presence of carbonate in solution (Morley); it can be obtained quite pure by electrolysing a solution of pure recrystallised baryta (Baker, Chem. Soc. Trans. 1902, 81, 400).

These electrolytic methods are employed on a commercial scale, dilute sulphuric acid being electrolysed between lead electrodes, or sodium hydroxide between iron electrodes. The chief difficulty encountered is that of preventing diffusion between the hydrogen and the oxygen simultaneously produced. The introduction of diaphragms increases the resistance of the cell, and is therefore to be avoided if possible. Various patterns of cell have been devised, and are described in J. Soc. Chem. Ind. 1900, 19, 1120; 1901, 20, 258; Eng. Pats. 2820, 1902, and 27249, 1903; Fr. Pats. 355652, 1905, and 397319, 1908; D. R. P. 198626, 1906.

(2) *Chemical decomposition of water.*—Hydrogen may be prepared by decomposing water; a large number of readily oxidisable substances can be employed for this purpose.

The alkali metals and the metals of the alkaline earths decompose water at ordinary temperatures, liberating hydrogen and producing the corresponding metallic hydroxide. The action is very violent, particularly with potassium, rubidium, and cæsium. The reactions can be readily controlled, however, by employing the amalgams of these metals. The action of steam on pure sodium has been used for the preparation of pure hydrogen (Scott, Phil. Trans. 1893, 184, 548; Mellor and Russell, Chem. Soc. Trans. 1902, 81, 1279), and the use of sodium, mixed with oil, aluminium, and infusorial earth, for the preparation of hydrogen on a commercial scale has been patented (U.S. Pats. 883531, 1908; 909536, 1909).

Magnesium decomposes water at temperatures above 70° (Ditte, Compt. rend. 1871, 73, 108), and burns vigorously when heated in steam. Magnesium amalgam decomposes cold water (Fleck and Basset, J. Amer. Chem. Soc. 1895, 17, 789).

Aluminium does not decompose water unless some means is afforded of removing the oxide from the surface of the metal. This is easily effected by amalgamating it with $\frac{1}{15}$ its weight of mercury, when the amalgam produced readily decomposes water and can be employed as a source of pure hydrogen (Baille and Féry, Ann. Chim. Phys. 1889, [vi.] 17, 248; Wislicenus and Kauffmann, Ber. 1895, 28, 1323). Hydrogen is readily obtained pure by slowly adding water to a mixture of fine aluminium filings containing 1 to 2 p.c. of mercuric chloride and 0·5 p.c. of potassium cyanide, keeping the temperature at 70° (Mauricheau-Beaupré, Compt. rend. 1908, 147, 310; Fr. Pat. 392725, 1908). One kilo. of this mixture yields 1300 litres of hydrogen.

At a red heat, water vapour is easily decomposed by iron, hydrogen and triferric tetroxide being produced (Lavoisier, Œuvres, 2, 360). This method is employed on a large scale and has been the subject of numerous patents (Eng. Pats. 7518, 1887; 20752, 1890; 4134, 1891; 28721, 1896; 10356, 1903; 21479, 1908; Fr. Pats. 373271, 1907; 386991, 1908; 395132, 1908; U.S. Pat. 971206, 1908; D. R. P. 226453, 1909). The oxide produced is reduced to metal by heating with coal or by some other process, and used again.

Steam is readily decomposed by passing it over red-hot coke, when a mixture consisting essentially of carbon monoxide and hydrogen in approximtaely equal volumes, is produced, known as *water-gas* (*v.* GAS, WATER). Numerous methods have been proposed for the purpose of preparing hydrogen commercially from this mixture. In one process (Frank, Fr. Pat. 371814, 1906), the dried mixture is passed over calcium carbide at a temperature above 300°; carbon monoxide and dioxide are removed as calcium oxide, calcium carbonate, and carbon, while the nitrogen present is converted into calcium cyanamide. The oxides of carbon may be partially removed by a preliminary cooling process, whereby the monoxide is liquefied and the dioxide solidified. Jouve and Gautier (Fr. Pat. 372045, 1906) propose to pass the gas through a porous partition in order to separate the hydrogen by reason of its rapid power of diffusion. It is said that by one such operation the percentage of carbon monoxide may be reduced from 45 to 8 p.c. In other processes, the carbon monoxide is removed by chemical means; for this purpose it is decomposed by heating to bright redness with excess of steam, when the monoxide is replaced by an equal volume of hydrogen, carbon dioxide being produced, which may be removed by solution in water or by absorbing it in milk of lime (Henry and Hembert, Compt. rend. 1885, 101, 797; D. R. P. 224862, 1907).

The oxidation of carbon monoxide by steam with the liberation of hydrogen can be effected at 400°–500° in the presence of reduced iron or nickel (Fr. Pats. 355324, 1905; 375164, 1906; *cf.* Mond and Langer, Eng. Pat. 12608, 1888, and Fr. Pat. 361429, 1905).

Hydrogen free from compounds of carbon and oxygen, can be prepared by heating coke, impregnated with 10 p.c. potassium carbonate and mixed with five times its weight of burnt lime, in a current of steam at 550°–750° (Eng. Pat. 8734, 1910).

The decomposition of steam may also be effected by passing it over red-hot barium sulphide, which becomes oxidised to sulphate, with the simultaneous formation of hydrogen (Fr. Pat. 361866, 1905). The sulphate is reduced with coal or producer gas to sulphide, and used again.

(3) *Action of metals on acids.*—The commonest method of preparing hydrogen for laboratory purposes consists in acting upon granulated zinc with either dilute hydrochloric acid (1 of acid to 2 of water), or sulphuric acid (1 of acid to 8 of water), when hydrogen is evolved and zinc chloride or sulphate left in solution. Very pure hydrogen is obtained from pure zinc and pure diluted acid, but the action is extremely slow. A regular stream of the gas may be obtained, however, by adding a little platinic chloride solution. Platinum is deposited over the surface of the zinc, and the liberated hydrogen escapes freely from the surface of the platinum, leaving the zinc surface free from bubbles of gas (Gourdon, Compt. rend. 1873, 76, 1250). A similar effect is produced by adding a small quantity of a salt of copper, silver, gold, tin, antimony, bismuth, nickel, or cobalt.

Other metals, *e.g.* aluminium, magnesium, and iron, may be used instead of zinc for generating hydrogen from acids. Pure hydrogen is readily prepared by acting upon aluminium with mercuric chloride solution slightly acidified with hydrochloric acid (Bodenstein, Zeitsch. physikal. Chem. 1897, 22, 3). The use of zinc, and more particularly of iron and sulphuric acid upon a commercial scale is very common (*v.* Eng. Pats. 15509, 1897; 16277, 1896; 17515, 1898; 25084, 1897).

(4) *Action of metals and non-metals on alkalis.*—The metals, zinc, aluminium, and tin, readily dissolve in warm concentrated alkali hydroxide solutions, liberating hydrogen and forming alkali zincate, aluminate, and stannate respectively. Very pure hydrogen is thus produced from aluminium free from carbon. The non-metallic element, silicon, similarly dissolves, and considerable quantities of hydrogen are now prepared by heating powdered silicon with sodium hydroxide solution and milk of lime (D. R. P. 216768, 1908; Eng. Pat. 21032, 1909) (*v. infra, Hydrogen for Balloons*).

Hydrogen may be prepared by heating slaked lime with either zinc dust (Schwarz, Ber. 1886, 19, 1141) or coal. The resulting calcium carbonate in the latter process may be reconverted into slaked lime by heating in steam (Bloxam).

(5) *Decomposition of metallic hydrides.*—The hydrides of the alkali metals and those of the alkaline earths readily decompose water at ordinary temperatures, liberating hydrogen and forming the corresponding metallic hydroxide. The use of calcium hydride for preparing hydrogen is very convenient, since the hydride is readily portable, and each gram of the substance yields more than 1 litre of hydrogen when decomposed by water. The hydrogen liberated is twice that which is absorbed by the metallic calcium in the preparation of the hydride (Fr. Pat. 327878, 1902); (*v. infra, Hydrogen for Balloons*).

Palladium foil is capable of directly absorbing large quantities of hydrogen; from the substance thus produced, pure hydrogen is readily obtained by heating it under reduced pressure (*v. infra*, p. 65).

Purification.—The electrolysis of either dilute sulphuric acid or a solution of pure baryta, yields practically pure hydrogen, as also does the action of steam on pure sodium. Most methods of preparation, however, yield hydrogen containing more or less of a number of impurities, nearly all of which may be removed by treating the gas with reagents capable of absorbing them. The precise nature of most of the impurities depends upon the method of preparation employed, but one in particular, viz. atmospheric air, is common to nearly all methods. Its presence in the gas is due partly to its presence in the liquids employed in the preparation of the gas, a source of error which may be diminished by previously boiling the solution, partly to the difficulty of completely expelling air from the apparatus, and partly owing to leakage into the apparatus through cork or rubber joints, which should therefore be reduced to a minimum. The oxygen thus introduced may be removed by passing the gas over red-hot copper or spongy platinum or through chromous chloride solution, but the nitrogen cannot be similarly removed.

A convenient but expensive method of obtaining pure hydrogen consists in passing the dried, approximately pure gas over palladium, the metal having been previously strongly heated, introduced into a tube fitted with a stopcock and the tube evacuated. The metal is allowed to cool during the absorption of the gas. The gas left in the apparatus is finally pumped out. From the palladium-hydrogen, pure hydrogen is readily obtained by attaching the palladium tube to the apparatus into which the gas is to be introduced, and gently warming the metal.

Hydrogen prepared from acid and ordinary iron, which contains a certain amount of carbide, invariably contains gaseous hydrocarbons which give the gas a most unpleasant odour, and this method of preparation is never used for laboratory purposes. The hydrocarbons may be removed by passing the gas through alcohol, or a tube filled with pieces of wood-charcoal or paraffin (Stenhouse, Annalen, 1858, 106, 125; Varenne and Hèbré, Bull. Soc. chim. 1877, [ii.] 28, 523).

According to Morley, the purest redistilled zinc always contains a little occluded oxides of carbon, which find their way into hydrogen prepared from the metal and acid. The commercial metal may also contain, besides a little lead, traces of sulphur, arsenic, antimony, carbon, silicon, and even phosphorus, which cause the hydrogen generated from the metal by means of acid to contain the corresponding gaseous hydrides. Sulphuric acid may contain sulphur dioxide, which will be partly evolved with the hydrogen and partly reduced to hydrogen sulphide (Kolbe, Annalen, 1861, 119, 174), and also nitrogen compounds, which lead to the formation of nitrogen and nitrous oxide in the hydrogen. Frequently sulphuric acid contains arsenic and selenium, which lead to the formation of the corresponding hydrides. Hydrochloric acid prepared from sulphuric acid may contain the same impurities.

Sulphur dioxide, the hydrides of sulphur, selenium, silicon, and hydrogen chloride carried over by the hydrogen may be absorbed in a solution of potassium hydroxide. The hydrides of phosphorus, arsenic, and antimony may be absorbed by solutions of various metallic salts, *e.g.* mercuric chloride, lead nitrate, or silver sulphate (Dumas, Ann. Chim. Phys. 1843, [iii.] 8, 189).

All the above impurities are decomposed when the hydrogen is passed over red-hot copper turnings. The small quantity of nitrogen that may be introduced by the decomposition of oxides of nitrogen is usually not inconvenient.

For laboratory purposes, hydrogen is best purified from phosphine, arsine, and stibine, by passing it through saturated permanganate solution and then through 5–10 p.c. silver nitrate. After washing hydrogen with concentrated permanganate solution, however, the gas contains traces of oxygen. For removing traces of arsine from large quantities of hydrogen, bromine is the best absorbent; on a technical scale potassium hypochlorite or bleaching powder may be substituted (Reckleben and Lockemann, Zeitsch. angew. Chem. 1908, 21, 433).

Arsine is said to be completely removed from hydrogen by bubbling the gas through petroleum spirit cooled by liquid air to −110°, and the process has been recommended for technical use (Compt. rend. 1903, 136, 1317).

An elaborate method for purifying hydrogen by freezing out the impurities is described by Kamerlingh Onnes (Proc. K. Akad. Wetensch. Amsterdam, 1909, 11, 883); using 25 litres of liquid air, 10,000 litres of hydrogen can be purified in 8 hours.

Hydrogen may be dried for ordinary purposes by passing it over anhydrous calcium chloride or through concentrated sulphuric acid. The latter process, however, slightly contaminates the gas with sulphur dioxide (Dittmar and Henderson, Proc. Roy. Soc. Glasgow, 1891, 22, 33; Berthelot, Compt. rend. 1897, 125, 743; Milbauer, Zeitsch. physikal. Chem. 1907, 57, 649). The use of phosphoric anhydride, free from lower oxides, is to be preferred.

Properties.—Hydrogen is a colourless, odourless, tasteless gas. It is the lightest gas known, 1 litre of hydrogen at N.T.P. and at sea-level in lat. 45°, weighing 0·089873±0·0000027 grams (Morley, Zeitsch. physikal. Chem. 1896, 20, 242; *cf.* Regnault, Relation des Expér. 2, 121; Leduc, Compt. rend. 1891, 113, 186; Thomsen, Zeitsch. anorg. Chem. 1896, 12, 1). The density of hydrogen compared with air is therefore 0·0694. The coefficient of expansion at constant pressure is 0·003661 (Regnault), and at constant volume the pressure coefficient is 0·0036624 (Chappuis). The thermal conductivity of hydrogen is seven times that of air (Stefan). Between 0° and 200° the molecular specific heat at constant pressure is 6·81 and at constant volume is 4·81 calories. The specific heat increases with rise of temperature. According to Mallard and le Chatelier (Compt. rend. 1887, 104, 1780), the mean molecular specific heat of hydrogen at constant pressure between 0° and t° is 6·5+0·0006 (t+273); the value at constant volume is

4·700+0·00045t (Pier. Zeitsch. Elektrochem. 1909, 15, 536). The ratio of the specific heats is 1·405 (Röntgen). Hydrogen is diamagnetic.

Hydrogen is very slightly soluble in water, its absorption-coefficient between 0° and 25° being given by the formula

$$0{\cdot}021528-0{\cdot}00019216t+0{\cdot}000001728t^2$$

(Timofejeff, Zeitsch. physikal. Chem. 1890, 6, 141; *cf.* Winkler, Ber. 1891, 24, 89; Bohr and Bock, Wied. Ann. 1891, 44, 316; Geffken, Zeitsch. physikal. Chem. 1904, 49, 257). For its solubility in alcohol, *v.* Timofejeff. *l.c.*, and in various aqueous salt solutions, *v.* Geffken, *l.c.*

The liquefaction of hydrogen for many years presented the most difficult problem to experimenters on the liquefaction of gases. In 1877, Cailletet submitted hydrogen to the same process as he had successfully used in the liquefaction of oxygen and nitrogen, and observed the formation of a fine mist when hydrogen was subjected to a pressure of 280 atmos. and then suddenly released. In 1884 Wroblewski (Compt. rend. 1884, 100, 979) liquefied hydrogen by cooling the gas, under a pressure of 190 atmos., by means of boiling nitrogen, and then quickly releasing the pressure. By a similar method, Olszewski (Compt. rend. 1884, 99, 133; 1885, 101, 238) succeeded in obtaining colourless drops of liquid hydrogen. Dewar (Chem. Soc. Proc. 1895, 229; Chem. Soc. Trans. 1898, 528; Proc. Roy. Soc. 1901, 68, 360) was the first to succeed in preparing liquid hydrogen in sufficient quantity to show a definite meniscus by applying the regenerative process to the compressed gas after first cooling it to −205°. Travers (Phil. Mag. 1901, [vi.] 1, 411), Olszewski (Ann. Chim. Phys. 1903, [vii.] 29, 289), and Nernst and Pollitzer (Zeitsch. Elektrochem. 1911, 17, 735) have since described processes whereby liquid hydrogen may be prepared in quantity.

Liquid hydrogen forms a clear, colourless liquid, boiling at −252·5° (Dewar, Proc. Roy. Soc. 1898, 63, 256; Travers, Phil. Mag. 1902, [vi.] 3, 535). The vapour pressures of the liquid at various temperatures have been measured by Travers and Jacquerod (Zeitsch. physikal. Chem. 1904, 46, 447). At its boiling point the density of the liquid is only 0·07. Liquid hydrogen has the greatest specific heat of any liquid, namely 6·4 (Dewar). When cooled by rapid evaporation under diminished pressure, the liquid solidifies to a transparent solid, melting at −257° (Dewar) or −258·9° (Travers, Proc. Roy. Soc. 1902, 70, 484), and having a sp.gr. at −259·9° of 0·0763 (*ibid.* 1904, 73, 251). The critical pressure of hydrogen is 15 atmos. and its critical temperature is −243° to −241° (Dewar).

The spectrum of hydrogen consists essentially of four bright lines—one in the red, corresponding with Fraunhofer's dark line C, and one in the greenish-blue, coincident with the dark line F. Their wave-lengths are (Angström) C=6562, F=4861, blue = 4340, indigo=4101 in ten-millionths of a millimetre.

Hydrogen is an inflammable gas, burning in air or oxygen with an extremely hot, almost colourless flame, and producing water. Even with pure hydrogen, however, the centre of the flame is coloured green, while the external portions are of a violet-blue colour. On reducing the pressure, the blue colour is transformed to green, and from that successively to yellow, orange, and red. Under increased pressure, hydrogen burns with a luminous flame.

The combination of hydrogen and oxygen proceeds slowly at ordinary temperatures in the presence of sunlight (Baker, Chem. Soc. Trans. 1902, 81, 400). The rate of combination is slow at 180° (Gautier and Hélier, Bull. Soc. chim. 1896, [iii.] 15, 468), but with rise of temperature it becomes quicker and quicker, and explosion occurs at about 550° (Gautier and Hélier, *l.c.*; Berthelot, Compt. rend. 1897, 125, 271; Ann. Chim. Phys. 1898, [vii.] 13, 30; Meyer and Raum, Ber. 1895, 28, 204; Bone and Wheeler, Phil. Trans. 1906, A, 206, 1; Rowe, Zeitsch. physikal. Chem. 1907, 59, 41). Mixtures of the two gases, if perfectly pure and dry, may be heated to the melting-point of silver without combination occurring (Baker, *l.c.*). The ignition-points of various mixtures of oxygen and hydrogen, from $3H_2+O_2$ to H_2+4O_2, vary between 557° and 507° when fired by adiabatic compression, electrolytic gas having an ignition-point of 536° (Dixon, Chem. Soc. Trans. 1910, 97, 661; *cf.* Falk, J. Amer. Chem. Soc. 1906, 28, 1517; 1907, 29, 1536). The union of hydrogen and oxygen proceeds quickly at ordinary temperatures in the presence of finely divided palladium, platinum, iridium, osmium, or gold.

Hydrogen unites at 250° with sulphur and selenium, and at 400° with tellurium. It can be made to unite directly with nitrogen under the influence of the silent discharge (Chabrier, Compt. rend. 1872, 75, 489; Donkin, Proc. Roy. Soc. 1881, 31, 281) or of electric sparks (Berthelot, Ann. Chim. Phys. 1880, [v.] 21, 385); compounds of hydrogen with arsenic, phosphorus, antimony, boron, and silicon, can be prepared indirectly.

Hydrogen unites with pure carbon directly when heated to 1150°, methane being produced (Bone and Jerdan, Chem. Soc. Trans. 1897, 71, 41; Bone and Coward, 1908, 93, 1975; 1910, 97, 1219). By passing an electric arc between carbon poles in an atmosphere of hydrogen, acetylene is produced, accompanied by a little methane and ethane (Berthelot, Compt. rend. 1862, 54, 640; Bone and Jerdan, Chem. Soc. Trans. 1901, 79, 1062).

Gaseous hydrogen combines with fluorine even in the dark and at ordinary temperatures, with explosive violence, hydrofluoric acid being produced (Moissan, Ann. Chim. Phys. 1891, [vi.] 24, 224). With liquid fluorine at −210°, explosion also occurs, and a similar result follows on mixing solid fluorine and liquid hydrogen (Moissan and Dewar, Bull. Soc. chim. 1897, [iii.] 17, 932; Compt. rend. 1903, 136, 641).

Chlorine does not combine appreciably with hydrogen at ordinary temperatures in the dark, but only when heated above 400° or exposed to light. In diffused light, combination occurs slowly, and there is usually an initial *period of induction* (Bunsen and Roscoe, Phil. Trans. 1857, ii. 378) during which the rate of combination slowly increases to its maximum value and afterwards remains constant. This period of induction is due to the presence of traces of volatile impurities (Burgess and Chapman, Chem. Soc. Trans. 1906, 89, 1399). Under the direct action of actinic rays, mixtures of hydrogen and chlorine explode.

Hydrogen combines directly with bromine above 400°, and slowly even at 100° in the presence of light (Kastle and Beatty, Amer. Chem. J. 1898, 20, 159). With iodine, the rate of combination becomes measurable above 200°.

The alkali metals, when heated to 360° in hydrogen, directly absorb the gas, forming white solid hydrides of the type MH (Guntz, Compt. rend. 1896, 122, 244; Moissan, Bull. Soc. chim. 1902, 27, 1141; Ann. Chim. Phys. 1905, [viii.] 6, 289, 323; Holt, Chem. Soc. Abstr. 1909, ii. 807). The alkaline-earth metals similarly combine with hydrogen, yielding solid hydrides of the type RH_2 (Moissan, Bull. Soc. chim. 1899, [iii.] 21, 876; Guntz, Compt. rend. 1901, 133, 1209). According to Winkler (Ber. 1891, 24, 884), hydrogen combines directly with various finely divided metals, *e.g.* cerium, yttrium, lanthanum, obtained by reducing their oxides with magnesium powder.

Hydrogen is a reducing agent, and readily displaces a large number of metals from their compounds with oxygen, sulphur, chlorine, &c. Thus the oxides of copper, lead, iron, antimony, &c., are easily reduced to the metallic state, with the formation of water, when heated in a current of hydrogen to a more or less elevated temperature. Silver oxide is slowly reduced at ordinary temperatures, and rapidly and completely at 100° (Colson, Compt. rend. 1900, 130, 330), a reaction which may be used to determine hydrogen in gaseous mixtures. Palladous oxide is reduced in the cold by hydrogen (Wöhler, Annalen, 1874, 174, 60), as also is the corresponding chloride, either in the anhydrous state or in solution (Phillips, Amer. Chem. J. 1894, 16, 255; Campbell and Hart, *ibid.* 1896, 18, 294).

When hydrogen is passed through a solution of silver nitrate, sulphate or acetate, metallic silver is precipitated; the amount of metal thus separated is small compared with that left in solution. The reaction is carried further by raising the temperature, and the precipitated metal is very pure. Palladium, platinum, and gold are similarly precipitated. Under great pressures, such reductions are much more complete. Thus silver and mercury are quantitatively precipitated from solutions of their salts at ordinary temperatures under 200 atmos. pressure. At higher temperatures, nickel, cobalt, lead, and bismuth are similarly precipitated, the deposition of nickel being complete at 200° and 180 atmos. (Ipatieff and Werchowsky, Ber. 1909, 42, 2078).

Occluded hydrogen (*v. infra*, p. 65) is capable of bringing about a great number of chemical changes that the free gas is unable to effect. Thus hydrogen occluded in palladium will unite with chlorine, iodine, and oxygen, even in the dark, at ordinary temperatures (Böttger, Ber. 1873, 6, 1396). It also reduces chlorates to chlorides; nitrates to nitrites, and even to ammonia; mercuric chloride to mercurous chloride; ferric salts to ferrous salts; ferricyanides to ferrocyanides; and indigo-blue to indigo-white (Gladstone and Tribe, Chem. News, 1878, 37, 68). A number of these reactions can be utilised in quantitative analysis (Chapman, Analyst, 1904, 29, 346). Hydrogen occluded in platinum or copper produces similar changes.

Hydrogen also becomes much more chemically active in contact with various finely divided metals, such as platinum black and nickel, cobalt, iron and copper reduced from their oxides. Thus, hydrogen and oxygen combine rapidly, at ordinary temperatures, in the presence of platinum black. The union of the gases is started by the heat evolved as they are occluded, and, once started, combination proceeds quickly, the metal being heated so much that it becomes incandescent. Similarly, at 400° hydrogen and iodine vapour rapidly unite in the presence of platinum black.

A very general method of reduction and hydrogenation has been based upon the fact that hydrogen becomes intensely chemically active in the presence of finely divided nickel that has been just previously reduced from its oxide. By passing the vapours of a large number of substances, mixed with hydrogen, over reduced nickel at quite moderate temperatures, reductions are easily effected; thus nitrous oxide produces nitrogen and water, nitric oxide and nitrogen peroxide are reduced to ammonia, and the oxides of carbon are converted into methane. Organic nitro compounds, fatty or aromatic, are reduced to amines. Unsaturated fatty hydrocarbons are transformed into paraffins, while benzene and numerous derivatives are easily converted into hexahydrobenzene and its substitution-products. Aldehydes and ketones are reduced to alcohols with remarkable ease. The nickel is not altered, and permits of hydrogenation being carried on indefinitely (Sabatier and Senderens, Compt. rend. 1897, 124, 1358; 1899, 128, 1173; 1900, 130, 1559, 1628, 1761; 131, 140; 1901, 132, 210, 566, 1254; 133, 321; 1902, 134, 514, 689, 1127; 135, 87, 225; 1903, 136, 738, 921, 983; 137, 301, 1025; 1904, 138, 457, 1257; 1905, 140, 482; Bull. Soc. chim. 1905, [iii.] 33, 263; Ann. Chim. Phys. 1905, [viii.] 4, 319, 433; Sabatier and Mailhe, Compt. rend. 1903, 137, 240; 1904, 138, 407, 245; 1905, 140, 350; 1906, 142, 553; 1907, 144, 824, 955, 784, 1086; 145, 18, 1126; 1908, 146, 457, 1193; Ann. Chim. Phys. 1909, [viii.] 16, 70).

Certain chemical systems which lead to the liberation of hydrogen are capable of acting as reducing agents when another substance is added to them that is capable of being reduced. Thus a solution of potassium chlorate remains unaffected when hydrogen is passed through it, but reduction to chloride readily occurs if zinc and sulphuric acid are added to the solution. Other systems are furnished by the alkali metals or their amalgams in contact with water, which are capable, among other things, of reducing aldehydes and ketones to alcohols; and zinc, iron, or tin, with either hydrochloric, sulphuric, or acetic acid, systems which are capable of reducing nitro compounds to amines, &c. Hydrogen evolved from such systems therefore appears to possess an activity superior to that of the ordinary gas; it is termed *nascent* hydrogen.

The superior activity possessed by hydrogen at the moment of its liberation is supposed by some chemists to be due to the fact that the gas is liberated in the atomic state, and is therefore more capable of entering into chemical reactions than after it has assumed the molecular state, since the combination of atoms to form molecules is accompanied by the degrading of a certain amount of energy. That this cannot be a full explanation is seen, however, by the fact that a reduction effected by one system evolving nascent hydrogen is not necessarily effected by another system, *e.g.* the system zinc and dilute sulphuric acid will reduce chlorates to chlorides, but the system sodium-amalgam and water will not.

Adsorption of hydrogen by metals. In 1863, Deville and Troost (Compt. rend. 1863, 57, 894) observed that red-hot platinum and iron were permeable to hydrogen. Upon further investigating this subject, Graham (Proc. Roy. Soc. 1867, 15, 223; 1868, 16, 422; 1869, 17, 212, 500) found that palladium possessed this property in a much higher degree, and, further, he showed that there was no need to assume a porosity in the structure of these metals to account for this phenomenon, but that it was due to the fact that such metals absorb hydrogen, yielding substances which still retain metallic lustre and characteristic metallic properties, but which readily evolve the absorbed gas under altered conditions. To this property, Graham gave the name *occlusion.* It may be studied by placing the metal within a porcelain tube, glazed inside and out, evacuating it by means of a mercury pump and heating to redness. Hydrogen is then admitted and allowed to flow over the metal while it cools. The tube is then evacuated again and the contents heated to redness once more, by which means the occluded hydrogen is expelled from the metal, and may be pumped off and measured.

The amount of hydrogen adsorbed depends to some extent on the physical condition of the metal. In one experiment, a palladium wire was found by Graham to absorb 935 times its own volume of hydrogen. Mond, Ramsay, and Shields (Phil. Trans. 1895, A, 186, 657; 1897, A, 190, 129; 1898, A, 191, 105) have shown that palladium black adsorbs at the ordinary temperature 873 to 889 volumes of hydrogen and that palladium wire and sponge adsorb a similar amount. Palladium-hydrogen readily evolves hydrogen in a vacuum, that prepared from the 'black' at the ordinary temperature, while the substance obtained from the foil requires warming to 100°. In all cases, however, a red heat is required to drive off the last traces of gas. Even at a red heat, however, palladium still adsorbs large quantities of hydrogen if the pressure is sufficiently increased (Dewar, Chem. Soc. Proc. 1897, 192).

Palladium readily adsorbs 935 vols. of hydrogen if it is employed as negative electrode in a water voltameter. Should the electrolysis be continued beyond this point, the metal becomes supersaturated with gas; the excess is, however, evolved as soon as the current ceases (Thoma, Zeitsch. physikal. Chem. 1889, 3, 69).

Colloidal palladium and platinum solutions adsorb hydrogen very readily and in large amounts (Kernot and Niguesa, Rend. accad. Sci. Fis. Mat. Napoli, 1909, [iii.] 15, 168). Various other metals, *e.g.* iron, nickel, cobalt, gold, and copper, also adsorb small quantities of hydrogen.

The process of occlusion is accompanied by an evolution of heat, 4370 calories being evolved per gram of hydrogen occluded; the thermal effect is the same for each successive fraction of gas absorbed (Favre, Compt. rend. 1869, 68, 1306; Mond, Ramsay, and Shields, *l.c.*).

The nature of the substances formed when hydrogen is occluded by metals has not yet been determined with certainty. The metals are unaltered in appearance, and such physical properties as thermal and electrical conductivity, sp.gr., and tenacity are only slightly diminished. Graham was of opinion that no chemical union occurs, but that the hydrogen assumes the solid form and acts as a quasi-metal. This adsorbed form of hydrogen he proposed to call *hydrogenium.*

From the expansion of alloys of palladium with platinum, gold, and silver, when charged with hydrogen, Graham calculated the sp.gr. of hydrogen to be 0·733; subsequent determinations by Dewar gave the figure 0·620, a figure which does not compare at all with the actual sp.gr. of solid hydrogen.

Troost and Hautefeuille (Compt. rend. 1874, 78, 686) believed that their experiments indicated the existence of a definite compound, Pd_2H, whilst Dewar (Chem. News, 1897, 76, 274) suggested the existence of Pd_3H_2. The fact that when fully charged with hydrogen, the composition of palladium-hydrogen approximates closely to this latter formula is, however, almost the only evidence that can be adduced in support of the existence of this compound (Mond, Ramsay, and Shields, *l.c.*). The experiments of Hoitsema (Zeitsch. physikal. Chem. 1895, 17, 1) have shown that between 20° and 200° no definite compounds of palladium and hydrogen exist; at constant temperature the relationship between the vapour tension of the system palladium-hydrogen and the percentage of hydrogen in the solid phase is such, however, as would be expected if two partially-miscible solid solutions of hydrogen in the metal are formed, the miscibility of which increases with rise of temperature.

The meteoric iron of Lenarto, containing 91 p.c. of iron, yields 2·85 times its volume of occluded gas, mainly hydrogen (Graham, Proc. Roy. Soc. 1867, 15, 502). Since under ordinary pressure iron absorbs only half its volume of hydrogen, this would seem to show that the meteorite has come from an atmosphere containing hydrogen under a pressure much greater than that of our own atmosphere, thus affording a confirmation of the conclusions drawn from spectroscopic observations regarding the existence of dense and heated hydrogen atmospheres in the sun and fixed stars.

Atomic weight of hydrogen. This has been determined by measuring the ratio of the combining weights of oxygen and hydrogen. Since this ratio is of fundamental importance, a very considerable amount of attention has been directed towards its accurate measurement. The methods used may be grouped under two headings: (*a*) synthesis of water; and (*b*) determinations of the relative densities of hydrogen and oxygen.

(*a*) The classical method, first employed by Dulong and Berzelius (1820), and used later by Dumas (Ann. Chim. Phys. 1843, [iii.] 8, 189) in his elaborate series of determinations, consists in reducing heated cupric oxide in a stream of pure, dry hydrogen, and estimating the water produced and the loss in weight experienced by the cupric oxide. The result obtained by Dumas, viz. H : O :: 1 : 15·9607, corroborated as it was by the experiments of Erdmann and Marchand (J. pr. Chem. 1842, 26, 461) was for many years accepted as the true value; but subsequent work has shown that this result deviates considerably from the truth, and has disclosed numerous sources of error in the older determinations. The method of Dumas, with various modifications, has been used by Cooke and Richards (Amer. Chem. J. 1888, 10, 81, 191); Keiser (*ibid.* 1888, 10, 249); Noyes (*ibid.* 1889, 11, 155; 1890, 12, 441); Dittmar and Henderson (Proc. Roy. Soc. Glasgow, 1891, 22, 33), and Leduc (Compt. rend. 1892, 115, 41); their results are given in the table below.

The synthesis of water has been effected by other methods than the above. In 1889, Rayleigh (Proc. Roy. Soc. 45, 425) weighed pure hydrogen and oxygen in glass globes, mixed them and then gradually exploded the mixture in a eudiometer. The residual gas was then analysed, and hence the ratio of hydrogen to oxygen determined. The first complete quantitative syntheses of water, in which both gases were weighed separately, and afterwards in combination, are due to Morley (Smithsonian Contributions to Knowledge, 1895, 29). The hydrogen was weighed in palladium (a method due to Keiser) and the oxygen in compensated globes, after the manner of Regnault. After weighing, the gases were burned by means of electric sparks in a suitable apparatus, from which the unburned residue could be withdrawn for examination. Finally, the apparatus containing the water produced was closed by fusion and weighed.

The syntheses of water by Keiser (Amer. Chem. J. 1898, 20, 733) were effected by the direct oxidation of hydrogen occluded in palladium; the hydrogen, oxygen, and water were all determined. The experiments recorded in the elaborate investigation by Noyes (J. Amer. Chem. Soc. 1907, 29, 1718) were performed partly by this method and partly by the method employed in his earlier work (*v. supra*). A novel, but indirect method for measuring the ratio of oxygen to hydrogen has been employed by Thomsen (Zeitsch. anorg. Chem. 1895, 11, 14).

The results of these experiments are collected in the following table :—

Experimenter	Date	Ratio O/H	At.wt. of Hyd. (O=16)
Dumas . . .	1842	15·9607	1·00246
Erdmann & Marchand	1842	15·9750	1·00156
Cooke & Richards .	1888	15·8690	1·00825
Keiser . . .	1888	15·9514	1·00305
Noyes . . .	1889	15·8966	1·00650
Dittmar & Henderson	1891	15·8677	1·00834
Leduc . . .	1892	15·8810	1·00750
Rayleigh . . .	1889	15·8900	1·00692
Morley . . .	1895	15·8790	1·00762
Keiser . . .	1898	15·8799	1·00756
Noyes . . .	1907	15·8745	1·00783
Thomsen . . .	1895	15·8690	1·00825

The weighted mean of these results is H=1·00769 according to Clarke (A Recalculation of the Atomic Weights, 3rd edit. 1910, 29).

(*b*) The ratio of the densities of oxygen and hydrogen is, subject to a correction to be mentioned later, equal to the ratio of their atomic weights. The first accurate measurements of these densities were made by Dumas and Boussingault in 1841 (Compt. rend. 12, 1005); the results obtained four years later by Regnault (*ibid.* 20, 975) were adopted as standard values for many years, and gave for the ratio a value of 15·9611. The remarkable agreement of this figure with that deduced from Dumas' synthesis of water is only, however, accidental, for in 1885, Agamennone, and independently, Rayleigh in 1888 (Proc. Roy. Soc. 43, 356) pointed out a serious error in all previous determinations of gaseous densities, owing to the fact that the glass globes in which the gases are weighed are elastic, and shrink to a measurable extent when evacuated. The effect of neglecting to correct for this shrinkage is that the apparent weight of gas is slightly lower than its true value. The corrected value for the density ratio from Regnault's experiments is 15·9105 (Crafts, Compt. rend. 1888, 106, 1662).

In recent years, the densities of hydrogen and oxygen have been frequently determined with the utmost care; *v.* Rayleigh (Proc. Roy. Soc. 1892, 50, 448; Cooke, Amer. Chem. J. 1889, 11, 509); Leduc (Compt. rend. 1891, 113, 186); Thomsen (Zeitsch. anorg. Chem. 1896, 12, 4) and especially Morley (Smithsonian Contributions, 1895). The table below summarises the results obtained :—

Experimenter	Date	Density ratio O/H
Dumas & Boussingault .	1841	15·9015
Regnault . . .	1845	15·9105
Rayleigh . . .	1888	15·8840
Rayleigh . . .	1892	15·8820
Cooke	1889	15·8900
Leduc	1891	15·9060
Morley . . .	1895	15·8955
Thomsen . . .	1896	15·8878

The weighted mean is 15·8948 (Clarke. *l.c.*).

This result is subject to a slight correction for the fact that hydrogen and oxygen do not combine together by volume exactly in the ratio of two to one; according to Morley (*l.c.*), the exact ratio is 2·00274 (*cf.* Scott, Phil. Trans. 1893, 184, 543; Leduc, Compt. rend. 1892, 175, 311; Rayleigh, Proc. Roy. Soc. 1904, 73, 153). Correcting the above mean value for the density ratio in accordance with this result, the figure 15·8726 is obtained, which leads to the value 1·00803 for the atomic weight of hydrogen on the oxygen scale.

According to Clarke (*l.c.*), the probable mean derived from the results of methods (*a*) and (*b*) combined, is H=1·00772. The value at present adopted is H=1·008.

Applications of hydrogen. Hydrogen is used in conjunction with oxygen for the production of the Drummond or oxy-hydrogen lime light. For this purpose, the gases are compressed in iron bottles furnished with taps and jets, so that they can be allowed to escape, and burned as required. They are allowed to impinge on a cylinder of lime which is thereby heated to whiteness, and gives a light almost equal to the electric arc.

For the autogenous welding of metals, the working of platinum, and the manufacture of laboratory utensils and mercury vapour lamps from fused quartz, hydrogen in the form of the oxyhydrogen blowpipe flame is used in large quantities, although it has here to meet the competition of acetylene, which is cheaper and readily obtainable as required from calcium carbide.

Autogenous soldering.—This process is much used for uniting the edges of the sheets of lead which are employed in making vessels for the purpose of holding acids. Joints made in this way are much more durable than those made with solder. The apparatus for this purpose is made so that hydrogen can be generated at pleasure, and when not in use the pressure of gas inside the apparatus lifts the acid out of contact with the zinc. The hydrogen generator consists of a cylindrical copper vessel lined with lead; there is an upper and lower chamber connected by a pipe, and they are filled with arrangements which admit of easy renewal of acid or zinc and the removal of the zinc sulphate formed. The apparatus gives a very constant flame, which may be used with advantage in soldering lead in the way which is practised in the construction of sulphuric acid chambers. The hydrogen is delivered from a platinum-tipped nozzle through which a jet of air also issues from a foot bellows; this is effected by attaching the nozzle by means of india-rubber tubing to a tube which branches out V-shaped into two limbs each provided with a stopcock; each of these limbs is provided with an india-rubber tube, one of which is attached to the bellows and the other to the delivery tube of the hydrogen generator. The operator can, therefore, carry the nozzle in his hand and direct the flame where he pleases, and by means of the stopcock he can readily regulate the supply of air or hydrogen.

Tungsten lamps.—The manufacture of tungsten filament lamps requires a regular supply of hydrogen to prepare the inert atmosphere in which the filaments are heated to a high temperature during the final treatment. It is almost the universal custom to employ a mixture of equal volumes of hydrogen and nitrogen when the filaments are electrically heated to whiteness. Since incandescent tungsten filaments are very sensitive to oxidation, it is of great importance that the hydrogen employed should be of a high degree of purity. The process devised by Lane (*v. infra*) is frequently adopted for obtaining the gas, since besides preparing hydrogen, it also admits of nitrogen being collected.

Hydrogen for balloons.—Soon after Cavendish published his researches on 'inflammable air,' Charles, in 1783, suggested the application of hydrogen for the inflation of balloons. Montgolfier had, during the same year invented the balloon which he inflated with rarefied air. In hydrogen, however, Charles recognised a much more suitable means of inflation, although the cost was very considerable, 500 lbs. of sulphuric acid and twice that amount of iron being consumed in the inflation of a balloon about 13 feet in diameter.

The first balloon sent up from English soil, on Nov. 25, 1793, was inflated with hydrogen. In the following year, the French Government instituted a series of experiments at Meudon under Guyton de Morveau, Contelle, and Comté with the view of perfecting the balloon for reconnoitring, signalling, and other warlike purposes. For the preparation of the hydrogen, Guyton de Morveau suggested a method invented by Lavoisier, that of passing steam over red-hot iron, and a furnace was accordingly built, which after many trials, was capable of producing sufficient gas to fill a balloon, 27 feet in diameter, in 4 hours. This balloon, with one filling, remained in use for a month.

Balloons inflated with hydrogen were used in the American Civil War in 1861. The gas was generated from old scrap iron and sulphuric acid in wooden tanks lined with lead: the apparatus was carried from place to place on two carts.

In 1878, Giffard made a gigantic captive balloon for the Paris Exhibition. It was spherical in form, 118 feet in diameter, and had a capacity of 882,902 cb. feet. To fill this great aerial ship with hydrogen gas, 190 tons of sulphuric acid and 80 tons of iron were consumed (Jour. United Service Inst. 27, 735–756).

Hydrogen was also used in the Soudan War for inflating balloons. For this purpose, the gas was compressed in strong iron cylinders, 12 feet long by 1 foot in diameter; these were for a reserve supply, and weighed half a ton each. A gas factory and pumping station were put up. To meet first requirements about 100 lighter cylinders, 9 feet long, and containing 120 feet of gas in a compressed condition, were taken out; these were so constructed as to be easily carried by men. One waggon containing a ton of stores was sufficient for a balloon ascent; a volume of gas occupying 4,150 feet was sufficient to lift a man 1,000 yards (Illus. Nav. and Mil. Gaz. 11, 172).

At the present time it is highly important for the maintenance of large dirigible balloons to be assured of a regular supply of pure hydrogen gas. The chief drawback to the use of hydrogen is its high rate of diffusion, a drawback which is being minimised by improvements in the manufacture of balloon fabrics.

Most of the hydrogen now used for inflating the gas bags of dirigible airships is produced either electrolytically or by the action of steam on red-hot iron. The former method has been largely developed in Germany, and depends for success upon a cheap supply of electrical energy. It yields pure hydrogen and the plant requires very little attention.

The other method is now used in this country as described by Lane (Eng. Pat. 17591, 1909); iron is heated to redness in a current of steam, and the oxide produced is reduced by heating in a current of water gas, the resulting metal being used again. By carrying on the reduction process in a number of the retorts and the preparation of hydrogen simultaneously in the others, it is possible to make the production of hydrogen more or less continuous.

The need for rapid convenient methods for preparing hydrogen for military purposes has led to the introduction of the '*hydrolith*' and '*hydrogenite*' processes for its preparation, which are employed by the French army. In the former process, 'hydrolith,' a white crystalline powder consisting of calcium hydride (90 p.c. pure, the remainder being oxide and nitride), is decomposed by water. One kilo. of the solid yields about 1 cubic metre of hydrogen. The portable apparatus used by the French army can fill an army dirigible in 4 hours. For speed, convenience, and reliability, hydrolith is unexcelled, but its high cost renders its use almost prohibitive for private aeronautics. 'Hydrogenite' is a compressible powder, consisting of ferrosilicon (90–95 p.c. Si) 25 pts., sodium hydroxide 60 pts., and slaked lime 20 pts. (Sander, Chem. Zeit., 1911, 35, 1273); when ignited by a suitable 'match,' it reacts spontaneously, much as do thermit mixtures, with the evolution of hydrogen and the production of sodium and calcium silicates. The material is hygroscopic, and is sold in a compressed cake in metal cartridges. One kilo. of substance yields from 270 to 370 litres of hydrogen. (For the method of using the substance for filling balloons, *v.* Jaubert, Rev. gén. chim. 13, 341, 357; and *cf.* D. R. P. 218257, 1908.)

HYDROGENIUM *v.* HYDROGEN.

HYDROGEN PEROXIDE. Symbol H_2O_2. This compound was discovered in 1818 by Thenard. It occurs at times in small quantities in the atmosphere, in dew, in rain, and in snow (Schöne, Ber. 1874, 7, 1695; *ibid.* 1893, 26, 3011; *ibid.* 1894, 27, 1233; Zeitsch. anal. Chem. 1894, 33, 137); but Ilosva (Ber. 1894, 27, 920) maintains that the tests used for detecting it in these media would also be given by the oxides of nitrogen, which are always present. It is said to be contained in many green plants (Bach, Compt. rend. 1894, 119, 1218; Chodat and Bach, Ber. 1902, 35, 1275, 3943; 1903, 36, 1756; 1904, 37, 36). It is also contained in solution in the water produced by the combustion of hydrogen in oxygen (Schuller and Bach, Compt. rend. 1897, 124, 951; Keiser and McMaster, Amer. Chem. J. 1908, 39, 96), and in the flames of alcohol, coal gas, ether, and carbon disulphide (Engler, Ber. 1900, 33, 1109).

Hydrogen peroxide is formed in small quantities in the electrolysis of aqueous solutions (Richarz, Zeitsch. anorg. Chem. 1903, 37, 75; Ber. 1909, 42, 4674; Riesenfeld and Reinhold, *ibid.* 2977); when a Tesla brush discharge, or the silent electric discharge is passed through water vapour (Findlay, Zeitsch. Elektrochem. 1906, 12, 129; Nernst, *ibid.* 1905, 11, 710; Löb, Ber. 1908, 41, 1517; Ringe and Fischer, *ibid.* 945); during the slow oxidation of many metals, particularly their amalgams, in the presence of water (Traube, Ber. 1893, 36, 1471; Smith, Chem. Soc. Trans. 1906, 481; Barnes and Shearer, J. Phys. Chem. 1908, 12, 155, 468; Rankin, Proc. Roy. Soc. 1910, B, 82, 78); with zinc amalgam and in the presence of an alkaline earth a better yield is said to be obtained (D. R. P. 48542; J. Soc. Chem. Ind. 1890, 213).

Hydrogen peroxide is also formed under several other circumstances, as, *e.g.*, when freshly-ignited bone black is moistened with as much water as it will take up, and exposed to light and air. Even in a few minutes a perceptible amount of hydrogen peroxide is formed (Dingl. poly. J. 256–519). A carbonic oxide flame (when the gas has been previously passed through water) is said to produce it in quantity, or if burnt in contact with the surface of water the same effect is produced (J. Soc. Chem. Ind. 1884, 496).

When turpentine oil or any other hydrocarbon containing a terpene is oxidised by air or ozone in the presence of water, hydrogen peroxide is formed and passes into solution in the water. In this way it is possible to prepare a solution of two volumes strength, that is to say, of such a strength that when fully decomposed it is capable of yielding twice its own volume of oxygen gas (Kingzett, Eng. Pat. 12274; J. Soc. Chem. Ind. 1898, 691).

It is also said to be produced by the oxidation of a number of organic compounds, such as urine, ether, &c., in direct sunlight (Richardson, Chem. Soc. Trans. 1893, 1110; *ibid.* 1896, 1349).

Preparation.—1. By passing a copious stream of well-washed carbon dioxide through cooled distilled water to which is added very gradually pure barium peroxide, finely powdered and suspended in water. The cautious addition of the barium peroxide is necessary, as an excess of it would cause the decomposition of any hydrogen peroxide formed, with evolution of oxygen and formation of water. After allowing the gas to pass some considerable time, the barium carbonate is filtered off, and the solution evaporated *in vacuô* over sulphuric acid until it acquires a syrupy consistency;

$$BaO_2+CO_2+H_2O=H_2O_2+BaCO_3$$

(D. R. P. 179771, 179826; J. Soc. Chem. Ind. 1906, 117).

2. The preparation is also effected by the decomposition of barium peroxide with hydrofluoric, silicofluoric, phosphoric, sulphuric, borofluoric, or hydrochloric acid, of which the last is to be preferred, owing to its cheapness, whilst the purest peroxide is obtained with phosphoric or borofluoric acids. The barium peroxide, which must be of the purest quality and very finely ground, is made into a thin paste with water, and introduced very gradually into the acid solution, the temperature of which must never exceed 10°–15°, and must be constantly agitated. When the solution is nearly neutralised, the liquid is decanted from the precipitate, and freed from iron and aluminium oxides by treatment with sodium phosphate solution, then with sufficient barium peroxide or waste barium oxide to make the liquid neutral, lastly with ammonia, after which it is rapidly pumped through a filter press. It is then freed from dissolved baryta by the addition of sodium sulphate. The most stable peroxide is that prepared with phosphoric acid, and contains a small amount of that acid in the free state (Chem. Zeit. 9, 949 and 976; Bourgougnon, J. Amer. Chem. Soc. 12, 64; Fawsitt, J. Soc. Chem. Ind. 1902, 229; *see* also Eng. Pats. 10476, 3628, 21333; J. Soc. Chem. Ind. 1891, 482; *ibid.* 1892, 707; *ibid.* 1900, 70). Nitric acid has also been employed (Fr. Pat. 359523; J. Soc. Chem. Ind. 1906, 374).

3. Hydrogen peroxide has also been conveniently, but not so cheaply, prepared by treating sodium peroxide with hydrofluoric or hydrochloric acids (U.S. Pat. 692139; J. Soc. Chem. Ind. 1902, 364; Forcrand, Compt. rend.

1899, 129, 1246; Merck, Chem. Zentr. 1904, ii. 67); and by treating persulphates, percarbonates, and perborates, obtained by electrolysis of the ordinary acids with dilute acids (Jaubert, Chem. Zentr. 1905, ii. 99; D. R. PP. 217538, 217539, 195351, 199958, 179826; J. Soc. Chem. Ind. 1905, 379; *ibid.* 1906, 321, 379; *ibid.* 1908, 448, 856; *ibid.* 1910, 489).

Pure concentrated solutions of hydrogen peroxide have been prepared by the action of alcohol and dilute sulphuric acid on sodium peroxide in earthenware, glass, or lead vessels at −10°. The alcohol is then removed by distillation *in vacuô* (Dony-Hénault, Fr. Pat. 403294; J. Soc. Chem. Ind. 1909, 1314). A mixture of a perborate with an equivalent amount of a dry solid organic or inorganic acid, or of a solid acid salt has been prepared, which, on treatment with water, yields hydrogen peroxide (Fr. Pat. 401911; J. Soc. Chem. Ind. 1909, 1198).

Hydrogen peroxide has also been prepared by blowing superheated steam against a heated body (Eng. Pat. 20868, 1907; Fr. Pat. 382189, 1907; D. R. P. 205262, 1908; J. Soc. Chem. Ind. 1906, 808; *ibid.* 1908, 123, 226; *ibid.* 1909, 140; Fischer and Ringe, Ber. 1908, 41, 945), and by blowing moist air against a spark or arc discharge (D. R. PP. 197023; 228425; J. Soc. Chem. Ind. 1910, 1462).

(For other methods *see* D. R. P. 185597; Bornemann, Zeitsch. anorg. Chem. 34, 1; Fr. Pat. 371043; Scheuer and Vernet, Bull. Soc. Ind. Mulhouse, 1907, 77, 336; *ibid.* 1908, 78, 184, 187; J. Soc. Chem. Ind. 1910, 1306; Fr. Pat. 415361.)

Commercial hydrogen peroxide is liable to contain hydrochloric, sulphuric, phosphoric, and hydrofluoric acids, alumina, lime, magnesia, potash, and soda, derived from water or other materials used in its manufacture, whilst baryta and traces of iron, copper, lead, and manganese are sometimes found if it has been carelessly made.

When these last are present, the product is tolerably stable only if it be sufficiently acid, though even then it is less stable than in the absence of these impurities.

The commercial liquid of so-called 10 volume or about 3 p.c. strength may be purified by the addition of about $\frac{1}{4}$ p.c. of concentrated phosphoric acid (preferably pure) to precipitate iron, copper, lead, and manganese, and prevent the subsequent formation of their peroxides which would otherwise take place. Saturated baryta water (hot or cold) is then added very gradually, until neutrality is reached. No excess must be used or hydrated BaO_2 will be precipitated, which will induce decomposition of a portion of the hydrogen peroxide.

The clear liquid is now drawn off, and is poured into an excess of cold saturated baryta water, when hydrated BaO_2 is thrown down, and is then washed until no metal except barium can be detected in the washings.

The BaO_2 is then suspended in water and added drop by drop to a solution consisting of 90 parts of distilled water to 10 parts of pure concentrated sulphuric acid until only traces of acid remain free; these are best removed by weak baryta water, for an accidental excess of BaO_2 will induce decomposition of some of the already formed hydrogen peroxide, whilst an excess of BaO will have no such effect. The barium sulphate is allowed to settle, and the clear liquid drawn off, if found free from both barium and sulphuric acid. The resulting product is about 3 p.c. strength, fairly stable and of great purity (Mann, Chem. Zeit. 12, 857; J. Soc. Chem. Ind. 1889, 640).

The commercial solutions can be concentrated to 95–99 p.c. by evaporating in air at 75° to 20 p.c. strength, then *in vacuô* to 50–55 p.c., after which it is treated with ether, in which the peroxide is readily soluble. The ethereal extract is then carefully distilled and fractionated *in vacuô* (Wolffenstein, Ber. 1894, 27, 3307; Staedel, Zeitsch. angew. Chem. 1902, 15, 642; Tyrer, *l.c.*; Merck, *l.c.*); also by distilling the solutions at a temperature below 85° in a powerful current of an inert gas (D. R. P. 219154).

The concentrated solution remains liquid at −20°, but when immersed in a mixture of ether and carbon dioxide, it crystallises to a solid mass, consisting of the anhydrous peroxide. Clear colourless crystals of the latter can also be obtained by introducing a fragment of the solid into a freshly prepared 90-80 p.c. solution at −8° (Staedel, *l.c.*). Hydrogen peroxide should be kept in paraffin or paraffin-lined vessels.

A number of substances have been proposed as suitable for increasing the stability of hydrogen peroxide, such as sulphuric or phosphoric acids (Tyrer, Pharm. J. 63, 100); sodium pyrophosphate (Eng. Pat. 23676; J. Soc. Chem. Ind. 1910, 152); organic substances such as alcohol, ether, glycerol, &c. (Sanders, Bull. Soc. Ind. Mulhouse, 1897, 95; Freyes, *ibid.* 97 Eng. Pat. 15993); 1 gram pure crystalline naphthalene to 1 litre of solution (Zinno, Bull. Soc. Ind. Mulhouse, 1895, 78); gallic acid or pyrogallol (Arndt, D. R. P. 196370); uric or barbituric acids (D. R. PP. 216263, 203019, J. Soc. Chem. Ind. 1908, 1204; *ibid.* 1909, 1314); phenacetin or an amide or imide or acetyl derivative of an aromatic base (J. Soc. Chem. Ind. 1906, 1219); oxalic acid (Fischer, Pharm. Zentr. 1907, 48, 57, 79).

According to Allain (J. Pharm. Chim. 1906, 24, 162) sodium or calcium chloride in the proportion of 1 p.c. are more efficient preservatives for medicinal hydrogen peroxide than sulphuric or phosphoric acids. They are also less objectionable than the latter, from a therapeutic point of view. *See* also Kingzett (J. Soc. Chem. Ind. 1890, 3).

The amount of hydrogen peroxide in an aqueous solution may be conveniently determined by titration with a solution of potassium permanganate containing 7·9 grams $KMnO_4$ per litre. 2 c.c. of hydrogen peroxide solution are introduced into a graduated tube of 35 c.c. capacity, 5 or 6 drops of hydrochloric acid are added, and then the solution of permanganate is gradually introduced with constant agitation until the contents of the tube are of a red or brownish colour; the quantity of solution is then read off, 5 c.c. representing 1 p.c. of hydrogen peroxide. The results are accurate to within 0·1 p.c. and can be obtained in a few minutes[1] (Chem. Zeit. 9, 940 and 976).

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[1] The reaction between hydrogen peroxide and potassium permanganate in acid solution may be utilised for preparing oxygen gas. In this way a good stream of tolerably pure oxygen may be readily

In the presence of persulphates, however, accurate results can only be obtained by using a minimum volume of solution, a large excess of sulphuric acid and performing the titration very rapidly; for this purpose an excess of permanganate is added, and the latter is then titrated back with sodium thiosulphate (Friend, Chem. Soc. Trans. 1904, 597, 1533; *ibid.* 1905, 1367; Skrabal and Vacek, Chem. Zeit. 1910, 34; Rep. 121).

If oxalic acid is present, this must first be removed (Sisley, J. Soc. Chem. Ind. 1901, 1028; *ibid.* 1904, 685; Roche, *ibid.* 1902, 190).

Another and more accurate method is to strongly acidify the solution of hydrogen peroxide with sulphuric or hydrochloric acid, then add a solution of potassium iodide free from iodate, and determine the iodine liberated by means of a standard solution of sodium thiosulphate (Kingzett, Chem. Soc. Trans. December, 1880, and The Analyst, 1888, 13, 62; Rupp, Arch. Pharm. 238, 156; Planés, J. Pharm. Chim. 1904, 20, 538).

Hydrogen peroxide can also be estimated by titrating against ferrous ammonium sulphate in presence of ammonium sulphate and phosphoric acid (Mathewson and Calvin, Amer. Chem. J. 1906, 36, 113); and by estimating the quantity of arsenious acid it will oxidise to arsenic acid (Grützner, Arch. Pharm. 237, 705).

According to Dehn the most rapid, convenient, and accurate method of estimating hydrogen peroxide is to measure the volume of oxygen evolved when a known quantity of the solution is treated with sodium hypobromite in a special apparatus described by him (J. Amer. Chem. Soc. 1907, 29, 1315). The following reaction takes place $H_2O_2+NaBrO=NaBr+H_2O+O_2$. By this method the presence of preservatives may be neglected. (For the estimation of the peroxide retained by fabrics, *see* Scheuer and Vernet, *l.c.*)

To determine the quantity of acid present in commercial hydrogen peroxide, the best method is by direct titration in the cold, with N/10 sodium hydroxide solution, using phenolphthalein as indicator (Brown, J. Ind. Eng. Chem. 1910, 377; Endemann, Zeitsch. angew. Chem. 1909, 22, 673; Lüning, *ibid.* 1549).

Properties.—Pure anhydrous hydrogen peroxide forms colourless prismatic crystals; m.p. −2°, b.p. 84°–85°/68 mm., 69·2°/26 mm. It forms a syrupy transparent acid liquid, which is colourless in thin layers, but bluish-green when viewed in bulk (Spring, Chem. Zentr. 1895, i. 1105). It has sp.gr. 1·4584 at 0° (Brühl, Ber. 1895, 28, 2854). It forms hydrates H_2O_2,H_2O, $H_2O_2.2H_2O$ (Wolffenstein, *l.c.* 3311).

When heated to the boiling-point of water it decomposes with explosive violence into oxygen and water, but when the peroxide or its solutions are quite pure it is not so readily decomposed by heat; the vapours of hydrogen peroxide are said to be quite stable (Wolffenstein, Ber. 1894, 27, 3307; Nernst, Zeitsch. physikal. Chem. 1904, 46, 720).

The liquid evaporates slowly *in vacuô* without the residue undergoing any change (Thenard). It bleaches organic colouring matters, but not so quickly as chlorine; when brought in contact with the skin it forms a white blister, which, after a time, produces an irritable, itching sensation (Wolffenstein, *l.c.*).

One volume of the concentrated solution yields at 14° and 760 mm. pressure, 475 volumes of oxygen, the theoretical amount being 501·8 volumes (Thenard). The compound is most stable in dilute aqueous solution; when the solution is subjected to great cold, part of the water freezes out.

Hydrogen peroxide is a remarkable oxidising agent. It converts arsenious into arsenic acid, and sulphurous acid into sulphuric acid; lead and other sulphides into the corresponding sulphate; manganese monoxide into dioxide and monoxides of iron and cobalt into the sesquioxides. The monoxides of barium, strontium, and calcium are converted by it into their respective peroxides. The concentrated solution of hydrogen peroxide acts with violence on selenium, arsenic, molybdenum, and chromium, converting them at once into their oxides.

It decomposes alkaline copper, silver, and bismuth nitrate solution with evolution of oxygen and formation of the metallic oxide, or in the last case the hydroxide (Berthelot, Compt. rend. 1901, 132, 897; Moser, Zeitsch. anorg. Chem. 1906, 50, 33; Gutbier and Bünz. Chem. Zentr. 1909, i. 732).

Hydrogen peroxide oxidises organic sulphides into sulphoxides (Gazdar and Smiles, Chem. Soc. Trans. 1908, 1833). It also reacts with benzene in presence of ferrous sulphate, forming phenol (Young, Chem. Soc. Proc. 1899, 131), and with α-diketones, and generally with substances possessing a quinonoid structure, and can therefore be employed for oxidising phenolic substances like brazilein and aurin, without having to protect the hydroxyl group by methylation (Perkin, Chem. Soc. Proc. 1907, 166). Hydrogen peroxide reacts with a number of opium alkaloids forming new crystalline bases (Freund and Speyer, Pharm. Zeit. 1907, 52, 115). According to Schaer (Arch. Pharm. 1910, 248, 458), it may be used as a test for other alkaloids. A few milligrams of the alkaloid to be tested are added to a cooled mixture of the peroxide and sulphuric acid. Quinine gives a lemon or canary yellow colour; berberine a cherry red; hydrastine a chocolate; emetine a dark orange, and nicotine a blood-red colour.

In presence of ferrous sulphate hydrogen peroxide also reacts with a number of sugars, forming osones (Cross, Bevan, and Smith, Chem. Soc. Trans. 1898, 403; Morell and Bellars, *ibid.* 1905, 280; Chem. Soc. Proc. 1902, 55; Chem. News, 1904, 90, 158). It also reacts with other organic compounds (Cross, Bevan, and Heiberg, Chem. Soc. Proc. 1899, 130; Harden, *ibid.* 158; Wolffenstein, Ber. 1895, 28, 1459; Bevan and Heiberg *ibid.* 1900, 33, 2015; Clover and Haughton, Amer. Chem. J. 1904, 32, 43).

Pure hydrogen peroxide reacts with potassium cyanide thus:

$$KCN+H_2O_2=KCNO+H_2O$$
$$KCNO+2H_2O=K(NH_4)CO_3.$$

Potassium formate and ammonia are also produced, but if the peroxide contains acid, then oxamide is formed (Masson, Chem. Soc. Trans. 1907, 1449).

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prepared. Crystals of the $KMnO_4$ should be placed in a Woulff's bottle containing 1 : 9 sulphuric acid, and the 3 p.c. solution of H_2O_2 allowed to drop regularly into the solution from a suitable reservoir.

With potassium persulphate it reacts thus:

$$H_2O_2+K_2S_2O_8=2KHSO_4+O_2$$

an unstable intermediate compound is also formed (Friend, Chem. Soc. Trans. 1906, 1092).

With sodium thiosulphate it gives the reaction:

$$Na_2S_2O_3+4H_2O_2=Na_2S_3O_6+2NaOH+3H_2O$$
$$Na_2S_2O_3+2NaOH+4H_2O_2=2Na_2SO_4+5H_2O$$

(Willstätter, Ber. 1903, 36, 1831).

In presence of certain solid substances, especially when finely divided, hydrogen peroxide undergoes violent decomposition, the substances themselves remaining unchanged (Fillippi, Chem. Zentr. 1907, ii. 1890; Antropoff, Zeitsch. physikal. Chem. 1908, 62, 513; Bredig Wilkie, Biochem. Zeitsch. 1908, ii. 67). This is the case with carbon, many metals, and oxides, and iodine (Walton, Zeitsch. physikal. Chem. 1904, 47, 185; Abel, Zeitsch. Elektrochem. 1908, 14, 589). Gold, platinum, and particularly silver, act most violently and evolve great heat. The presence of acids retards this decomposition, whilst the presence of alkalis facilitates it.

This decomposition is still more readily brought about by these metals when in the colloidal state (Bredig and Reinders, Chem. Zentr. 1901, ii. 87; Bredig, Zeitsch. physikal. Chem. 1899, 31, 258; *ibid.* 1901, 37, 323; *ibid.* 38, 122; Price and Denning, *ibid.* 1903, 46, 89; Brossa, *ibid.* 1909, 66, 162; Spear, J. Amer. Chem. Soc. 1908, 30, 195; *see* also Kastel and Loevenhart, Amer. Chem. J. 1903, 29, 563; Liebermann, Ber. 1904, 37, 1519; Bredig, *ibid.* 798; Poppada, Gazz. chim. ital. 1907, 37, ii. 172).

Hydrogen peroxide is also decomposed by *catalases*, a class of organic ferments which are widely distributed in the animal and vegetable kingdoms (Senter, Proc. Roy. Soc. 1904, 74, 201; Wender, Chem. Zeit. 1904, 28, 300, 322; Euler, Chem. Zentr. 1905, i. 941; Bach, Ber. 1904, 37, 3785; *ibid.* 1905, 38, 1878; Laer, Bull. Soc. chim. Belg. 1906, 19, 337; J. Inst. Brewing, 1906, 12, 313; Rywosch, Centr. Bakt. Par. 1907, i. 44, 295).

Hydrogen peroxide also acts as a deoxidising agent; thus silver oxide when brought in contact with it causes a mutual decomposition of the two compounds $Ag_2O+H_2O_2=H_2O+O_2+Ag_2$, an atom of oxygen is liberated from each compound, and a molecule of free oxygen is thus obtained. A similar reaction occurs when hydrogen peroxide and ozone are brought together, $H_2O_2+O_3=H_2O+2O_2$ (Mulder, Rec. trav. chim. 1903, 22, 388; Baeyer and Villiger, Ber. 1902, 34, 749; 2769; Inglis, Chem. Soc. Trans. 1903, 1013).

Hydrogen peroxide is reduced by manganese dioxide and peroxide of lead in presence of an acid, $H_2O_2+MnO_2=MnO+O_2+H_2O$.

Alkaline mercury salts are reduced to the metallic state by hydrogen peroxide (Kolk, Chem. Zeit. 1901, 25, 21). Direct sunlight accelerates the decomposition of hydrogen peroxide. The effect of hydrogen peroxide on a photographic plate is similar to that of light, and is probably due to the hydrogen peroxide vapour itself, and not to a radiation from it (Russell, J. Soc. Chem. Ind. 1899, 516; Otsuki, *ibid.* 1905, 575; Precht and Otsuki, *ibid.* 290; Dony-Hénault, *ibid.* 1904, 138; Graetz, Chem. Zentr. 1904, ii. 1561; Dony-Hénault, *ibid.* 1906, ii. 203; Bull. Soc. chim. Belg. 1908, 22, 224; Soeland, Ann. Physik. 1908, [iv.] 26, 899).

Hydrogen peroxide forms molecular compounds with certain inorganic and organic salts in which it appears to play the same part as water of crystallisation (Tanatar, Chem. Zeit. 1901, 25; Rep. 326; J. Russ. Phys. Chem. Soc. 1908, 40, 376; Staedel, *l.c.*; Jones and Carroll, Amer. Chem. J. 1902, 28, 284; Willstätter, Ber. 1903, 36, 1828; De Forcrand, Compt. rend. 1902, 134, 601).

An acidified solution of potassium dichromate in presence of hydrogen peroxide gives rise to an unstable combination of chromic acid and the dioxide; this, on mixing with ether, can be extracted from the aqueous solution, imparting to it a beautiful and characteristic blue colour.

A solution of guaiacum mixed with a small amount of blood gives a blue colouration on addition of hydrogen peroxide. This is a delicate test for the compound, and serves also as a test for blood.

Hydrogen peroxide gives a blue-green colouration with an alcoholic solution of guaiacol and sulphuric acid, and an intense yellow colour with a solution of quinine sulphate in concentrated sulphuric acid (Denigès, Pharm. J. 1909, July 31st).

In the presence of hydrogen peroxide, chlorates, bromates, iodates, phosphates, sulphates, and alkali hypohalites, also salts of organic acids, give a yellow-green colouration with 1 p.c. guaiacol solution. On addition of hydrochloric or sulphuric acid the colour changes to red (Baudran, Compt. rend. 1905, 141, 891). Solutions of vanadic and titanic acids are turned brown or red by the peroxide and with a mixture of potassium chlorate and aniline in the presence of acid a violet colour is formed after a short time (Bach, Compt. rend. 1894, 119, 1218); if dimethylaniline is used instead of aniline, a yellow colour is formed. By the latter reaction 1 part of peroxide in 5,000,000 can be detected.

When hydrogen peroxide is added to a solution of potassium iodide, even in presence of ferrous sulphate or copper sulphate, iodine is set free, which may be shown by the colouration of starch. Hydrogen peroxide is the only compound known which can liberate iodine in presence of ferrous sulphate (*cf.* Traube, Ber. 1884, 17, 1062), 1 part in 25,000,000 can thus be detected.

A very delicate reagent for hydrogen peroxide has been suggested by Charitschkoff (Chem. Zeit. 1910, 34, 50). It consists of the pinkish-red cobalt salts of the naphthenic acids obtained from the waste liquors from the refining of petroleum with alkali. A strip of filter paper is dipped into a petroleum solution of the cobalt salt, and, after drying, is moistened with the liquid to be tested. If the peroxide is present the colour changes immediately to olive-green. Ozone does not give this reaction.

For other tests *see* Denigès (Bull. Soc. chim. 1890, 797); Aloy (*ibid.* 1902, 27, 734); Precht and Otsuki (Zeitsch. physikal. Chem. 1905, 52, 236).

Technical applications.—Moistened lead sulphide in contact with hydrogen peroxide is quickly oxidised to lead sulphate. This fact has led to the employment of hydrogen peroxide as a *picture restorer.* The painting darkened by age or by exposure to air containing sulphuretted hydrogen, owing to the white lead employed as body colour being partially converted into lead sulphide, after careful treatment with an aqueous solution of the peroxide is found to be greatly improved in colour from the oxidation of the sulphide to the white sulphate.

Dilute solutions of hydrogen peroxide mixed occasionally with nitric acid, are also used as 'auricome,' 'golden hair water,' &c., for imparting a light colour to the hair (Schrötter, Ber. 1874, 7, 980; Lange, Dingl. poly. J. 1886, 259, 196).

It is also employed for removing the last traces of chlorine from vegetable fibres which have been bleached with the latter, and to remove the last traces of sulphur dioxide from bleached wool and silk.

Hydrogen peroxide may be used for bleaching in many cases where other agents, such as bleaching powder, sulphurous acid, chlorine, would be injurious. It is particularly valuable for bleaching ostrich feathers, bones, ivory, silk, wood, cotton, the teeth, &c.

The advantages of using hydrogen peroxide as a bleaching agent, particularly for wool, are claimed to be the following: a purer white can be obtained; the fibres are not tendered by it to the same extent as by the sulphur bleach; the wool, after bleaching, does not turn yellow, does not emit an unpleasant odour when in contact with perspiration, and purer tones and more even colours can be obtained on dyeing the bleached wool. It is also stated to be more convenient to use, more pleasant for the workpeople, and less corrosive on the machinery. With care, the process, moreover, need not be much more expensive than with the older bleaches, and it is now used very extensively and with good results, both in England and on the Continent (Wachtel, Färber-Zeit. 1900, 11, 268; Russell, Proc. Roy. Soc. 1899, 64, 409).

In the case of wool the scoured article is first soaked thoroughly in a dilute solution of sodium silicate (2 lbs. to 10 gallons). After saturation the wool is wrung out and placed in the peroxide bath, which is prepared by adding 3½ gallons of 10 volume peroxide to 6½ gallons of water in which ½ lb. of sodium silicate has been dissolved. The wool is kept in the bath for about 24 hours (or a shorter or longer interval depending on the quality of the wool and on the whiteness desired) at 80°F. Occasionally the wool is turned over, and the solution tested whether it is alkaline, which it must be for satisfactory results. It is then pressed through a wringing machine and dried at a temperature of 15°–17°C., and preferably in the sunlight. When quite dry the wool is well washed and redried (Fawsitt, J. Soc. Chem. Ind. 1902, 229; Luttringhaus, Färber-Zeit. 1901, 12, 328; Dommergne, Rev. Chim. Ind. 1896, 7, 73).

With slight modifications this process is also applicable to cotton, straw and silk, but for the two last, the peroxide solution is made up of 1 part 10 volumes peroxide to 2 of water, and for every 10 volumes of peroxide, 4 ozs. of sodium silicate is employed (Fawsitt, *l.c.*; Koechlin, J. Soc. Chem. Ind. 1899, 1119). In the case of silk the bath may be made strongly alkaline with caustic soda from the beginning of the process.

Bone and ivory are first cleansed by treatment with light petroleum, ammonia or other solvent; they are then immersed in a bath containing 1 of 10 volumes peroxide to 2 of water made slightly alkaline with ammonia. Feathers are bleached similarly, but are washed after bleaching with a dilute solution of sulphuric acid.

On a small scale lace can be bleached conveniently in the following way: The material, after being moistened with water, is immersed in a solution of potassium permanganate for a few minutes. It is then rinsed and treated for about 10 minutes with a very dilute solution of hydrogen peroxide, after which it is treated with acid to remove the manganous oxide formed in the previous operation (Thomas, J. Soc. Chem. Ind. 1900, 734).

For bleaching delicate materials the hydrogen peroxide should not be too strong; a solution of 1 in 10 is strong enough, and a bleaching vat of this solution may be used for a long time if the strength be kept up by fresh additions of hydrogen peroxide. In bleaching dead hair, it is first digested for 12 hours in a solution of 3 parts of ammonium carbonate in 100 of water at a temperature of 30°C., rinsed, then washed with soap and treated with ammonium carbonate until all fatty matter is removed. Thus prepared it is treated in a bath of hydrogen peroxide and water as in the first case.

Hydrogen peroxide has been used for tanning leather, also to disinfect hides that have been long stored, and to preserve extracts of tanning materials (Göhring, J. Soc. Chem. Ind. 1890, 84). It has also been recommended for use in photographic processes (Smith, J. 1873, 1131; Gros, D. R. PP. 147131; 153769; 158368; Otsuki, *l.c.*; Lüppo Cramer, Chem. Zeit. 1902, 26, Rep. 292, 336; Ebert, *ibid.* 27, Rep. 152).

Medicinal and surgical applications.—As an antiseptic and disinfectant it has the advantage of (1) being odourless; (2) yielding oxygen without leaving any residuum but pure water; (3) absence of injurious influence on the organism.

The antiseptic properties of hydrogen peroxide solution were first brought into notice by Richardson in 1860. They were also studied by Kingzett, and subsequently by Paul Bert and Regnard (Compt. rend. 1882, 94, 1383).

It is used in the treatment of syphilitic and scrofulous sores, alveolar abscesses, and purulent discharges. It is also of great value in cases of purulent discharge from the conjunctiva, and it is particularly efficient for destroying diphtheritic membranes.

Its behaviour is that of a powerful oxidising agent, but on healthy skin its action is slow. In contact with fistulous wounds or pus it is rapidly decomposed with effervescence, which continues till the wound is cleansed or the diseased secretion is destroyed (Kingzett, J. Soc. Chem. Ind. 1890, 3; Paneth, Chem. Zentr. 1890, 174; Schmidt, *ibid.* 1906, ii. 145; Jaubert, *ibid.* 1905, ii. 99).

Hydrogen peroxide may be used to bleach discoloured teeth. In cases where the teeth are covered with coloured matter (*Lichen dentalis*, &c.) peroxide of hydrogen in conjunction with finely levigated pumice-stone may be employed in place of water. A suitable liquid for cleansing the teeth and mouth is prepared by mixing 1 part of 3 p.c. peroxide of hydrogen with 9 parts of water (Chem. News, 45, 71; and Ch. Trade J. April 14, 1888).

It has been proposed to use mixtures of hydrogen peroxide containing starch, cooked or in viscid solution, with anhydrous calcium sulphate as dentrifices, the starch preventing loss of oxygen from the oxide and the latter preserving the starch from putrefaction (Queissier, Fr. Pat. 381924, 1907; J. Soc. Chem. Ind. 1908, 226).

Hydrogen peroxide has the power of freeing water from living organisms, a property which has been utilised in brewing. It also destroys the acid and mould ferments in the wort. In stronger doses it destroys the alcoholic ferment and stops fermentation (G. Reisenbichler, Chem. News, 56, 219; Miquel, Monit. Scient. 1884, [3] 14, 170; Chodat and Bach, Ber. 1902, 35, 1275; Loew, *ibid.* 2487; Bonjean, Compt. rend. 1905, 140, 50; Laer, J. Inst. Brewing, 1909, 15, 553).

Altenhöfer has recommended hydrogen peroxide as a disinfectant for drinking water (Zentr. Bakteriol and Parasitenkde, 1890, 129; Küster, Chem. Zentr. 1889, i. 411; 1891, ii. 272; 1895, i. 948; but see also Gourmont, Nagier, and Rochaix, Compt. rend. 1910, 150, 1453).

Hydrogen peroxide is one of the chief constituents of 'sanitas,' which is a solution of the products of oxidation of terpentine oil in the presence of water and air (Kingzett).

It has been tried with success in the preservation of beer; after a month the taste and aroma of the beer remained good (Weingartner, Bied. Zentr. 1884, 428).

Hydrogen peroxide has been suggested as a useful and harmless preservative of milk (Jablin and Gounet, Ann. Chim. anal. 1901, 6, 129; J. Soc. Chem. Ind. 1902, 420; *ibid.* 1905, 1184; Fr. Pat. 355547; Amberg, J. Biol. Chem. New York, 1906, i. 219).

To test milk for hydrogen peroxide, 10 drops of a 2 p.c. alcoholic solution of benzidine and a few drops of acetic acid are added to 10 c.c. of the milk. If hydrogen peroxide is present a blue colouration appears. The peroxide can be detected in this way in other liquids if a little milk serum is added (Wilkinson and Peters, Zeitsch. Nahr. Genussm. 1908, 16, 172, 515, 589; for other tests, *see* Feder, *ibid.* 15, 234; Arnold and Mentzel, *ibid.* 1903, 6, 305).

Hydrogen peroxide is used in the laboratory in the valuation of bleaching-powder, the principle depending upon the fact that hypochlorites, when mixed with hydrogen peroxide, instantly evolve all their oxygen, at the same time liberating the oxygen of the peroxide (J. Soc. Chem. Ind. 1887, 391). It is also employed in estimating the amount of active oxygen in potassium permanganate and in manganese dioxide (Schlossberg, Zeitsch. anal. Chem. 1902, 41, 735; Carnot, Compt. rend. 1893, 116, 1295). The amount of sulphur in sulphides is also determined by first oxidising the sulphate and then proceeding as usual (G. Lunge, Ber. 18, 1872; *see* also Baumann, Zeitsch. angew. Chem. 1890, 72; Talbot and Moody, J. Soc. Chem. Ind. 1893, 780).

Hydrogen peroxide has been employed in the separation of a number of metals from one another (Rose, Ber. 1894, 27, 2227; Lesinsky, *ibid.* 1893, 26, 1496, 2331, 2908; Jannasch and Röttgen, Zeitsch. anorg. Chem. 1895, 8, 202; Friedheim and Brühl, Zeitsch. anal. Chem. 1899, 38, 681). Also for the separation of the halogens (Jannasch and Zimmermann, Ber. 1906, 39, 196, 3655), and for separating vanadium from ores and slags (Fr. Pat. 357397; J. Soc. Chem. Ind. 1906, 72).

Hydrogen peroxide has also been used as a solvent for Indian gum (Bull. Soc. Ind. Mulhouse, 1894, 36), but its use in the estimation of the quantity of flour in a mixture of the latter with bran, is considered to be untrustworthy by Bremer (Zeitsch. Nahr. Genussm. 1906, 11, 569).

Hydrogen peroxide has been employed with success in determining the amount of sulphur in coal gas. The solution used for this purpose consists of the commercial product diluted to a 1 p.c. solution. This solution is run into the Referees' 'apparatus,' through which the coal gas passes at a measurable rate, and the sulphurous acid gas in it is oxidised to sulphuric acid $SO_2+H_2O_2=SO_4H_2$. The amount of sulphur is then determined by titration or precipitation (J. Soc. Chem. Ind. 1887, 285).

Higher oxides of hydrogen.—The oxides H_2O_4 and H_2O_3 have been described (Bach, Ber. 1900, 33, 1506, 3111; *ibid.* 1902, 35, 158; Berthelot, Compt. rend. 1900, 131, 637), but it is doubtful whether they really exist (Armstrong, Chem. Soc. Proc. 1900, 134; Ramsay, Chem. Soc. Trans. 1901, 1324; *see* also Baeyer and Villiger, 1900, 33, 2488; Clover, Amer. Chem. J. 1903, 24, 463; Brühl, Chem. Zentr. 1896, i. 86; Nagel, Pharm. Zeit. 1898, 43, 556). Kastner (J. 1820, 472) described a *suboxide*, but its existence has not been confirmed.

HYDROGEN SULPHIDES *v.* SULPHUR.

HYDROLITES *v.* AGATE.

HYDROLYSIS. The term hydrolysis (or hydrolytic dissociation) is given to a number of different chemical reactions, all of which consist in the addition of water to a complex, and the subsequent resolution of the product into simpler substances.

Some of the best-known types of hydrolysis are those of metallic salts, esters, acid chlorides, amides, &c., or generally acyl derivatives, complex carbohydrates, and glucosides, and finally, polypeptides and proteins.

1. **Hydrolysis of salts.** The hydrolysis of a salt by water may be represented by means of an equation of the type:

$$KCN+H{\cdot}OH \leftrightarrows HCN+KOH.$$

The reaction is a balanced one, and may be regarded as due to the incomplete neutralisation of the acid and base from which the salt is derived; in terms of the ionic theory the acid in question (HCN) does not yield sufficient hydrions to combine with the hydroxyl ions of an equivalent quantity of the strong base (KOH). When equivalent quantities of a strong acid and a strong base are brought together in aqueous solution complete neutralisation takes place, and a normal salt with a neutral reaction towards common indicators is formed. (Basis of methods of acidimetry and alkalimetry.) In the cases of such salts appreciable hydrolysis would not be expected even in dilute solution. The following are the common types of salts which are hydrolysed by water: (1) salts derived from feeble acids and strong bases; (2) salts from strong acids and feeble bases; (3) salts from feeble acids and feeble bases. As examples of the first type we have potassium cyanide and sodium phosphate.

$$KCN+H{\cdot}OH \rightleftarrows HCN+KOH$$

$$Na_3PO_4+H{\cdot}OH \rightleftarrows Na_2HPO_4+NaOH$$

and even

$$Na_2HPO_4+H{\cdot}OH \rightleftarrows NaH_2PO_4+NaOH$$

Solutions of such salts invariably have an alkaline reaction towards common indicators, *e.g.* litmus, phenolphthalein. The water may be regarded as a feeble acid, which, like any other feeble acid, liberates a certain amount of acid from the salt with which it is brought into contact. In many cases acid salts are first formed, *e.g.* sodium phosphate, sodium carbonate, but free acid and free base may be liberated. The alkaline reaction of the solution can be accounted for by the fact that the feeble acid, or the acid salt formed, is ionised to a slight extent only, whereas with moderately dilute solutions the strong base is almost completely ionised, and thus there is a great excess of hydroxyl ions over hydrions. As examples of the second type we have ferric chloride and cupric sulphate, which are derived respectively from the feeble bases, ferric hydroxide and cupric hydroxide. The aqueous solutions of such salts invariably give an acid reaction. The hydrolysis may be represented by means of the equations:

$$FeCl_3+H{\cdot}OH \leftrightarrows FeCl_2{\cdot}OH+HCl$$

or even $FeCl_3+3H{\cdot}OH \leftrightarrows Fe(OH)_3+3HCl$

and $CuSO_4+2H{\cdot}OH \leftrightarrows Cu(OH)_2+H_2SO_4$.

With moderately concentrated solutions basic salts, *e.g.* $FeCl_2{\cdot}OH$ are almost certainly formed, and it is only in very dilute solution that the hydrolysis will proceed to the formation of the metallic hydroxide, and even when this is formed it is not precipitated, but remains in solution in the form of a colloid. A group of salts which belongs to this type is that of the salts dervied from feeble organic bases such as aniline, and from the strong mineral acids, *e.g.*

$$\underset{\text{Aniline hydrochloride.}}{C_6H_5{\cdot}NH_3Cl}+H{\cdot}OH \rightleftarrows \underset{\text{Aniline hydroxide.}}{C_6H_5{\cdot}NH_3{\cdot}OH}+HCl$$

$$\rightleftarrows C_6H_5NH_2+H_2O+HCl.$$

As examples of the third type we have ferric phosphate, aluminium carbonate and sulphide, and aniline acetate. The hydrolysis in the first case is readily shown by washing finely divided ferric phosphate with distilled water, when it is found that the filtrate is always distinctly acid, owing to the free phosphoric acid which has been washed away by the water, and if the operation is continued nearly pure ferric hydroxide remains on the filter. In the case of the two aluminium salts, they are so readily hydrolysed that when brought into contact with water they yield the corresponding metallic hydroxide, and the free acids, carbonic acid and hydrogen sulphide, which escape and thus destroy the equilibrium.

In the case of salt formation we may regard the water as capable of acting as either a feeble base or a feeble acid. When in contact with equivalents of a strong acid and a feeble base the water competes with the base for the acid, and hence neutralisation is not complete, or, in other words, hydrolyis of the salt occurs and the feebler the base the greater the degree of hydrolysis. The mechanism of salt hydrolysis according to the ionic theory is as follows: In aqueous solution the given salt, *e.g.* potassium cyanide is ionised in the ordinary manner into $\overset{+}{K}$ and $\overset{-}{CN}$ ions, but water itself is ionised to a certain extent, $H_2O \rightleftarrows \overset{+}{H}+\overset{-}{OH}$, and as hydrogen cyanide is a very feeble acid, and therefore ionised to only a very slight extent in aqueous solution, there is a tendency for the $\overset{+}{H}$ ions of the water to combine with the $\overset{-}{CN}$ ions from the cyanide, yielding undissociated HCN, the result is that the equilibrium $H_2O \rightleftarrows \overset{+}{H}+\overset{-}{OH}$ is destroyed and more molecules of water are ionised, but this results in further combination between $\overset{+}{H}$ and $\overset{-}{CN}$ ions, and by this means an excess of $\overset{-}{OH}$ over $\overset{+}{H}$ ions is produced, and thus the alkaline reaction. The changes continue until ultimately an equilibrium is established between the KCN, $\overset{-}{CN}$, $\overset{+}{K}$, $\overset{+}{H}$, $\overset{-}{OH}$, HCN, and H_2O present. The degree of hydrolysis, *i.e.* the fraction of the salt hydrolysed, cannot be determined by direct titration of the free acid or free base present in the solution; the addition of standard acid to the solution of potassium cyanide would immediately destroy the equilibrium which previously existed, and more salt would be hydrolysed in order to restore the equilibrium, and the point of neutrality would not be reached until acid sufficient to decompose the salt completely had been added. The methods commonly adopted for determining the degree of hydrolysis are (*cf.* Farmer, B. A. Report 1901, 240): 1. Determination of the concentration of the free acid or free alkali present in the solution of the salt by its catalytic effect on the hydrolysis of an aqueous solution of ethyl acetate or on the inversion of a solution of cane sugar, and then determining the amount of pure acid or alkali required to produce the same effect (for acid, *cf.* Walker, Zeitsch. physikal. Chem. 1889, 4, 319; for alkali, *cf.* Shields, *ibid.* 1893, 12, 167; also Bruner, *ibid.* 1900, 32, 133; Ley, *ibid.* 1899, 30, 216; Walker and Aston, Chem. Soc. Trans. 1895, 67, 576). 2. Determination of the electrical conductivity of the solution (Walker, Zeitsch. physikal. Chem. 1889, 4, 333; Bredig, *ibid.* 1894, 13, 313; Denham, Chem. Soc. Trans. 1908, 93, 41). The molecular conductivity of a hydrolysed salt of the type aniline hydrochloride is made up of two quantities: (*a*) conductivity due to the non-hydrolysed salt; (*b*) conductivity due to the free acid formed on hydrolysis—since the free base (aniline) is not an electrolyte. $M=(1-x)u_1+xu_{HCl}$, where M = molecular conductivity, x=degree of hydrolysis, u_1=molecular conductivity of non-hydrolysed salt. The various quantities in the equation with the exception of x can be determined and then x calculated. 3. By determining the partition coefficient (Farmer, Chem. Soc. Trans. 1901, 79, 863). In the case of aniline hydrochloride the hydrolysis of the salt leads to the formation of free aniline and hydrochloric acid, and the concentration of the free base is determined by shaking the aqueous solution at a given temperature with a known volume of benzene, and finding the concentration of the aniline in the benzene layer. Since C_B/C_{Aq} is always constant (C_B=concentration of aniline in benzene and C_{Aq}=concentration of aniline in water) for a given temperature the concentration of free aniline in the aqueous layer can be calculated directly, and thus the degree of hydrolysis determined. The assumption is made that the salt present does not effect the partition coefficient to an appreciable extent. 4. By the change in colour produced by a solution of the hydrochloride of an organic base on a solution of methyl orange of known concentration, and a comparison of this change with that produced by the addition of known quantities of hydrochloric acid (Veley, Chem. Soc. Trans. 1908, 93, 652, 2114, 2122; 1909, 95, 758; Trans. Far. Soc. 1908, 4, 19).

Most of the methods give only rough approximations (*cp.* Beveridge, Proc. Roy. Soc. Edin. 1909, 29, 648). A few of the results obtained are as follows:—

Salt	Temp.	P.c. of salt hydrolysed in 0·1 N solution	Method
Glycine hydrochloride	25°	19·00	Hydrolysis of ester
Acetoxime ,,	25	36·00	,, ,,
Urea ,,	25	90·00	,, ,,
Urea ,,	60	81·00	Inversion of sugar
Sodium cyanide .	25	1·10	Saponification of ester
,, acetate .	25	0·008	,, ,,
,, carbonate .	25	3·17	,, ,,
,, phenate .	25	3·05	,, ,,
Aniline hydrochloride	60	2·60	Inversion of sugar
,, ,,	25	1·50	Conductivity
Zinc chloride . .	100	0·10	Inversion of sugar
Aluminium chloride .	100	6·10	,, ,,
,, ,, .	25	0·50	Conductivity
Ferric chloride . .	40	10·00	Inversion of sugar
Lead ,, . .	25	0·50	Conductivity

The whole question becomes more complicated when the acid or base formed by hydrolysis is unstable and is transformed into an isomeride (pseudo-acid or pseudo-base).

The influence of concentration on hydrolysis is given by Guldberg and Waage's law of mass action. According to this $\frac{C_S}{C_A \times C_B}$=constant, where C_S represents the concentration (molar) of the non-hydrolysed salt, C_A that of the acid formed by hydrolysis, and C_B that of the base. If originally 1 gram mol. of salt was dissolved in v litres of solution and x gram mols. were hydrolysed, then

$$\frac{1-x}{v}\bigg/\frac{x}{v}\cdot\frac{x}{v}=\text{constant, or}\frac{v(1-x)}{x^2}=\text{constant.}$$

It is obvious that as v increases, *i.e.* as the concentration is diminished, x, *i.e.* the degree of hydrolysis, must increase in order to keep the whole expression constant.

The relationships are not quite the same in the case of a salt derived from a feeble base and a feeble acid, *e.g.* aniline acetate.

$$C_6H_5{\cdot}NH_3{\cdot}O{\cdot}CO{\cdot}CH_3+H_2O \rightleftarrows C_6H_5{\cdot}NH_3{\cdot}OH+CH_3{\cdot}CO{\cdot}OH.$$

If the reaction is represented as taking place between the ions of the salt and the water, and the salt is practically completely ionised, and the base and acid not appreciably, then $C_{Cat}{\cdot}C_{An}/C_A{\cdot}C_B$=constant, where C_{Cat}=concentration of the cation and C_{An}=concentration of the anion. But $C_{Cat}=C_{An}=C_{Salt}$.

$$\therefore\ C^2_{Salt}/C_A{\cdot}C_B=\text{constant, or}\left(\frac{s}{v}\right)^2\bigg/\frac{a}{v}\cdot\frac{b}{v}=\text{constant}$$

where s, a, b are the gram mols. respectively of salt, acid, and base in v litres of solution. But this expression is independent of v, and hence dilution does not affect the degree of hydrolysis.

Another factor which affects the degree of hydrolysis is the addition to the solution of one of the products of hydrolysis, *e.g.* free acid or free base. Thus the hydrolysis of aniline hydrochloride in aqueous solution can be stopped completely by the addition of hydrochloric acid or of aniline. This follows again directly from the equation $C_S/C_A{\cdot}C_B$=constant. If C_A, *i.e.* the concentration of the acid is increased it is necessary, in order that the whole expression may remain constant, that either C_B should diminish or C_S increase or both, and the only way in which this can be affected is by a diminution in the degree of hydrolysis.

The velocity of salt hydrolysis has been determined in a few cases, *e.g.* ferric chloride (Goodwin, Zeitsch. physikal. Chem. 1896, 21, 1); potassium ruthenium chloride K_2RuCl_5 (Lind and Bliss, J. Amer. Chem. Soc. 1909, 31, 868).

A type of hydrolysis analogous to salt hydrolysis is that of the chlorides of certain non-metals, *e.g.* $PCl_3+3H_2O=3HCl+P(OH)_3$. This reaction proceeds to completion in the presence of an excess of water, and, as a rule, the chlorides of non-metals are hydrolysed more readily than those of metals. Nitrogen trichloride and carbon tetrachloride are, however, stable in the presence of water and many metallic chlorides derived from feeble electropositive metals are appreciably hydrolysed, *e.g.* $FeCl_3$, $BiCl_3$, &c.

2. **Hydrolysis of esters.** The hydrolysis of an ester may be brought about by water alone, by solutions of neutral metallic salts, by aqueous solutions of strong alkalis or acids, by water in the presence of finely divided solids, such as charcoal, and also by means of enzymes.

The reaction with water may be represented by an equation of the type:

$$CH_3{\cdot}CO{\cdot}OC_2H_5+H{\cdot}OH \rightleftarrows CH_3{\cdot}CO{\cdot}OH+C_2H_5OH$$

The reaction is the reverse of esterification, and is hence a balanced bimolecular reaction; in dilute solutions, however, the mass of the water may be regarded as remaining constant, and the reaction becomes practically non-reversible. The course of the reaction can be followed by estimating the amount of free acid in the solution after given intervals of time; this is accomplished by removing an aliquot part of the solution at the given time and titrating the free acid by means of standard alkali solution. In most cases it is necessary to use a feeble alkali for titration, *e.g.* ammonium hydroxide using litmus as indicator, as nearly all esters which are hydrolysed appreciably by water are decomposed very readily by strong alkalis, and it becomes impossible to tell the end point of the titration when sodium or barium hydroxide solutions are used. Comparatively few esters are hydrolysed to any appreciable extent by water at the ordinary temperature, the few that have been investigated are esters derived from comparatively strong acids, *e.g.* ethyl nitrate, ethyl formate, ethyl trichloroacetate, and ethyl pyruvate. In these cases the velocity of the reaction does not correspond with that of a simple unimolecular reaction, the values for K calculated by means of the usual equation $K=1/t \log a/a-x$, increase as t increases, and the probable reason is that the acid formed during the hydrolysis reacts catalytically on the reaction (*see* under hydrolysis by acids). Hydrolysis of natural glyceryl esters by means of superheated steam is used as a commercial method for the production of stearic acid for the manufacture of candles.

The hydrolysis of esters by means of dilute mineral acids is slow and readily lends itself to study as a time reaction. The velocity is directly proportional to the concentration of the mineral acid, *i.e.* probably to the hydrions which act as a catalyst, and the reaction may be represented by the differential equation

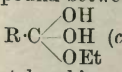
$$dx/dt=K{\cdot}C_{\text{Ester}}{\cdot}C_{H_2O}{\cdot}C_{\overset{+}{H}}.$$

In dilute solution, and most esters are somewhat sparingly soluble in water, C_{H_2O} can be regarded as not changing, and $C_{\overset{+}{H}}$ is also constant, since the catalyst is not used up during the reaction. The process thus becomes a typical unimolecular reaction, and the velocity constant can be determined with the aid of the usual formula $K=1/t \log_e a/a-x$.

The concentration of the organic acid at any given time is obtained by titrating a portion of the solution with standard barium hydroxide solution and phenolphthalein (unless the ester is derived from a strong acid when ammonia and litmus are used) and subtracting from the total alkali used the amount required by the mineral acid. The following relative values have been obtained at 25°, using 0·1 N-hydrochloric acid as catalyst working with the methyl, ethyl, and propyl esters of acetic, propionic, and butyric acids:

K methyl ester : K ethyl ester=0·97
and K ethyl ester : K propyl ester=1·01.
K acetate ester : K propionate ester=1·07
K propionate ester : K butyrate ester=1·75
K butyrate ester : K valerate ester=2·93.

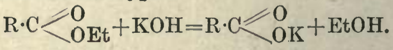
From these values it is clear that in the hydrolysis of an ester R·CO·OR′ by means of a strong mineral acid the acyl group R·CO has a much greater influence than the alkyl group R′ on the velocity of hydrolysis (Hemptinne, Zeitsch. physikal. Chem. 1894, 13, 562). Lowenherz (*ibid.* 1894, 15, 389) working at a temperature of 40° found that ethyl formate is hydrolysed much more readily than ethyl acetate (ratio 20 : 1); that methyl and ethyl monachloroacetates are hydrolysed at much the same rates, ratio 1·01 : 1, that the ratio K ethyl acetate : K ethyl monochloroacetate=1·7 and that K ethyl dichloroacetate : K ethyl monochloroacetate =1·6, and that ethyl benzoate is hydrolysed extremely slowly.

The majority of chemists are of opinion that the process of hydrolysis consists first of all in the formation of an additive compound between the ester and the water, *e.g.*  $\mathrm{R{\cdot}C}\begin{cases}\mathrm{OH}\\ \mathrm{OH}\\ \mathrm{OEt}\end{cases}$ (*cp.* esterification), and the subsequent breaking up of this into acid and alcohol. The manner in which the complex dissociates, *e.g.* into water and ester, or into alcohol and acid, will depend largely on the relative amounts of water and alcohol present. A view put forward by Stieglitz, and supported by many chemists (*cp.* Acree and Johnson, Amer. Chem. J. 1907, 38, 335), is that the ester, being a feeble base, combines with the strong mineral acid used as catalyst, forming a salt, *e.g.* $R{\cdot}CO_2Et,HCl$, only small amounts of such salts would be formed, as the base is an extremely feeble one. The salt would be ionised in the usual manner into $\overset{-}{Cl}$ ions and complex cations $R{\cdot}C\overset{+}{O_2}Et,H$. It is these complex cations which then react with the water and undergo hydrolysis

$$R{\cdot}CO_2\overset{+}{E}t,H+H_2O=R{\cdot}CO_2H+EtOH+\overset{+}{H}$$

and the assumption has to be made that the hydrolysis of the complex cations proceeds more rapidly than the hydrolysis of the ester molecules. The view that it is the complex cation and not the unionised salt (ester hydrochloride) which reacts with the water is supported by the fact that the rate of hydrolysis is directly proportional to the concentration of the mineral acid, *i.e.* to the concentration of the hydrion and not to the square of the concentration of the hydrion.

The hydrolysis of an ester by means of an alkali hydroxide can be represented by an equation of the type:



$$\mathrm{R{\cdot}C}\begin{cases}\mathrm{O}\\ \mathrm{OEt}\end{cases}\!\!+KOH=\mathrm{R{\cdot}C}\begin{cases}\mathrm{O}\\ \mathrm{OK}\end{cases}\!\!+EtOH.$$

The reaction is non-reversible, as the alkali salt cannot react directly with the alcohol, and as both ester and alkali are used up as the hydrolysis proceeds the reaction should be bimolecular. Hydrolysis by alkalis proceeds more rapidly than that by mineral acids (*cp.* Van Dikjen, Rec. trav. chim. 1895, 14, 106), and is the common method used in the laboratory. The ester is boiled for some time with an excess of sodium (or potassium) hydroxide solution in a flask fitted with a reflux condenser. If the ester is an oil only sparingly soluble in water, the completion of the reaction is denoted by the disappearance of the oily layer, unless the alcohol formed is also insoluble in water. If, however, the ester itself is soluble in water, but has a characteristic odour, the disappearance of the odour indicates complete hydrolysis. In order to separate the acid and alcohol formed, the mixture is (*a*) boiled, when the alcohol passes over together with water, provided the alcohol is a comparatively simple monohydric one; (*b*) extracted with ether if the alcohol is complex and is not readily volatile. To obtain the acid the alkaline solute left after treatment (*a*) or (*b*) is acidified with hydrochloric acid, when the organic acid is directly precipitated if it is sparingly soluble in water, or can be extracted with ether if soluble in water.

An alcoholic solution of potassium hydroxide is sometimes used for hydrolysing purposes, especially when the ester is practically insoluble in water.

The decomposition of esters by alkaline hydroxide solutions is the basis for the usual methods for the manufacture of hard and soft soaps (*see* SOAP; SAPONIFICATION), and hence a common name for the process is '*saponification.*' The common fats are glyceryl esters of monobasic acids of high molecular weight, more especially of palmitic, stearic, and oleic acids, and on saponification yield the trihydric alcohol glycerol and the sodium or potassium salts of the acids, *e.g.*

$$C_3H_5(O{\cdot}CO{\cdot}C_{17}H_{35})_3+3NaOH$$
$$=C_3H_5(OH)_3+3C_{17}H_{35}{\cdot}COONa.$$

Reicher (Annalen, 1885, 228, 257) was one of the first to determine the velocity of saponification under varying conditions. When the alkali and ester are not used in equivalent quantities the differential equation is of the type

$$dx/dt=K(a-x)(b-x)$$

where a and b are the original concentrations, and $a-x$ and $b-x$ the concentrations at the time t. When integrated this gives an equation

$$K=\frac{1}{t(a-b)}\log_e\frac{b(a-x)}{a(b-x)}$$

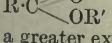
for calculating K. The concentration of the alkali at any given time is determined by titration with standard acid and the concentration of the ester calculated from that of the alkali, as with an ester of the type of ethyl acetate, the disappearance of each gram molecule of alkali entails the disappearance of a gram molecule of ester (*cf.* Warder, Amer. Chem. J. 1882, 3, 340; Ber. 1881, 14, 1311). The velocity constant K can be calculated by means of the equation

$$K=\frac{1}{C_\infty t}\log_e\frac{C_t(C-C_\infty)}{C(C_t-C_\infty)}$$

where C, C_t, and C_∞ denote the concentration of the alkali just after mixing, the concentration after time t and the concentration after complete hydrolysis (24–48 hours).

Reicher's experiments were carried out at 9·4°, and show that the velocity is practically the same whether sodium, potassium, or calcium hydroxide is used as saponifying agent. With strontium or barium hydroxide the velocity constants are somewhat smaller and with a feeble alkali, such as ammonium hydroxide, the value for K is much less, *e.g.*

$$K_{NaOH}:K_{NH_4OH}=200:1.$$

The results obtained by using different esters show that the alkyl group R′ in the ester  $R{\cdot}C\begin{smallmatrix}\nearrow O\\ \searrow OR'\end{smallmatrix}$ influences the rate of hydrolysis to a greater extent than it does when mineral acids are used for hydrolysing; thus the values for K using sodium hydroxide at 9·4° are: methyl acetate 3·49, ethyl acetate 2·31, propyl acetate 1·92, *iso*butyl acetate 1·62, and *iso*amyl acetate 1·64. The influence of the acyl group R·CO is also marked, as shown by the following values for K at 14·4°, using sodium hydroxide and ethyl esters: acetate 3·2, propionate 2·8, butyrate 1·7, *iso*butyrate 1·73, *iso*valerate 0·62, and benzoate 0·83. Later experiments by Sudborough and Feilmann (Chem. Soc. Proc. 1897, 13, 243) prove that the introduction of methyl groups into the ethyl acetate molecule retards hydrolysis by means of alcoholic potassium hydroxide, whereas the introduction of chlorine atoms facilitates the decomposition. The investigations of Gyr (Ber. 1908, 41, 4308) show that two or three phenyl groups in the ethyl acetate molecule also retard hydrolysis, whereas the ethyl ester of phenylacetic acid is hydrolysed more readily than ethyl acetate itself. The results obtained by Hjelt (Ber. 1896, 29, 1864) with substituted derivatives of ethyl malonate also show that the introduction of an alkyl group into the ethyl malonate molecule retards hydrolysis, and that when two such groups are present the effect is still more noticeable. The influence of the strength of the acid from which the ester is derived also appears to be a determining factor. The investigations of Kellas (Zeitsch. physikal. Chem. 1897, 24, 243) on the hydrolysis of ethyl esters of substituted benzoic acids show that the esters of many substituted benzoic acids are hydrolysed by alcoholic potash more readily than ethyl benzoate itself. This appears to be true of all esters derived from acids much stronger than benzoic acid, *e.g.* the bromo-, chloro-, and nitro-benzoic acids, but does not hold good when the esters are derived from acids with small dissociation constants, *e.g.* the toluic acids. Kellas's results also show that when the rates of hydrolysis of a group of three isomeric esters are compared the ortho-compounds are invariably hydrolysed more slowly than the isomeric, meta-, and para- compounds, even when the ortho- acid is a much stronger acid than the isomers.

Findlay and Turner (Chem. Soc. Trans. 1905, 87, 747) and Findlay and Hickmans (*ibid.* 1909, 95, 1004) show that an *a*-hydroxyl group increases the readiness with which the ester is hydrolysed by alkalis. The ratio K ethyl glycollate : K ethyl acetate=11·5; and K ethyl lactate : K ethyl propionate=11·9, and K methyl mandelate : K methyl phenylacetate =5·7. The introduction of a phenyl group in the *a*-position does not necessarily increase the rate of hydrolysis. The ratio K ethyl phenylacetate : K ethyl acetate=1·9, but K ethyl mandelate : K ethyl glycollate=0·88. It is shown that there is no direct proportionality between the affinity constant of the acid and the saponification constant of its ester, although in any given series of compounds the two constants follow the same order. The results obtained by different authorities point to the general conclusion that two factors at least determine the rate of hydrolysis of ethyl esters by alkalis or acids. (*a*) The complexity of the acyl group, especially as regards the presence of substituents in close proximity to the carbonyl group, *e.g.* in the *a*-position in aliphatic, the ortho- position in aromatic, and probably the cis- position in unsaturated esters. (*b*) The strength of the acid from which the ester is derived. When mineral acids are used as hydrolysing agents the rate of hydrolysis appears to be determined largely by the first factor, although the second factor also has an effect, as shown by the fact that ethyl trichloroacetate is hydrolysed more readily than the dichloroacetate. When alkalis are used and also probably when water alone is used, the second factor has a much more marked effect than when acids are used; the effect is so marked in certain cases that the influence of the first factor is almost completely obscured, *e.g.* with the esters of the chloroacetic acids, of the α-hydroxy acids and of nitro substituted benzoic acids.

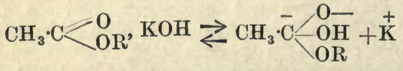
The generalisation drawn by V. Meyer (Ber. 1895, 28, 1263; *cp.* Wegscheider, *ibid.* 2536) viz. that there is a simple relationship between the rate of hydrolysis of an ester by alkalis and its rate of formation by the catalytic method of esterification does not hold. It is highly probable that there may be a relationship between the rate of esterification of an acid by the direct method and the rate of saponification of the ester, and also a relationship between the rate of hydrolysis of the ester by acids and the rate of esterification by the catalytic method. No relationship between the rate of saponification or by hydrolysis by acids and the constitution of the alkyl group R′ in the ester $R{\cdot}C\begin{array}{l}\diagup O\\ \diagdown OR'\end{array}$, can be deduced as the data available are not sufficiently numerous.

Since sodium, potassium, and calcium hydroxides as saponifying agents have practically the same effect when solutions of equivalent strengths are used, the conclusion has been drawn that the hydrolysis is due to the hydroxyl ions present. The reaction cannot be a simple addition of the alkali to the ester followed by the elimination of alcohol, as then the reaction with calcium hydroxide would be termolecular

$$2R{\cdot}CO_2Et+Ca(OH)_2=(R{\cdot}CO_2)_2Ca+2EtOH$$

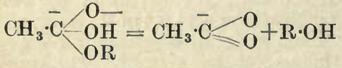
whereas it can be shown to be bimolecular.

It is possible that the reaction consists in the addition of water (not alkali) to the ester and the subsequent resolution of this complex into acid and alcohol. The alkali in this case would act first as a catalyst, and secondly as a base for neutralising the acid formed. According to Acree (Amer. Chem. J. 1907, 38, 344) the ester can function as a feeble acid and form small amounts of salts with the alkali, *e.g.*



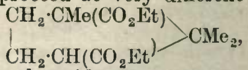
$$CH_3{\cdot}C\begin{array}{l}\diagup O\\ \diagdown OR'\end{array}, KOH \rightleftarrows CH_3{\cdot}\overset{-}{C}\begin{array}{l}\diagup O—\\ —OH\\ \diagdown OR\end{array}+\overset{+}{K}$$

and it is the complex anion which reacts with the water yielding the anion of the acid and alcohol



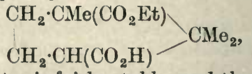
$$CH_3{\cdot}\overset{-}{C}\begin{array}{l}\diagup O—\\ —OH\\ \diagdown OR\end{array}=CH_3{\cdot}\overset{-}{C}\begin{array}{l}\diagup O\\ \diagdown O\end{array}+R{\cdot}OH$$

Esters of dibasic acids. J. Meyer (Zeitsch. physikal. Chem. 1909, 66, 81, and 67, 257) by the study of the hydrolysis of esters of dibasic acids (tartaric, succinic, and camphoric) with hydrochloric acid as catalyst, has been able to prove that the reaction proceeds in two distinct stages: (*a*) normal ester+water⟶acid ester +alcohol; (*b*) acid ester+water⟶acid+alcohol. With the ethyl esters of symmetrical dibasic acids, *e.g.* tartaric and succinic, the whole reaction appears to be unimolecular as the velocity constant for the first stage is almost exactly double that for the second stage, and the whole is pseudo-unimolecular. In the case of ethyl camphorate, the ester of an unsymmetrical acid, the two stages proceed at very different rates, the normal ester



$$\left.\begin{array}{l}CH_2{\cdot}CMe(CO_2Et)\\ |\\ CH_2{\cdot}CH(CO_2Et)\end{array}\right\rangle CMe_2,$$

is rapidly hydrolysed to the acid ester,



$$\left.\begin{array}{l}CH_2{\cdot}CMe(CO_2Et)\\ |\\ CH_2{\cdot}CH(CO_2H)\end{array}\right\rangle CMe_2,$$

but this latter is fairly stable, and the method is a convenient one for the preparation of the acid ester. For different esters of the same acid the influence of the alcoholic group on the rate of esterification is scarcely noticeable, whereas the constitution of the acyl group has a marked effect. Experiments carried out with the same esters using alkali hydroxide as hydrolysing agent show that here also the reaction proceeds in two distinct stages, but the relationship between the velocity constants of the two is not so simple as when hydrochloric acid is used. With ethyl malonate the first stage proceeds about 100 times as quickly as the second, but with ethyl succinate the ratio is about 10 : 1, and in neither case can the whole process be represented as a simple bimolecular reaction. With the esters derived from symmetrical dihydric alcohols, *e.g.* glycol diacetate $C_2H_4(OAc)_2$, although the saponification proceeds in two distinct stages the velocity constants of the two stages bear a simple relationship to one another, *e.g.* 2 : 1, and hence the whole appears to be a bimolecular reaction. The same holds good for the hydrolysis of glyceryl triacetate, where the three distinct stages proceed at the relative rates 3 : 2 : 1.

Esters of sulphonic acids. Esters of sulphonic acids can also be hydrolysed by water, mineral acids, or alkalis, and since most of the sulphonic acids are very strong acids, their esters are hydrolysed quite readily by water alone. The esters are also converted into the corresponding acids when heated with alcohol (Krafft and Roos, Ber. 1892, 25, 2225; Kastle and Murrill, Amer. Chem. J. 1895, 17, 290), a reaction in which an alkyl ether is also formed

$$R{\cdot}SO_2{\cdot}OEt+EtOH=R{\cdot}SO_2{\cdot}OH+Et_2O$$

This decomposition proceeds slowly at the ordinary temperature, and is brought about more readily by methyl than by ethyl alcohol.

Kastle, Murrill, and Frazer (Amer. Chem. J. 1897, 19, 894) have shown that 0·1 N-solutions of sulphuric and acetic acids have no effect on the hydrolysis of esters of sulphonic acids by water. Hydrochloric and hydrobromic acids, on the other hand, have an apparent retarding effect, but this is due to the fact that the halogen hydracids can react with the ester according to the equation:

$$R{\cdot}SO_2{\cdot}OEt+HCl \rightleftarrows R{\cdot}SO_2{\cdot}OH+EtCl$$

a reaction which does not affect the total acidity of the solution. A more detailed investigation has proved that this second reaction proceeds more rapidly and to a greater extent than the hydrolysis of the ester by water. The hydrolysis of a sulphonic ester by means of a large excess of water or alcohol in acetone solution gives concordant values for K when the equation for a monomolecular reaction is used. Alkalis are much more efficient hydrolysing agents than water for sulphonic esters; this may be due to the alkali acting independently of the water or to the alkali catalytically affecting the hydrolysis by water. The constants at 25° for methyl benzenesulphonate, using water and N-potassium hydroxide solution, are 1 : 90 (Wegscheider and Furcht, Monatsh. 1902, 23, 1903). When the neutral ester of a mixed carboxylic sulphonic acid is hydrolysed, *e.g.* $OEt\cdot SO_2\cdot C_6H_4\cdot CO_2Et$, the $\cdot SO_2\cdot OEt$ group is hydrolysed much more readily than the $\cdot CO_2Et$ group, and an acid ester of the type $OH\cdot SO_2\cdot C_6H_4\cdot CO_2Et$ is formed.

Esters can also be hydrolysed by water with finely divided metals as catalysts, *e.g.* Neilson (Amer. J. physiol. 1903, 10, 191) has shown that platinum black accelerates the hydrolysis of ethyl butyrate by water. The reaction is, however, very slow, and increases with the amount of platinum present. The maximum effect is obtained at 50°, and the activity of the catalyst is readily destroyed by various 'poisons.' The reaction is reversible as platinum black can also accelerate the esterification of butyric acid in ethyl alcoholic solution.

Sabatier and Maihle (Compt. rend. 1911, 152, 494) have shown that titanium dioxide is a good catalyst for the conversion of acids and alcohols into esters. The method adopted is to allow a mixture of molecular quantities of the vapours of the two compounds to pass over a column of the dioxide kept at 280°–300°. The yield of ester is much the same as in Berthelot and Menschutkin's experiments, but the process is extremely rapid. The reaction is reversible, and using equivalent quantities of acid and alcohol an approximately 70 p.c. yield of ester was obtained in most cases examined. A similar method may also be used for hydrolysis of esters. It consists in allowing a mixture of the vapour of the ester with an excess of steam to pass over the titanium dioxide at 280°–300°.

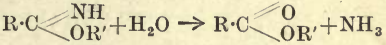
Similar results can be obtained with thorium oxide as catalyst provided aromatic acids of the type of benzoic are used (*ibid.* 358).

Certain neutral metallic salts also act catalytically on the hydrolysis of esters by water (Kellog, J. Amer. Chem. Soc. 1909, 31, 403, 886). The salts which have been investigated are potassium chloride, bromide, and iodide. The catalytic effects are comparatively small when compared with those of strong acids, the chloride has the greatest effect and the iodide the least, and when the concentration of the salt reaches a certain value the catalytic effect is negative. No simple explanation of the results can be given.

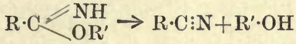
Hydrolysis of halogen derivatives. The hydrolysis of chloroacetic acid $CH_2Cl\cdot CO_2H$ and of its sodium salt to glycollic acid $OH\cdot CH_2\cdot CO_2H$ has been studied. With water at high temperatures the reaction is unimolecular and non-reversible, and when salts of the acid are used the velocity appears to be independent of the base with which the chloroacetic acid is combined. The velocity coefficients of N-, 0·3 N-, and 0·1 N-solutions of salts of monochloro- and monobromoacetic acids are inversely proportional to the affinity constants of the two acids. The rate diminishes with dilution and reaches a minimum at about 0·1 N, and from that point to $v=1000$ the velocity of decomposition is practically constant (Kastle and Keiser, Amer. Chem. J. 1893, 15, 471).

Senter (Chem. Soc. Trans. 1907, 91, 460) has shown that N solutions of hydrochloric acid and neutral salts have but little effect, and that the hydrolysis of the monochloroacetic acid is directly proportional to the concentration of the acid within wide limits. At 102° it is shown that the reaction is strictly unimolecular in dilute solution, but that slight deviations are met with in more concentrated solutions. The reaction is presumably between unionised water and unionised acid, and when the sodium salt is used the reaction is between unionised water and both unionised salt and the anion. When sodium hydroxide is used for hydrolysis at 102° the reaction is bimolecular in dilute solutions, although deviations are met with in more concentrated solution, and the reaction with the alkali proceeds some 10 times as fast as with water alone. For comparison of rates of various α-bromo acids and sodium salts, *cp.* Chem. Soc. Trans. 1909, 95, 1835. The velocity reaction between the sodium salt of the acid and water is appreciably increased by the introduction of methyl and ethyl groups into the acid molecule, whereas the reaction between the sodium salt and sodium hydroxide is retarded by the presence of alkyl substituents.

The *esters of imino acids* can be hydrolysed in two different ways:

(1) 

$$R\cdot C{<}^{NH}_{OR'}+H_2O \rightarrow R\cdot C{<}^{O}_{OR'}+NH_3$$

(2) 

$$R\cdot C{<}^{NH}_{OR'} \rightarrow R\cdot C{:}N+R'\cdot OH$$

The former reaction is enormously accelerated by acids and the latter by alkalis. According to Steiglitz (Amer. Chem. J. 1908, 39, 29, 166) the former reaction consists in the hydrolysis of the complex cation $(R\cdot C(:NH)\cdot OR',\overset{+}{H})$, and the latter in the decomposition of the anion $R\cdot C(:N)\cdot OR'$. The effect of alkalis is much more pronounced than that of acids. When water alone is used it is the non-ionised ester which is decomposed.

3. **Hydrolysis of acyl derivatives.** The chlorides, amides, anilides, and anhydrides of organic acids can be hydrolysed in much the same manner as esters, *e.g.*

$$R\cdot CO\cdot Cl+H\cdot OH=R\cdot CO\cdot OH+HCl;$$
$$R\cdot CO\cdot NHPh+K\cdot OH=R\cdot CO\cdot OK+NH_2Ph.$$

As a rule the derivatives of aliphatic acids are hydrolysed more readily than those derived from aromatic acids, *e.g.* acetamide more readily than benzamide. The hydrolysis is usually effected by boiling with alkali hydroxide, but the presence of ortho- substituents in derivatives of benzoic acid retards hydrolysis to an appreciable extent (V. Meyer, Ber. 1894, 27, 2153; Sudborough, Chem. Soc. Trans. 1894, 65, 1030; 1895, 67, 587; 1897, 71, 229; Reed, Amer. Chem. J. 1899, 21, 281). When two such substituents are present the amide cannot be hydrolysed by boiling with potassium hydroxide solution, but the hydrolysis may be accomplished by heating with concentrated hydrochloric or hydrobromic acid under pressure in sealed tubes. One of the most convenient methods for converting a diortho- substituted benzonitrile into the corresponding acid is to hydrolyse to the amide $R\cdot CN+H_2O=R\cdot CO\cdot NH_2$ by heating at 120°–130° with 90 p.c. sulphuric acid, and when cold to replace the amino group by hydroxyl by the addition of sodium nitrite solution (Bouveault, Bull. Soc. chim. 1892, [iii.] 9, 368; Sudborough, Chem. Soc. Trans. 1895, 67, 602).

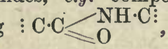
The hydrolysis of acetamide by hydrochloric acid has been studied by Acree and Nirdlinger (Amer. Chem. J. 1907, 38, 489). The amount of hydrolysis after given intervals of time was determined by introducing known volumes of the reaction mixture into a Lunge nitrometer containing sodium hypobromite solution and measuring the nitrogen evolved. Their results show that at 65° the reaction is practically unimolecular when dilute solutions are used, but that the values for K tend to increase with the time, probably owing to a slight catalytic effect of the ammonium chloride formed on hydrolysis. These chemists conclude that the hydrolysis of an acid amide by mineral acids is analogous to the hydrolysis of an ester or the inversion of cane sugar by acids, and that the first stage consists in the formation of a small amount of salt between the acid and the amide, the final stage consisting in the hydrolysis of the complex cation derived from the salt.

$$
\begin{aligned}
&CH_3{\cdot}CO{\cdot}NH_2+\overset{+}{H}+\overset{-}{Cl}+H_2O\\
&\qquad\rightleftharpoons CH_3{\cdot}\overset{+}{CO}{\cdot}NH_3+H_2O+\overset{-}{Cl}\\
&\qquad\qquad\rightarrow CH_3{\cdot}CO_2H+\overset{+}{NH_4}+\overset{-}{Cl}.
\end{aligned}
$$

Croker and Lowe (Chem. Soc. Trans. 1907, 91, 593, 952) have studied the hydrolysis of the amides of the simple aliphatic acids with hydrochloric acid, and also with sodium hydroxide solution, using the electrical conductivity method in order to determine the amount of amide hydrolysed. The order of the amides when hydrochloric acid is used is formamide, propionamide, acetamide, *iso*butyramide, capronamide, butyramide, and valeramide; but with sodium hydroxide the order is formamide, acetamide, propionamide, capronamide, butyramide, *iso*butyramide, and valeramide, in both cases formamide is the amide most readily hydrolysed, and in every case the hydrolysis with alkali proceeds more rapidly than that with hydrochloric acid under similar conditions.

E. Fischer (Ber. 1898, 31, 3266) has pointed out that uric acid and similar cyclic nitrogen derivatives are less readily hydrolysed by dilute alkalis than their alkylated derivates, *e.g.* 1:3:9-trimethyl uric acid. Similarly the amide and methyl ester of the methyl ether of salicylic acid are more readily hydrolysed than the corresponding derivatives of salicylic acid itself, and in all such cases the compounds most resistant to the hydrolysing agent are those which can form metallic salts with the alkalis.

These facts support Stieglitz's view that in hydrolysis by alkalis a salt of the alkali and amide (or ester) is formed and that the complex anion of this salt undergoes hydrolysis. When the amide or ester contains a replaceable hydrogen atom, salt formation of a different type occurs, and the characteristic complex anion is not formed.

Most compounds of the type of alkylated acid amides, *e.g.* compounds containing the grouping  $\vdots C{\cdot}C\genfrac{}{}{0pt}{}{\diagup NH{\cdot}C\vdots}{\diagdown\!\!\diagdown O}$, can be hydrolysed. Thus hippuric acid (benzoylglycine)

$$C_6H_5{\cdot}CO{\cdot}NH{\cdot}CH_2{\cdot}CO_2H$$

is hydrolysed to benzoic acid and glycine hydrochloride when boiled with concentrated hydrochloric acid. The hydrolysis of naturally occurring protein derivatives by means of acids or alkalis consists in the addition of water to such groups and the subsequent resolution into simpler cleavage products, ultimately into amino acids (*see* PROTEINS). (For hydrolysis of sulphonic acids, *cp.* Crafts, Bull. Soc. chim. 1907, [iv.] 1, 917.)

4. **Hydrolysis of di- and poly-saccharoses.** As a rule compounds of the ether type, *i.e.* compounds containing two alkyl or substituted alkyl groups attached to oxygen, are not readily hydrolysed when boiled with alkali or acid solutions.

All the carbohydrates of the di- or poly-saccharose type take up water when warmed with dilute mineral acid and are resolved into mono-saccharoses. The best known examples are:

sucrose (cane sugar)+water
=glucose (dextrose)+fructose (lævulose)
malt sugar+water=dextrose
lactose (milk sugar)+water
=dextrose+galactose.

All these reactions can be represented by the equation:

$$C_{12}H_{22}O_{11}+H_2O=C_6H_{12}O_6+C_6H_{12}O_6.$$

Starch is also hydrolysed by dilute mineral acids yielding as final product dextrose:

$$(C_6H_{10}O_5)n+n(H_2O)=n(C_6H_{12}O_6).$$

The hydrolysis of cane sugar (sucrose) by means of dilute mineral acid has been examined in detail; it is usually referred to as the inversion of sucrose, as the optical rotatory power changes from + to − during the reaction. The investigations of Wilhelmy (Pogg. Ann. 1850, 81, 413, 499) proved that in dilute solution the amount of sugar inverted is proportional to the amount present, or, in other words, the reaction is unimolecular. The method of determining the concentration of the sucrose at any given time is based on polarimetric readings. If the original rotation of the sucrose solution be $+x°$, and after complete inversion be $-y°$, then the total change is $x+y°$. If after an interval of time t the rotatory power of the solution is $+z°$, then the fraction of sucrose which has undergone inversion is $\frac{x-z}{x+y}$, and the velocity constant can be determined by substituting the values for t, C_o, and C_t in the equation

$$K=1/t \log_e C_o/C_t$$

where C_o represents the concentration of the sucrose at the beginning and can be expressed by $x+y$, C_t represents the concentration at time t, and is equal to $x-z$. The velocity of inversion is directly proportional to the concentration of the hydrochloric acid, and increases with rise in temperature. J. Meyer (Zeitsch. physikal. Chem. 1908, 62, 59) states that the reaction between sucrose and dilute mineral acid is not a simple unimolecular reaction, but is complicated by the mutarotation of the glucose and fructose.

Hudson (J. Amer. Chem. Soc. 1908, 30, 1165), on the other hand, claims that the reaction is typically unimolecular, and that the question of mutarotation does not arise, as both the α-glucose and α-fructose first formed undergo mutarotation immediately in the presence of the acid giving the usual rotatory values for invert sugar. Even in the earlier readings deviations from the unimolecular reaction are not encountered.

The hydrolysis of other di-saccharoses, and even of glucosides by dilute mineral acids, also follows Wilhelmy's Law, but the relative rates are very different; the following values have been obtained for *N*-sulphuric acid at 20°: lactose 1, maltose 1·27, sucrose 1240; or again α-methylglucoside 100, and β-methylglucoside 179. The hydrolysis of carbohydrates by means of dilute mineral acids is the basis of certain commercial methods for the manufacture of glucose. Large quantities of this carbohydrate are manufactured by boiling starch (*e.g.* potato or maize starch) with dilute sulphuric acid, removing the acid by precipitating as calcium sulphate and evaporating the clear solution under reduced pressure.

Neutral salt action. The investigations of Ostwald (J. pr. Chem. 1883, [ii.] 28, 460), Spohr (*ibid.* 1886, [ii.] 33, 265), and Arrhenius (Zeitsch. physikal. Chem. 1889, 4, 234; 1899, 31, 207) prove that the addition of a substance which is largely ionised in aqueous solution accelerates the hydrolysis of esters or of carbohydrates by aqueous solutions of strong acids. This has been proved by the addition of metallic chlorides to mixtures in which hydrogen chloride is the catalyst, the addition of bromides to hydrogen bromide, and of nitrates to nitric acid. The majority of chlorides have much the same effect if readily ionised, whereas a salt such as mercuric chloride, which is only partially ionised, has a much feebler action. Non-electrolytes, such as methyl and ethyl alcohols have but little effect on the hydrolytic activity of hydrogen ions. The neutral salt action has been shown to be independent of the concentration of the compound hydrolysed, and is stated to be proportionately greater the more dilute the acid solution, but Lunden (Med. Nobel Institut. 1910, 2) disputes this statement.

Caldwell (Proc. Roy. Soc. 1906, A, 78, 272), working with weight normal solutions, shows that the presence of metallic chlorides increases the catalytic activity of hydrogen chloride on the inversion of cane sugar, and that calcium chloride has the most pronounced effect. Similar effects on the activity of nitric acid are produced by nitrates (Whymper, *ibid.* 1907, A, 79, 576). Salts also tend to increase the activity of hydrogen chloride when used as a catalyst in the hydrolysis of methyl acetate (Armstrong and Watson, *ibid.* 1907, A, 79, 579), but their effect is not so marked as in the case of the inversion of sucrose (*cp.* Armstrong, *ibid.* 1908, A, 81, 90; Armstrong and Crothers, *ibid.* 102). According to Armstrong and Caldwell the salts act by removing part of the water in the form of definite hydrated compound, and in this manner increase the concentration of the reacting substance. Senter (Chem. Soc. Trans. 1907, 91, 462) is of opinion that this view cannot be correct, as the relative neutral salt action of different salts is not that of their ordinary degree of hydration (*cf.* chlorides and nitrates), and as in equivalent solutions the effect is practically independent of the nature of the salt (*cp.* Jones, Zeitsch. physikal. Chem. 1906, 55, 355, 429). A further argument used by Senter is that whereas rise of temperature affects hydration to an appreciable extent, alteration of temperature has but little effect on neutral salt action. It is concluded that probably the earlier suggestion of Arrhenius is correct, namely, that the ions of the neutral salt have some action on the hydrions or hydroxyl ions of the catalyst.

Reed (Amer. Chem. J. 1899, 21, 342) states that neutral salts retard the hydrolysis of acid amides by alkalis; and Arrhenius (Zeitsch. physikal. Chem. 1887, 1, 110) and Spohr (*ibid.* 1888, 2, 1194) claim that the same effect is produced by salts on the rate of hydrolysis of esters by alkalis. Senter, on the other hand (*l.c.* 473), shows that they accelerate the hydrolysis of sodium chloroacetate by sodium hydroxide. Since neutral salts have no effect on the decomposition of sodium chloroacetate by water, it is claimed that the effect of the salts cannot be due to their action on the reacting substance (the chloroacetate), and probably is due to their action on the hydroxyl ions (*cf.* Zeitsch. physikal. Chem. 1910, 70, 517).

5. Hydrolysis by enzymes. Many of the hydrolytic processes induced by aqueous solutions of acids or alkalis can also be brought about by certain complex organic substances found in animal and plant tissues. Such substances are termed unorganised ferments or *enzymes*; they act not merely as catalysts in processes of hydrolysis, but certain of them induce processes of oxidation—the oxidases—and others can effect complex decompositions as exemplified by the decomposition of glucose into ethyl alcohol and carbon dioxide under the influence of zymase. The enzymes are somewhat unstable, nitrogenous, organic compounds of colloidal nature, but not necessarily proteins; they act as catalysts, in the majority of cases as positive, but in a few as negative catalysts. The catalytic nature is shown by the fact that the rate of reaction is directly proportional to the concentration of the catalyst, but that the total decomposition is the same whatever the amount of catalyst used, provided sufficient time is allowed, and provided the enzyme does not undergo decomposition owing to secondary reactions. One of the most characteristic proofs of their catalytic nature is that due to Henri, who showed that when sugar was added after given intervals of time to a solution in which cane sugar was undergoing hydrolysis by invertase, the added sugar in each case began to be inverted by the enzyme at a rate irrespective of the amount already decomposed. Unlike most organic ferments the enzymes are sensitive to high temperatures; thus when heated to just below 100° their activity is completely destroyed; they are, however, resistant towards certain antiseptics which destroy protoplasm and kill fermenting organisms. A colloidal solution of an enzyme can often be prepared free from living organisms by treatment with a mild antiseptic, *e.g.* toluene, and filtration through a porous clay filter. Strong antiseptics such as formaldehyde are to be avoided, as they tend to destroy the enzyme also. A study of enzyme action is often complicated by the fact that it is impossible to isolate, in a state of purity, the particular enzyme required, and it may be accompanied by another enzyme capable of causing the destruction (autolysis) of the first, and thus bringing the reaction to an end long before all the substrate is decomposed.

The name given to a particular hydrolysing enzyme usually indicates the substance it is capable of hydrolysing and in all cases the termination *ase* is used. Thus maltase is the enzyme which hydrolyses maltose, amylase the enzyme which hydrolyses starch; but in some cases older names which were in use before this scheme was adopted, are still retained, *e.g.* sucrase, the enzyme which inverts sucrose (cane sugar), is still called invertase or even invertin, the common digestive enzymes are termed trypsin and pepsin. The substance which is decomposed by the enzyme is usually termed the substrate.

Although the processes of hydrolysis by acids and by enzymes are frequently compared it should be borne in mind that the rate at which a given substance is hydrolysed by the two different types of catalysts is frequently quite different, *e.g.* sucrose is hydrolysed by invertase much more readily than by a N-solution of hydrochloric acid; in fact, with a concentrated solution of invertase at 0° the inversion is practically instantaneous. It is not essential that the products obtained by the two processes should be identical. Thus in the case of the inversion of cane sugar by invertase the products are α-glucose and α-fructose, whereas when mineral acids are used the products are equilibrium mixtures of α- and β-glucose and α- and β-fructose, as the α-glucose and the α-fructose undergo immediate mutarotation in the presence of the mineral acid. Another example of a similar type is met with in the tri-saccharose, raffinose; when hydrolysed by acids this yields galactose, fructose, and glucose, the same sugar with raffinase yields melibiose and fructose, and with emulsin it yields galactose and sucrose, Similarly natural products of protein character yield comparatively simple amino acids when hydrolysed with acids or alkalis, whereas with enzymes more complex intermediate products are formed.

An important point of difference between hydrolysis by means of acids or alkalis and hydrolysis under the influence of enzymes is that any particular enzyme has a very restricted use as a catalyst or the action of enzymes is essentially selective. Thus lipase can hydrolyse esters and not carbohydrates; maltase can hydrolyse maltose but not sucrose. That a slight difference in the configuration of two isomeric compounds is sufficient to affect their reactivities with a particular enzyme is shown in the case of the two stereoisomeric α-methylglucosides. (For further details, *see* art. FERMENTATION.) Further examples are met with among the numerous polypeptides prepared within recent years (*cp.* Fischer and Bergell, Ber. 1903, 36, 2592; 1904, 37, 3103; Fischer and Abderhalden, Zeitsch. physiol. Chem, 1905, 46, 52; 1907, 51, 264).

The behaviour of some of the natural and artificial glucosides (*see* GLUCOSIDES) towards the two enzymes maltase and emulsin has been made use of in determining their configurations. Thus maltose, which is hydrolysed by maltase but not by emulsin, is regarded as an anhydride of α-glucose having a configuration similar to that of the α-methylglucoside; most of the natural glucosides, on the other hand, are hydrolysed by emulsin, but not by maltase, and therefore are probably analogous to β-methylglucoside. As a rule a natural glucoside is accompanied in the plant tissue by the enzyme which is able to hydrolyse it. The commonest glucosidoclastic enzymes, *i.e.* enzymes capable of hydrolysing glucosides are emulsin (β-glucase), myrosin, which hydrolyses sulphur glucosides, rhamnase, and tannase.

The products formed by the hydrolysis of naturally occurring compounds by enzymes are various; thus the natural glucosides can give rise to sugars, alcohols, phenols, aldehydes, acids, mustard oils, anthracene derivatives, indigo, &c.

It has been proved in many cases that a specific enzyme can act not merely as a hydrolysing, but also as a synthesising agent. The process of hydrolysis is thus, in certain cases, a balanced reaction, but the equilibrium is mainly in the direction of analysis and not synthesis. The synthesising activity of an enzyme was first demonstrated by Croft Hill (Chem. Soc. Trans. 1898, 73, 634; 1903, 83, 578) in the case of maltase. The greater portion of the maltose is hydrolysed by the enzyme to glucose, but a certain proportion of di-saccharose is always present.

Emulsin and lipase have also been shown to possess synthesising properties; in the latter case natural fats have been synthesised by the action of lipases on mixtures of glycerol and the higher fatty acids in the absence of a large excess of water. The lipatic enzymes present in certain seeds are made use of on a commercial scale for the preparation of fatty acids from natural fats (*cp.* Welter, Zeitsch. angew. Chem. 1911, 24, 385; Pottevin, Bull. Soc. chim. 1906, [iii.] 35, 693). For details of the synthetic functions of enzymes, *see* art. FERMENTATION.

In some of these balanced actions between carbohydrates or esters and enzymes it has been shown that the equilibrium mixture is the same, whether mineral acid or enzyme is used, *e.g.* Visser's experiments using invertase and emulsin; in other cases, however, the equilibrium mixture with the enzyme is quite different from that obtained when an acid is used, *e.g.* Dietz's experiments with lipase and *iso*-amyl *n*-butyrate (Zeitsch. physiol. Chem. 1907, 52, 279).

A considerable amount of work has been done on the velocities of different reactions in which enzymes play a part. Henri (Lois general de l'action des diastases, 1903) and others claim that the rate of inversion of sucrose by invertase, unlike that by mineral acids, does not agree with the unimolecular formula. The investigations of O'Sullivan and Tompson (Chem. Soc. Trans. 1890, 57, 834) and of Hudson (J. Amer. Chem. Soc. 1908, 30, 1160, 1564; 1909, 31, 655) prove conclusively that the unimolecular formula holds for any given solution, if the birotation of the α-glucose and a-fructose first formed is taken into consideration. The complications attending the mutarotation of the glucose and fructose can be avoided by adding a small amount of alkali, *e.g.* 10 c.c. of 0·4 N-sodium carbonate solution for each

100 c.c. of sugar solution, a short time before the polarimetric reading is taken. The alkali stops the hydrolysis and rapidly brings about equilibrium between the α- and β-glucoses and α- and β-fructoses, so that the normal rotatory power of invert sugar is given. Hudson's results clearly prove that the α-modifications of glucose and fructose are first formed, and that these are stable in the presence of enzyme, but rapidly undergo mutarotation in the presence of a little alkali. Hudson's experiments also show that a trace of hydrochloric acid, *e.g.* 0·0006 *N*, accelerates the action of the invertase to an appreciable extent.

The decomposition of the cane sugar is directly proportional to the concentration of the enyzme, and in very dilute solutions (under 5 p.c.) is also proportional to the concentration of the sugar, but with more concentrated solutions it is not even approximately proportional, but decreases and becomes practically zero in the strongest solutions. According to O'Sullivan and Tompson, and to Hudson, the diminution in the velocity in concentrated solutions is due principally to the viscosity of the medium; it may also be partly due to the formation of a definite compound between the sugar and enzyme. According to A. J. Brown (Chem. Soc. Trans. 1902, 81, 373) a given quantity of invertase decomposes a nearly constant weight of sugar in unit time (*i.e.* the decomposition is independent of the sugar concentration), provided the solution is moderately concentrated; but after an appreciable amount of sugar is decomposed the further inversion is directly proportional to the concentration of the sugar. This change of velocity from a linear to a logarithmic period is in harmony with the view that the sugar unites with the enzyme, and that it is the additive compound which is hydrolysed, and that the enzyme thus liberated immediately combines with a further amount of sugar. *Cp.* the hydrolysis of milk sugar by enzymes (E. F. Armstrong, Proc. Roy. Soc. 1904, 73, 500).

The reaction between salicin and water in the presence of emulsin is also a unimolecular reaction (Hudson and Paine, J. Amer. Chem. Soc. 1909, 31, 1242), provided alkali is added to bring about mutarotation of the β-glucose, which is the primary product

$$C_{13}H_{18}O_7+H_2O=C_6H_{12}O_6+C_7H_8O_2$$

Salicyl alcohol.

The reaction between lipase and *iso*amyl butyrate or between the same enzyme and *iso*amyl alcohol and *n*-butyric acid in the presence of a large excess of alcohol is a normal unimolecular reaction, although it proceeds in a heterogeneous medium. Dietz concludes that the reaction takes place in the solid phase, and that the diffusion of the ester or acid into the colloidal enzyme takes place so rapidly when compared with the velocity of reaction that the rates of diffusion do not affect the determination of the velocity of the reaction.

The hydrolysis of ethyl butyrate by lipase (Pierce, J. Amer. Chem. Soc. 1910, 32, 1517) points to the formation of an additive compound of the ester and enzyme. In many other cases the velocity relationships are not so simple. In some of these the reaction is retarded after a certain time owing to the product or products formed combining with the enzyme, or to negative autocatalysis, or to the gradual destruction of the enzyme.

In the reaction between pepsin and albumen the amount of albumen transformed in given time by different amounts of pepsin is proportional to the square root of the pepsin concentrations. The same relationship holds good with regard to trypsin and albumen, and is due to the fact that the velocity is inversely proportional to the amount of substance transformed, and this points to the formation of a definite compound between the enzyme and one of the products.

Most decompositions by enzymes are characterised by a high temperature coefficient when compared with catalytic reactions in which acid or alkali is used. In the latter case the coefficient is about 2–3 for a rise of 10°; with emulsin, however, the coefficient is 7·14 for a rise from 60° to 70°, with trypsin 5·3 for a rise from 20° to 30°; but like most colloidal catalysts enzymes exhibit an optimum temperature, at which the activity is greatest, and then falls again with further rise of temperature. This may be due to the coagulating effects which a moderately high temperature usually has on the majority of colloids.

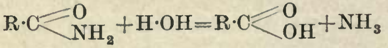
In certain cases it has been found possible to obtain by dialysis from a given enzyme two portions, a dialysate and a residue; neither portion alone is active, but the hydrolytic activity is restored when the dialysate is added to the dialysed residue. This residue is decomposed when boiled with water, and is the enzyme proper, whereas the dialysate is not decomposed when boiled and contains the co-enzyme (*see* art. FERMENTATION). In the case of liver lipases it has been proved that both enzyme and co-enzyme are essential for the hydrolysis of esters, and it has also been proved that the co-enzyme is a metallic salt of taurocholic acid. In living tissues a number of complex substances are present which are capable of interfering with the specific action of an enzyme. These are termed anti-enzymes; some are normally present in tissues, others appear to be formed when an enzyme is injected into the tissue.

A view generally held with regard to the mechanism of enzyme reaction is that compounds perhaps of the type of 'absorption compounds' (Bayliss) are formed between the enzyme and substrate, and that the absorbed material then reacts with water (*see* art. FERMENTATION). The fact that a specific enzyme can hydrolyse only certain particular substrates is in harmony with this view, as it is known that chemical constitution plays an important part in absorption phenomena (Zung, Arch. inter. Physiol. 1907, 5, 245; Hedin, Bio-Chem. J. 1907, 2, 112; Acree, J. Amer. Chem. Soc. 1908, 30; 1755; *cp.* also Freundlich, Zeitsch. physikal. Chem. 1907, 57, 385).

6. **Alcoholysis.** Reactions in which alcohols play much the same part as water in hydrolysis are usually grouped together under the name alcoholysis. The reaction with methyl alcohol is termed '*methanolysis*,' and that with ethyl '*ethanolysis*.'

The ethanolysis of an acid amide in the

presence of a mineral acid is analogous to the hydrolysis of the amide by dilute mineral acids as shown by the two equations :



$$R\cdot C\Big<\begin{smallmatrix}O\\ NH_2\end{smallmatrix}+H\cdot OH=R\cdot C\Big<\begin{smallmatrix}O\\ OH\end{smallmatrix}+NH_3$$

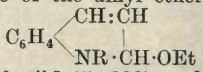
$$R\cdot C\Big<\begin{smallmatrix}O\\ NH_2\end{smallmatrix}+H\cdot OEt=R\cdot C\Big<\begin{smallmatrix}O\\ OEt\end{smallmatrix}+NH_3.$$

The latter reaction has been studied in detail by Reed (Amer. Chem. J. 1909, 41, 483). The reaction is bimolecular as the catalyst is gradually neutralised by the ammonia formed in the reaction, and proceeds at an easily measurable rate at 50° in the case of benzamide. A comparison of the values of K for *p*- and *m*-nitrobenzamide shows that this is 1·16, a value practically identical with the ratio for the hydrolysis of the two amides. The ratio of the constants for benzamide and *m*-nitrobenzamide varies considerably with the concentration of the hydrogen chloride. The presence of small amounts of water on the rate of alcoholysis is also marked, just as in the case of the esterification of an acid, and similarly ortho-substituents appear to have inhibiting effects. The general conclusion drawn is that the mechanism of alcoholysis is analogous to that of hydrolysis, and consists in the formation of salts between the amide and the mineral acid and the reaction of the complex cation with the alcohol.

Another common type of alcoholysis met with is the conversion of an ester of a given acid into another ester of the same acid by means of an alcohol, *e.g.* :

$$R\cdot CO\cdot OEt+MeOH \rightleftarrows R\cdot CO\cdot OMe+EtOH.$$

This change does not take place readily except in the presence of a catalyst, the most efficient being sodium alkyl oxide (Purdie, Chem. Soc. Trans. 1885, 47, 862 ; 1887, 51, 627 ; 1888, 53, 391 ; Claisen, Ber. 1887, 20, 646), hydrogen chloride (Patterson and Dickinson, Chem. Soc. Trans. 1901, 79, 280), sodium hydroxide (Henriques, Zeitsch. angew. Chem. 1898, 338 ; Pfannl, Monatsh. 1910, 31, 301 ; Kommenos, *ibid.* 1910, 31, 111, 687 ; 1911, 32, 77 ; Kremann, *ibid.* 1905, 26, 783 ; 1908, 29, 23) or ammonia (Leuchs and Theodorescu, Ber. 1910, 43, 1239). As a rule only a small amount of the catalyst need be used, but with the esters of aromatic acids saturation with hydrogen chloride is necessary. The reaction appears to be reversible, as it is possible to transform an ethyl into a methyl and conversely a methyl into an ethyl ester. The reaction is not limited to methyl and ethyl esters, but can be applied to more complex esters, such as benzyl and phenyl, and also to glyceryl esters (*cp.* Haller, Compt. rend. 1906, 143, 657 ; 1908, 146, 259 ; Fanto and Stritar, Monatsh. 1908, 29, 299), and is a most convenient laboratory method for the conversion of a given ester into another ester derived from the same acid. The esters of the great majority of aliphatic and aromatic acids react in this manner, but Sudborough and Edwards have shown that when the esters are derived from diortho-substituted benzoic acids the transformation cannot be affected by using either sodium alkyl oxide or saturating with hydrogen chloride and boiling for some time. Even when several substituents are present transformation occurs, provided the ortho- positions are free. This indicates that the transformation of esters under the influence of hydrogen chloride is analogous to the esterification of an acid by the same catalyst (*see* ESTERIFICATION).

Similar transformations can be brought about in the case of the alkyl ethers of carbonium bases, *e.g.*  $C_6H_4\Big<\begin{smallmatrix}CH:CH\\ \vert\\ NR\cdot CH\cdot OEt\end{smallmatrix}$ (Decker, J. pr. Chem. 1890, [ii.] 45, 182), and of the oxygen ethers of substituted thiocarbamides, *e.g.*

$$OEt\cdot CH_2\cdot NH\cdot CS\cdot NHPh \rightarrow OMe\cdot CH_2\cdot NH\cdot CS\cdot NHPh$$

(Johnson and Guest, J. Amer. Chem. Soc. 1910, 32, 1279). Comp. also Kuntze (Arch. Pharm. 1908, 246, 110). An interesting case of alcoholysis observed by Willstätter and Stoll (Annalen, 1910, 378, 18) is the conversion of amorphous chlorophyll into crystalline chlorophyll by ethyl alcohol in the presence of an enzyme 'chlorophyllase,' which accompanies chlorophyll in plant tissues. The reaction consists in the replacement of the complex phytyl group by the simpler ethyl group

$$CO_2H\cdot C_{31}H_{29}N_4Mg(CO_2Me)(CO_2C_{20}H_{39})+EtOH$$
$$=C_{20}H_{39}OH+CO_2H\cdot C_{31}H_{29}N_4Mg(CO_2Me)(CO_2Et).$$

J. J. S.

HYDROMAGNESITE *v.* MAGNESIUM.

HYDROMETER *v.* SPECIFIC GRAVITY.

HYDROPYRIN *v.* SYNTHETIC DRUGS.

HYDROQUININE *v.* VEGETO-ALKALOIDS.

HYDROQUINONE, HYDROTOLUQUINONE *v.* PHENOL AND ITS HOMOLOGUES.

HYDROQUINONE CARBOXYLIC ACID *v.* PROTOCATECHUIC ACID.

HYDROSOLS *v.* COLLOIDS.

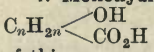
HYDROSULPHITES *v.* SULPHUR.

HYDROXY ACIDS. *Oxy acids.* The organic hydroxy acids are derived from the corresponding non-hydroxylated acids by the replacement of one or more hydrogen atoms in the hydrocarbon radicle of the acid by the same number of hydroxyl groups. According as the hydroxyl group is introduced into a fatty radicle or into a benzenoid radicle, the resulting acid is an alcohol-acid or a phenol-acid.

HYDROXY ACIDS OF THE ALIPHATIC SERIES.

There are several groups of hydroxy acids of the aliphatic series and these will be discussed *seriatim.*

I. Monohydroxymonocarboxylic acids

 $C_nH_{2n}\Big<\begin{smallmatrix}OH\\ CO_2H\end{smallmatrix}$ The most important members of this group are glycollic, lactic, hydracrylic, hydroxybutyric, and hydroxystearic acids (*q.v.*). They occur naturally, *e.g.* glycollic acid in unripe grapes and in the leaves of *Ampelopsis* (*Vitis*) *hederacea* (D. C.), lactic acid in the juice of the muscles, in sour milk, in pickles and in the gastric juice.

General methods of preparation.

(i) By the careful oxidation of diprimary, primary secondary, and primary tertiary glycols with dilute nitric acid or with platinum black and air, *e.g.* lactic acid from glycol.

(ii) By the reduction of aldehyde acids, keto-acids, and dicarboxylic acids with sodium amalgam or with zinc and hydrochloric or sulphuric acids, *e.g.* lactic acid from pyroracemic acid and glycollic acid from oxalic acid.

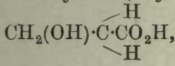
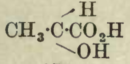
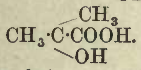
(iii) By boiling monohalogen fatty acid

with silver oxide, alkali, or with water or by distilling them, *e.g.* glycollic acid from monochloroacetic acid; hydracrylic acid from β-chloropropionic acid; γ-butyrolactone from γ-chlorobutyric acid.

(iv) By the action of nitrous acid on amino acids of the fatty series, *e.g.* glycollic acid from glycine.

(v) By the action of hydrogen cyanide followed by hydrochloric acid on aldehydes, ketones, and glycolchlorhydrins, *e.g.* lactic acid from acetaldehyde; hydracrylic acid from glycolchlorhydrin.

(vi) By treating unsaturated acids with hydrobromic acid, or with dilute sulphuric acid or by distilling them, *e.g.* γ-valerolactone from allylacetic acid.

Properties.—These acids may be sub-divided into three groups, primary, secondary, and tertiary acids, *e.g.* hydracrylic acid,  $CH_2(OH)\cdot\overset{H}{\underset{H}{C}}\cdot CO_2H$, lactic acid,  $CH_3\cdot\overset{H}{\underset{OH}{C}}\cdot CO_2H$ and α-hydroxy*iso*butyric acid,  $CH_3\cdot\overset{CH_3}{\underset{OH}{C}}\cdot COOH$. They also exhibit differences in their properties depending on the position of the hydroxyl group in the molecule, *i.e.* whether they are α-, β- or γ-hydroxy-acids. They are more soluble in water, but less soluble in ether than the corresponding fatty acids. They are also less volatile and, as a rule, cannot be distilled unchanged.

General reactions.

(i) Like the fatty acids they yield through change in the carboxyl group normal salts, esters, amides, and nitriles.

(ii) Like the alcohols, the hydrogen of the hydroxyl group may be replaced by alkali metals or by alkyl groups; also by the action of acyl chlorides or of a mixture of concentrated nitric and sulphuric acids, acid radicles or the nitro group may be substituted for it.

(iii) Phosphorus pentachloride replaces the two hydroxyl groups by chlorine, *e.g.* glycollic acid yields chloracetylchloride.

(iv) Hydriodic acid reduces the hydroxy acids to the corresponding fatty acids, *e.g.* propionic acid from lactic acid.

In the above reactions the hydroxy acids behave similarly, but on oxidation or by the application of heat, these acids show great differences.

(v) On oxidation these acids yield different products, according as whether they are primary, secondary, or tertiary acids.

(*a*) Primary acids yield aldehyde acids and dibasic acids, *e.g.* glycollic acid yields glyoxylic and oxalic acids.

(*b*) Secondary acids yield ketonic acids; the α-ketonic acids change to aldehyde and carbon dioxide, the β-ketonic acids to ketones and carbon dioxide, *e.g.* lactic acid yields pyruvic acid, which changes into acetaldehyde and carbon dioxide.

(*c*) Tertiary α-hydroxy acids yield ketones, *e.g.* α-hydroxy*iso*butyric acid yields acetone.

(vi) By the application of heat, differences in deportment are shown by these acids, according as they are, α-, β-, or γ-hydroxy acids.

(*a*) α-Hydroxy acids lose water and become cyclic double esters—the lactides, *e.g.* lactic acid becomes lactide, two molecules of the acid condensing with the loss of two molecules of water.

(*b*) β-Hydroxy acids lose water and become unsaturated acids, *e.g.* hydracrylic acid becomes acrylic acid.

(*c*) γ- and δ-Hydroxy acids lose water at the ordinary temperature and change more or less completely into simple cyclic esters—lactones.

II. **Aldehyde acids.** Formic acid is the simplest member of this group of acids, and also of the fatty acid series. The next member is glyoxylic acid, $CHO\cdot CO_2H$. Its claim to be considered here lies in the fact that all the salts are derived from the dihydroxy formula of glyoxylic acid $(OH)_2CH\cdot CO_2H$, and thus it behaves both as an aldehyde acid and as a dihydroxy acid. For details as to this group of acids *v.* Glyoxylic acid.

III. **Monohydroxydicarboxylic acids**

$$C_nH_{2n-1}(OH)(CO_2H)_2.$$

Various groups of monohydroxydicarboxylic acids are known, corresponding to the several groups of dibasic acids (*q.v.*). The most important acids of this type are tartronic, malic, α-glutanic, and paraconic acids. They occur in nature; thus malic acid in unripe gooseberries, and in rhubarb; α-hydroxyglutaric acid in molasses. The acids in which the hydroxyl group occupy the γ position with reference to the carboxyl group, when separated from their salts, readily part with water and become lactones, *e.g.* paraconic acid. The methods of preparation are very similar to those of the monobasic acids.

IV. **Dihydroxydicarboxylic acids.** The most important acid of this group is tartaric acid (*q.v.*). Mesoxalic acid, which is ketomalonic acid, exhibits tautomerism and behaves both as a keto-acid and as a dihydroxy acid.

V. **Hydroxytricarboxylic acids.** The most important acid of this group is citric acid (*q.v.*).

Hydroxy Acids of the Aromatic Series.

If the hydroxyl group is attached to the benzene nucleus of a carboxy acid derived from benzene or its homologues, the acid thus formed is a phenol acid. Examples of this class are the three isomeric hydroxy benzoic acids, which have the formula $C_6H_4(OH)COOH$. On the other hand, in the case of carboxy acids derived from homologues of benzene, a hydroxyl group, may be introduced into a fatty lateral chain, and in such a case the resulting acid is an alcohol acid; such an acid is *mandelic acid*

$$C_6H_5\cdot CH(OH)COOH.$$

I. **Monohydroxyaromatic acids.** The most important members of this group of acids are salicylic, *m*- and *p*-hydroxybenzoic and anisic acids (*q.v.*). They occur in nature; thus salicylic acid is found in the buds of *Spiræa Ulmaria* (Linn.) and as the methyl ester in oil of winter-green.

General methods of preparation.

(i) By the action of nitrous acid on the amino-acids, *e.g.* salicylic acid from anthranilic acid.

(ii) By fusing the sulphonic acids with alkalis, *e.g.* salicylic acid from *o*-toluenesulphonic acid.

(iii) By fusing the homologous phenols with alkalis, when the methyl group attached to the benzene nucleus will be oxidised to the carboxyl group, *e.g.* salicylic acid from *o*-cresol.

(iv) By fusing the phenol aldehydes with potash, *e.g.* salicylic acid from salicylaldehyde.

(v) By the action of carbon dioxide on the dry sodium salts of the phenols at high temperatures when the carbonic acid usually enters the ring in the position ortho to the hydroxyl group, *e.g.* salicylic acid from sodium phenate.

(vi) By boiling the phenols with carbon tetrachloride and caustic potash, the carboxyl group entering the ring generally in a position para to the hydroxyl groups: *o*-acids are formed in small amounts, *e.g.* *p*-hydroxybenzoic acid from phenol, carbon tetrachloride and caustic potash.

Properties.—When these acids react with carbonates only the hydrogen of the carboxyl group is replaced by metal; but with alkaline hydroxides they behave like feeble dibasic acids, and the hydrogen of the phenolic hydroxyl is also replaced: *e.g.* in *disodium salicylate* $C_6H_4(ONa)COONa$. Carbon dioxide will convert the latter into the former. The *o*-acids, unlike the *m*- and *p*-acids, volatilise in aqueous vapour, are coloured violet by ferric chloride and dissolve in chloroform. The *m*-acids are coloured red brown when heated with concentrated sulphuric acid and are converted into hydroxyanthraquinones: they are usually more stable than the *o*- and *p*-acids. Boiling hydrochloric acid decomposes the *p*-acids into carbon dioxide and phenols. All the hydroxy acids decompose into phenol and carbon dioxide when distilled with lime.

II. **Dihydroxyaromatic acids.** The most important member of this class is protocatechuic acid (*q.v.*). These acids may be prepared by the same methods as were used for the monohydroxy acids (*v. supra*). The carboxyl group is more readily introduced into the dihydroxybenzenes than into the monohydroxybenzenes. This may be effected by heating the compounds with a solution of ammonium or sodium carbonate at 100°–130°. The dihydroxybenzoic acids break down when heated, into carbon dioxide and dihydroxybenzenes.

III. **Trihydroxyaromatic acids.** The most important members of this group are gallic and tannic acids (*q.v.*).

HYDROXYANTHRAQUINONE *v.* ALIZARIN AND ALLIED COLOURING MATTERS.

HYDROXYBENZALDEHYDE *v.* SALICYLALDEHYDE.

HYDROXYBENZENES *v.* PHENOL AND ITS HOMOLOGUES.

HYDROXYBUTYRIC ACIDS $C_4H_8O_3$.

α-Hydroxybutyric acid

$$CH_3\cdot CH_2\cdot CH(OH)CO_2H.$$

Prepared by treating α-chloro- or α-bromo- butyric acid with baryta (Markownikow, Annalen, 153, 242) or with moist silver oxide (Naumann, Annalen, 119, 115; Friedel and Machuca, *ibid.* 120, 279); by treating the cyanhydrin of propionaldehyde with hydrochloric acid and saponifying the nitrile thus produced (Prbzibyek, J. Russ. Chem. Soc. 8, 335); by heating ethyltartronic acid at 180° (Guthzeit, Annalen, 209, 234); by boiling 100 grams of α-bromobutyric acid, 500 c.c. of water and 1 molecular proportion of potassium carbonate for 5 to 6 hours (Bischoff and Walden, *ibid.* 279, 104). Forms white crystals, m.p. 43°–44°, sublimes at 60°–70° and boils at 225°. Chromic acid oxidises it to acetic and propionic acids, whilst electrolysis of a concentrated solution of the sodium salt results in the production of propionaldehyde and formic acid (Miller and Hofer, Ber. 1894, 468). It has been resolved into its optically active components by fractional crystallisation of the brucine salts (Guye and Jordan, Compt. rend. 120, 562, 632, 1274).

β-Hydroxybutyric acid

$$CH_3\cdot CH(OH)CH_2\cdot CO_2H.$$

Prepared by the reduction of aceto-acetic ester with sodium amalgam (Wislicenus, Annalen, 149, 205); by the action of potassium cyanide on α-propylenechlorhydrin and saponification of the nitrile thus formed (Markownikow, *ibid.* 153, 237). It forms a thick syrup, which is volatile in steam and on heating decomposes into water and crotonic acid. It has been resolved into its optically active components by fractional crystallisation of the quinine salts (McKenzie, Chem. Soc. Trans. 1902, 1402). *l*-β-Hydroxybutyric acid occurs in the urine in considerable quantities in cases of *diabetes mellitus* (Laud, Chem. Zentr. 1899, ii. 63; Bergell, Zeitsch. physiol. Chem. 1901, 33, 310; Minkowski, Chem. Soc. Abstr. 1885, 413; Kulz, Zeitsch. Biol. 20, 165). (For estimation in urine *v.* Schaffer, J. Biol. Chem. 1908, 5, 211; Black, *ibid.* 207.) The liver cells contain an enzyme, *β-hydroxybutyrase*, which converts β-hydroxybutyric acid into aceto-acetic acid (Wakeman and Dakin, *ibid.* 1909, 6, 373).

γ-Hydroxybutyric acid

$$CH_2(OH)CH_2\cdot CH_2\cdot CO_2H$$

readily loses water even at the ordinary temperature passing into the cyclic ester, butyrolactone $\overline{CH_2\cdot CH_2\cdot CH_2\cdot CO\cdot O}$. Butyrolactone was discovered by Saytzeff in 1873, but he regarded it as the dialdehyde of succinic acid. He prepared it by the reduction of succinyl chloride in acetic acid with sodium amalgam (Annalen, 171, 261). It may also be prepared by the distillation of γ-chlorobutyric acid at 180°–200° (Henry, Bull. Soc. chim. [ii.] 45, 341); by the interaction of ethylene chlorhydrin and acetoacetic ester and decomposing the resulting product with baryta (Chanlaroff, Annalen, 226, 325); by treating a solution of succinic anhydride in ether with sodium amalgam and gradually adding hydrochloric acid to the product (Fichter and Herbrand, Ber. 1896, 1192); by heating γ-phenoxybutyric acid with fuming hydrobromic acid (Bentley, Haworth and Perkin, Chem. Soc. Trans. 1896, 168); by the reduction of aldehydopropionic acid with sodium amalgam (Perkin and Sprankling, *ibid.* 1899, 17). It is a colourless oil, b.p. 206° (Fittig and Roeder, Annalen, 227, 22); sp.gr. 1·1286 15°/0°; it is volatile in steam. Chromic acid oxidises it to succinic acid; heating with hydriodic acid converts it into iodobutyric acid (Saytzeff, J. pr. Chem. 25, [ii.] 70). It reacts with magnesium methyl iodide, forming δ-methylpentane-αδ-diol (Henry, Compt. rend. 1906, 143, 1221).

α-Hydroxyisobutyric acid (*Butyl-lactinic acid, Acetonic acid, Dimethyl oxalic acid*)

$$(CH_3)_2C(OH)\cdot CO_2H.$$

Prepared by treating acetone with prussic and hydrochloric acids (Staedeler, Annalen, 111, 320; Markownikow, *ibid.* 146, 339); by treating dimethyloxalic ester with zinc and methyl iodide (Frankland and Duppa, *ibid.* 135, 25); by heating acetonechloroform to 180° with water or by boiling with caustic soda (Willgerodt and Schiff, J. pr. Chem. 41, [ii.] 519; Ber. 1882, 2307); by heating α-bromo- or α-chloro*iso*butyric acid with water to 180°, with baryta, or with caustic soda (Markownikow, Annalen, 153, 228; Fittig, *ibid.* 200, 70; Ostropjatow, J. Russ. Phys. Chem. Soc. 28, 51); by treating α-amino-*iso*butyric acid with sodium nitrite (Tiemann and Friedländer, Ber. 1881, 1973); by treating *iso*butyric acid with potassium permanganate (Meyer, Annalen, 219, 240). It forms hygroscopic prisms which sublime at about 50°, and when freshly sublimed melt at 79°; b.p. 212°; volatile in steam. Oxidation with chromic acid converts it into acetic acid, acetone, and carbon dioxide; fusion with caustic soda yields acetone; heating with phosphorus pentoxide yields acetaldehyde, acetone, acetic acid, and other products (Bischoff and Walden, Annalen, 279, 111). *Acetone chloroform* (*q.v.*)

$$(CH_3)_2C(OH)CCl_3$$

is an interesting derivative of this acid.

HYDROXYLAMINE NH_2OH. Discovered by Lossen (Annalen, Suppl. 1868, 6, 220) in 1865, but until 1891 only known in the form of salts or in aqueous solution. Obtained by the reduction of nitric acid with metals under suitable conditions (Divers, Chem. Soc. Trans. 1883, 443 *et seq.*; 1885, 597 *et seq.*); by the reduction of nitrates, nitro bodies, &c., with finely divided metals (Wohl, Eng. Pat. 11216; J. Soc. Chem. Ind. 1895, 595); by the electrolytic reduction of nitric acid, nitrous acid, or their salts or other derivatives in the presence of a second acid electrolyte at a low temperature (Boehringer and Söhne, D. R. PP. 133457, 137697; Fr. Pat. 319187; J. Soc. Chem. Ind. 1902, 1458; Compagnie Parisienne de Couleurs d'Aniline, Fr. Pat. 322943; J. Soc. Chem. Ind. 1903, 425; Tafel, Zeitsch. anorg. Chem. 1902, 31, 289); by the reduction of nitrites with sodium amalgam (Divers, Chem. Soc. Trans. 1899, 89) or with sulphites (Raschig, Eng. Pat. 3028; J. Soc. Chem. Ind. 1888, 210; Eichkoff, Arch. Pharm. 27, [iii.] 713; Lidoff, J. Russ. Chem. Soc. 1884, 751; Divers and Haga, Chem. Soc. Trans. 1887, 661; 1896, 1665). It is best prepared by taking a concentrated aqueous solution of commercial sodium nitrite (2 mols.) and sodium carbonate (1 mol.) and passing in sulphur dioxide at −2° to −3° with constant stirring until it is just acid. The solution is warmed gently with a few drops of sulphuric acid and then kept at 90°–95° for two days. It is then neutralised with sodium carbonate, evaporated until the solution weighs about 10½–11 times as much as the sodium nitrite originally taken, when on cooling nearly all the sodium sulphate crystallises out. The hydroxylamine sulphate is obtained from the mother liquors and purified by recrystallisation (Divers and Haga, *l.c.*). Jouve (Compt. rend. 128, 434) has prepared hydroxylamine synthetically by the direct union of hydrogen and nitric acid in the presence of spongy platinum at 115°–120°. The anhydrous compound may be obtained by dissolving hydroxylamine hydrochloride in absolute methyl alcohol, adding a solution of sodium methoxide in the same solvent, separating the sodium chloride so formed and distilling off the greater part of the methyl alcohol under 100 mm. pressure. The residue is distilled in small portions under 20 mm. pressure with the addition of a little vaseline to prevent frothing. When the solid hydroxylamine begins to come over, the receiver is changed and cooled to 0°, care being taken that the hydroxylamine vapour does not come in contact with air at 60°–70°, as then explosions occur (Lobry de Bruyn, Rec. trav. chim. 10, 100; 11, 18; *v.* also Brühl, Ber. 1894, 1347). Crismer (Bull. Soc. chim. 6, [iii.] 793) obtains it by heating zinc dihydroxylamine chloride, and Uhlenhuth (Annalen, 311, 117) by the distillation of the phosphate under reduced pressure; the solid thus obtained may be purified by crystallisation from absolute alcohol at −18° (Ebler and Schott, J. pr. Chem. 1908, 78, [ii.] 289).

Hydroxylamine forms white inodorous scales or hard needles, sp.gr. 1·3 (*circa*), m.p. 33·05°, b.p. 58° under 22 mm. Heated to 100° it decomposes, ammonia, nitrous and hyponitrous acids being the first products of decomposition and these then interact with the formation of nitrogen and nitrous oxide. Readily soluble in water, and to a less extent in ethyl and methyl alcohols, and in boiling ether (De Bruyn, Ber. 1894, 967). When pure it is stable below 15°, but alkali decomposes it. The aqueous solution is colourless and odourless, has a strong alkaline reaction, and gives precipitates, insoluble in excess, with salts of Zn, Ni, Fe, Al, Cr, but not with those of the alkaline earths. In its general reactions resembles a solution of ammonia, although it is less basic than that substance. It acts as a strong reducing agent, *e.g.* with $CuSO_4$ solution it gives a red precipitate of Cu_2O; it reduces $HgCl_2$ to $HgCl$, and precipitates the metals from solutions of $AgNO_3$, $AuCl_3$, and $PtCl_4$. It can also act as an oxidising agent being itself reduced to ammonia (Haber, Ber. 1896, 2444; Biltz, *ibid.* 1896, 2080; Dunstan and Dymond, Chem. Soc. Trans. 1887, 646). Thus in alkaline solution it converts ferrous hydroxide into ferric hydroxide, whilst in acid solution it reduces ferric chloride to ferrous chloride. Oxidation converts hydroxylamine into nitrous oxide and nitric oxide (Arndt, Ber. 1900, 33) and caustic soda decomposes it into nitrogen, nitrous oxide, nitrous acid and water (Kolotoff, J. Russ. Phys. Chem. Soc. 25, 295).

The salts of hydroxylamine are readily soluble in water and alcohol; they crystallise well and are anhydrous.

By treating hydroxylamine sulphate in the cold with sodium nitrite and then adding silver nitrate, a yellow precipitate of silver hyponitrite is obtained (Wislicenus, Ber. 1893, 771; Tanatar, J. Russ. Phys. Chem. Soc. 25, 342; Ber. 1894, 187). By passing sulphur dioxide through a solution of the hydrochloride or sulphate, ammonium sulphate is produced (Tanatar, Ber. 1899, 241, 1016). Elber and Schott (J. pr. Chem. 1908, ii. 78, 289) have prepared metallic salts of the type $R(ONH_2)_2$, where R is any divalent metal: alkyl hydroxylamines have been prepared by the action of alkyl halides on hydroxylamine (Dunstan and Goulding, Chem. Soc. Trans.

1899, 792; *v.* also *ibid.* 1896, 839; De Bruyn, Rec. trav. chim. 15, 185).

Detection and estimation.—Hydroxylamine may be detected by its action in reducing Fehling's solution with the formation of cuprous oxide (Adams and Overman, J. Amer. Chem. Soc. 31, 637); by adding sodium nitroprusside to a neutral solution and then a little caustic soda, when a magenta red colouration is produced (Angeli, Gazz. chim. ital. 23, ii. 102); or by treating it with sodium acetate and benzoyl chloride with the formation of benzhydroxamic acid which gives a violet red colouration with ferric chloride (Bamberger, Ber. 1899, 1805). It may be estimated by titration in alkaline solution with mercury acetamide, which is reduced to metallic mercury (Forster, Chem. Soc. Trans. 1898, 785); by oxidation with vanadic sulphate, measuring the nitrogen evolved and titrating the vanadous sulphate with potassium permanganate (Hofmann and Küspert, Ber. 1896, 64); by adding excess of standard titanium trichloride and titrating back the excess with potassium permanganate (Stähler, *ibid.* 1904, 4732; *v.* also *ibid.* 1909, 2695); by titrating the solution with potassium permanganate after the addition of sodium oxalate (Simon, Compt. rend. 135, 1339); by boiling with excess of N/10 silver nitrate solution, ammonia, and caustic soda and estimating the silver nitrate unacted upon (Denigés, Ann. Chim. Phys. 7, [vi.] 427). Jones and Carpenter (Chem. Soc. Trans. 1903, 1394) add the solution containing the hydroxylamine to a hot solution of potassium copper carbonate or tartrate with stirring. The solution is boiled, filtered, the precipitate washed with hot water and dissolved in ferrous sulphate in an atmosphere of carbon dioxide. The ferrous salt is titrated back with potassium permanganate.

$$4 \text{ mols. } K_2Mn_2O_8 = 10 \text{ mols. } NH_2OH.$$

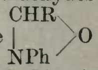
Schaeffer (Bull. Mulhouse, 1883) has applied the reducing properties of hydroxylamine in order to discharge manganese brown. The hydrochloride NH_2OH,HCl must be used. On printing this upon a manganese ground the latter is instantly reduced to manganese chloride. A very dark indigo, blue-dyed on manganese, is lowered to a lighter and brighter blue by the elimination of the MnO_2. In like manner nankin, chamois, and similar colours can be discharged white (J. Soc. Chem. Ind. 3, 166).

Hydroxylamine and its salts have been used as developers in photography, and for recovering silver from fixing bath solutions and waste liquors (Lainer, J. Soc. Chem. Ind. 1890, 890). It is a powerful antiseptic (Marpmann, Pharm. Centr. N.F. 10, 245) and has been used as a substitute for chrysarobin and pyrogallic acid, as it does not discolour the skin or bandages and has a strong reducing action (Schwarz, Pharm. Zeit. 33, 659).

Ethylhydroxylamines *v.* ETHYL.

β-Phenylhydroxylamine C_6H_5NHOH. Prepared by the reduction of nitrobenzene (1) in water with zinc (Bamberger, Ber. 1894, 27, 1348, 1548; Wohl, *ibid.* 1432); (2) in alcohol with zinc (Wohl, *ibid.* 1434; D. R. P. 84138; Frdl. iv. 44), or the zinc-copper couple (Wohl, D. R. P. 84891; *ibid.* 46) in the presence of anhydrous calcium chloride; (3) in aqueous alcohol with zinc amalgam in the presence of aluminium sulphate (Bamberger and Knecht, Ber. 1896, 29, 864); (4) in ether with zinc in the presence of anhydrous calcium chloride (Goldschmidt, *ibid.* 2307); (5) in aqueous ether with aluminium amalgam (Wislicenus, *ibid.* 494; J. pr. Chem. [ii.] 54, 57); (6) in ammonium chloride with zinc (Kalle & Co. D. R. P. 89978; Frdl. iv. 47); (7) electrolytically in acetic acid (Haber, Zeitsch. Elektrochem. 1898, 5, 77) or in alcoholic ammonia (Schmidt, Zeitsch. physikal. Chem. 32, 272); by the oxidation of aniline in ethereal solution with Caro's acid (Bamberger and Tschirner, Ber. 1899, 32, 343).

β-Phenylhydroxylamine forms colourless needles, m.p. 81°–82°; soluble in 10 parts of hot and 50 of cold water, readily soluble in alcohol, ether, carbon disulphide, and chloroform, sparingly so in petroleum. It dissolves in sulphuric acid with a deep blue colour. By heating at 100° azobenzene together with aniline, azoxybenzene, and other products are formed. Oxidation with potassium permanganate gives first nitrosobenzene, then nitrogen and azoxybenzene (Bamberger and Tschirner, Ber. 1899, 32, 342); in dilute neutral solution hydrogen peroxide yields azoxybenzene, in alkaline solution azoxybenzene and nitrobenzene (Bamberger, *ibid.* 1900, 33, 119). In the presence of hydroxylamine and air it is partly oxidised to azoxybenzene and partly reduced to aniline, phenylazoimide, and benzeneazohydroxyanilide also being formed (Bamberger, *ibid.* 1902, 35, 3893). It dissolves in sodium hydroxide forming a sodium salt which in the absence of air yields azoxybenzene, and in the presence of air azoxybenzene and nitrobenzene; alcoholic potash yields azobenzene (Bamberger and Brady, *ibid.* 1900, 33, 271). Mineral acids yield *p*-aminophenol and azoxybenzene; alcoholic sulphuric acid gives azoxybenzene, *o*- and *p*-phenetidine, *o*- and *p*-aminophenols, aniline and other compounds (Bamberger and Lagutt, *ibid.* 1898, 31, 1501). With aromatic aldehydes it yields phenylaldoximes of the type



$$\left.\begin{matrix} CHR \\ | \\ NPh \end{matrix}\right\rangle O$$

(Plancher and Piccinini, Atti. R. Acad. Lincei. 1905, [v.] 14, ii. 36). (For constitution, *v.* Brühl, Zeitsch. physikal. Chem. 1898, 26, 47.)

Nitrosophenylhydroxylamine $C_6H_5N(NO)OH$. Prepared by the action of sodium nitrite and dilute sulphuric acid on β-phenylhydroxylamine (Wohl, Ber. 1894, 27, 1435; Bamberger, *ibid.* 1553); or by the interaction of hydroxylamine and nitrobenzene in alcoholic solution in the presence of sodium ethoxide (Angeli, *ibid.* 1896, 29, 1885; Angelico, Atti. R. Accad. Lincei, [v.] 8, ii. 28).

It crystallises from petroleum in colourless needles, melting at 58°–59° and decomposing at 75°; sparingly soluble in water, readily so in most organic solvents. On heating it decomposes into nitrosobenzene and other substances (Bamberger, Ber. 1898, 31, 574, 1507). Alcoholic or ethereal solutions give a brownish-red colouration with a few drops of dilute ferric chloride (Bamberger and Ekecrantz, *ibid.* 1896, 29, 2412). Reduction with sodium amalgam yields phenylhydrazine; oxidation with potassium permanganate or sodium hypochlorite, nitrosobenzene. By heating with dilute mineral acids nitrosobenzene is formed, whilst nitrous acid yields benzenediazonium nitrite.

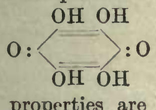
Cupferron, *Ammonium nitrosophenylhydroxylamine,* is prepared by dissolving β-phenylhydroxylamine in ether at 0°, passing in dry ammonia and adding excess of amyl nitrite, when a snow-white crystalline mass of ammonium nitrosophenylhydroxylamine is formed (Baudisch and King, J. Ind. Eng. Chem. 1911, 3, 629).

Cupferron is used in quantitative analysis for separating copper and iron from most of the metals. The iron and copper are precipitated in strongly acid solution with cupferron, the precipitate filtered, washed with water, and finally with ammonium hydroxide. The latter dissolves the copper, but not the ferric salt. The ferric salt is soluble in chloroform, ether, acetone, &c., and may be dissolved and separated from other salts, such as those of lead, silver, or tin, which may have been precipitated with it (Baudisch, Chem. Zeit. 1909, 33, 1298; Biltz and Hödtke, Zeitsch. anorg. Chem. 1910, 66, 426; Hanuš and Soukup, *ibid.* 68, 52; Fresenius, Zeitsch. anal. Chem. 1911, 50, 35). The use of cupferron as an analytical reagent is limited by virtue of its explosive properties.

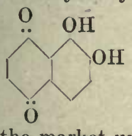
HYDROXYQUINOL *v.* PHENOL AND ITS HOMOLOGUES.

HYDROXYQUINOLINE *v.* QUINOLINE.

HYDROXYQUINONE COLOURING MATTERS. The hydroxyquinones form an important group of mordant colouring matters which are characterised by containing at least one hydroxyl group adjacent (ortho- or peri-) to an oxygen atom of a quinone, but usually two hydroxyl groups in the ortho- position with respect to one another. They possess the property of forming insoluble, coloured salts with certain metallic oxides, and therefore, when dyed on a fabric impregnated (mordanted) with such oxides, for example, the oxides of aluminium, chromium, and iron, lakes are formed which are extremely fast. The simplest compound possessing the above requirements is tetrahydroxy-*p*-benzoquinone

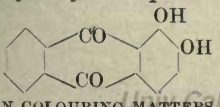


but its dyeing properties are not sufficiently intense for it to be of practical value. This desideratum is first reached in the naphthalene series in the case of dihydroxynaphthaquinone



which comes on the market under the name of Naphthazarin (*see* under NAPHTHALENE).

By far the most valuable and important hydroxyquinones are those belonging to the anthracene series, of which a large number are manufactured. The simplest and best known of these is dihydroxyanthraquinone or alizarin



(*See* ALIZARIN COLOURING MATTERS.) J. C. C.

HYDROXYSTEARIC ACIDS $C_{18}H_{36}O_3$.

α-Hydroxystearic acid

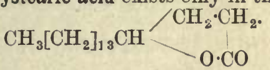
$CH_3[CH_2]_{15}CH(OH)CO_2H.$

Prepared by treating α-bromostearic acid with aqueous potash. Separates from a mixture of benzene and petroleum as a crystalline powder, m.p. 91°–92° (Hell and Sadomsky, Ber. 1891, 2391; Le Sueur, Chem. Soc. Trans. 1904, 827). By heating it to 270°, it yields margaric aldehyde $C_{16}H_{33}{\cdot}CHO$, a lactide $C_{36}H_{68}O_4$, formic acid, water and carbon dioxide.

β-Hydroxystearic acid

$CH_3[CH_2]_{14}CH(OH)CH_2{\cdot}CO_2H.$

Prepared by treating β-bromstearic acid with aqueous potash. Crystallises from chloroform in white plates, m.p. 89° (Ponzio, Atti. R. Accad. Sci. Torino, 1905, 40, 970).

γ-Hydroxystearic acid exists only in the form of a lactone  $CH_3[CH_2]_{13}CH\left<\begin{matrix}CH_2{\cdot}CH_2{\cdot}\\ O{\cdot}CO\end{matrix}\right.$ Obtained by treating the anhydride of γ-hydroxyoleic acid with potash (Geitel, J. pr. Chem. 37 [ii.] 85). Prepared by heating oleic acid with anhydrous zinc chloride. Oxidation with chromic acid in glacial acetic acid converts it into liquid monobasic and small quantities of dibasic acids, including succinic acid and γ-ketostearic acid $CH_3[CH_2]_{13}CO[CH_2]_2CO_2H$, m.p. 97° (Shukoff and Schestakoff, J. Russ. Phys. Chem. Soc. 1903, 35, 1).

ι-Hydroxystearic acid

$CH_3[CH_2]_7{\cdot}CH(OH)[CH_2]_8CO_2H.$

This acid was formerly described as *β-hydroxstearic acid* (A C. and M. Saytzew, J. Russ. Phys. Chem. Soc. 1886, 328; 17, 426; J. pr. Chem. 35, [ii.] 369, 384; Fremy, Annalen, 19, 296; 20, 50; 33, 10; Ann. Chim. Phys. 65, [ii.] 113; Sabanejew, J. Russ. Phys. Chem. Soc. 18, 41; Geitel, J. pr. Chem. 37 [ii.] 81; Leichti and Suida, Ber. 1883, 2458). Shukoff and Schestakoff (J. Russ. Phys. Chem. Soc. 1903, 35, 1) have shown that its constitution is that of ι-hydroxystearic acid. It is prepared from the sulpho or iodo derivative of oleic acid, or best by the action of sulphuric acid on oleic acid; m.p. 83°–85°. It may also be obtained from elaidic acid by the action of sulphuric acid and subsequent treatment with alcoholic potash (Tscherbakow and Saytzew, J. pr. Chem. 57, [ii.] 27). By heating to 100° it yields an anhydride; oxidation with chromic acid in glacial acetic acid converts it into sebacic, azelaic, and traces of suberic and liquid monobasic acids and ι-ketostearic acid $CH_3[CH_2]_7CO[CH_2]_7CO_2H$, m.p. 76°. Molinari and Barosi (Ber. 1908, 2794) have obtained an acid by the decomposition of the ozonide of oleic acid and consider it to be formed by the aldol condensation of monaldehyde with nonoic acid, and hence they consider it to ι-hydroxystearic acid; it melts at 41°, and hence is either impure or a hydroxystearic acid containing the hydroxyl group in some other position.

κ-Hydroxystearic acid

$CH_3[CH_2]_6CH(OH)[CH_2]_9CO_2H.$

This acid was formerly described as *α-hydroxystearic acid* (Saytzew, J. pr. Chem. 37, [ii.] 277, 284). Shukoff and Schestakoff (J. Russ. Phys. Chem. Soc. 1903, 35, 1) have shown that its constitution is that of κ-hydroxystearic acid; m.p. 84°–85°. Prepared by the action of sulphuric acid on *iso*oleic acid. Oxidation with chromic acid in glacial acetic acid yields sebacic acid, nonylene-$\alpha\iota$-dicarboxylic acid (m.p. 124°) and κ-ketostearic acid,

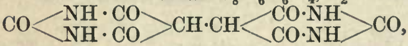
$$CH_3[CH_2]_6CO[CH_2]_9CO_2H,$$

m.p. 65°.

λ-Hydroxystearic acid (12-*Hydroxystearic acid*)

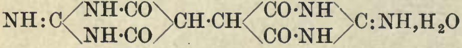
$$CH_3[CH_2]_5CH(OH)[CH_2]_{10}CO_2H.$$

Prepared from the methyl ester which is obtained by the reduction of the methyl ester of ricinoleic acid; m.p. 78° (Grün and Woldenberg, J. Amer. Chem. Soc. 1909, 31, 490). Kasansky (J. Russ. Phys. Chem. Soc. 1900, 32, 149) by acetylating ricinoleic acid, followed by bromination and reduction, obtained a hydroxystearic acid (m.p. 81°–82°) which is possibly identical with the above.

HYDURILIC ACID $C_8H_6O_6N_4,H_2O$ or $2H_2O$;  $CO\left<\begin{matrix}NH\cdot CO\\NH\cdot CO\end{matrix}\right>CH\cdot CH\left<\begin{matrix}CO\cdot NH\\CO\cdot NH\end{matrix}\right>CO$, was first prepared by Schlieper (Annalen, 1845, 56, 11), who obtained the acid ammonium salt together with alloxan by the action of nitric acid (sp.gr. 1·25) on uric acid. It is also prepared (2) in the form of its ammonium salt by prolonged boiling of alloxan or alloxantin with very dilute sulphuric acid (Finch, Annalen, 1864, 132, 303); (3) by heating crystallised alloxantin in a tube at 170° when it is converted quantitatively into hydurilic acid, according to the equation

$$2C_8H_4O_7N_4+3H_2O$$
$$=C_8H_6O_6N_4+4NH_3+(COOH)_2+2CO+4CO_2$$

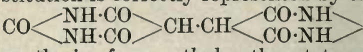
or alloxan is similarly decomposed (Murdoch and Doebner, Ber. 1876, 9, 1102); (4) in the form of its acid ammonium salt by heating dialuric acid with glycerol at 150°, formic acid and carbon dioxide being formed at the same time (Baeyer, Annalen, 1863, 127, 14); (5) together with glycine and carbon dioxide by heating uric acid with twice its weight of concentrated sulphuric acid (Schultzen and Filehne, Ber. 1868, 1, 150); (6) by reducing dibromobarbituric acid with hydrogen iodide (Baeyer, Annalen, 1864, 130, 133); and it is also formed to a small extent by reducing alloxantin with sulphuretted hydrogen (Murdoch and Doebner, *l.c.*); (7) by the condensation of ethyl ethanetetracarboxylate with carbamide in the presence of sodium ethoxide at 60°–70°; or by the hydrolysis of ethanetetracarbonylguanide



$$NH{:}C\left<\begin{matrix}NH\cdot CO\\NH\cdot CO\end{matrix}\right>CH\cdot CH\left<\begin{matrix}CO\cdot NH\\CO\cdot NH\end{matrix}\right>C{:}NH,H_2O$$

by means of dilute hydrochloric acid at 150° (Conrad, Annalen, 1907, 365, 24). Hydurilic acid is most conveniently purified by precipitating the sparingly soluble copper salt from a solution of the neutral ammonium salt, and decomposing this with hot hydrochloric acid, in which the hydurilic acid is only slightly soluble (Baeyer, Annalen, 1863, 127, 15).

Hydurilic acid crystallises from hot water in small four-sided prisms containing $2H_2O$, or is precipitated as a fine crystalline powder containing $1H_2O$ by the addition of hydrochloric acid to a hot aqueous solution. It is sparingly soluble in alcohol or cold water, more readily so in hot water; its heat of combustion is 658·5Cal. (Matignon, Ann. Chim. Phys. 1893, [vi.] 28, 328).

Hydurilic acid bears the same relation to dialuric and barbituric acids that alloxantin bears to alloxan and barbituric acid. Conrad (Annalen, 1907, 365, 24) has shown that its constitution is correctly represented by the formula  $CO\left<\begin{matrix}NH\cdot CO\\NH\cdot CO\end{matrix}\right>CH\cdot CH\left<\begin{matrix}CO\cdot NH\\CO\cdot NH\end{matrix}\right>CO$ by its synthesis from ethyl ethanetetracarboxylate and carbamide (*v. supra*), and also by the fact that on hydrolysis with concentrated hydrochloric acid at 200°–230° it is converted almost quantitatively into carbon dioxide, ammonia, and succinic acid; barbituric acid when similarly treated yields carbon dioxide, ammonia, and acetic acid.

Hydurilic acid is not attacked by reducing agents; it yields alloxan and dibromobarbituric acid when treated with bromine.

Fuming nitric acid oxidises it into alloxan, whilst weaker acid converts it into nitrobarbituric acid (dilituric acid), *iso*nitrosobarbituric acid (violuric acid) and violantin. Ferric chloride or silver oxide oxidises it to oxyhydurilic acid, which gives a blood-red colouration with ferric chloride. Hydurilic acid has marked acidic properties, and decomposes most metallic chlorides and acetates, yielding the corresponding hydrogen hydurilate. The heat of neutralisation of hydurilic acid with 2 mols. potassium hydroxide is 21·8Cal.; but on adding a further quantity of alkali (up to 16 mols.) there is a further evolution of 4·2Cal. of heat, thus pointing to the existence of a third very feeble acid function. The following salts have been described: the *ammonium hydrogen* salt

$$NH_4{\cdot}C_8H_5O_6N_4,$$

small octahedral sparingly soluble crystals precipitated by acetic acid from solutions of the *normal ammonium* salt $(NH_4)_2C_8H_4O_6N_4$ which crystallises in needles with $1H_2O$ or in large monoclinic crystals with $4H_2O$, $a:b:c=1{\cdot}0821:1:0{\cdot}7003$. *Sodium* salt

$$Na_2C_8H_4O_6N_4,4H_2O$$

crystallises in prisms; *potassium hydrogen* salt $KC_8H_5O_6N_4$ forms sparingly soluble microscopic needles; the *normal* salt $K_2C_8H_4O_6N_4,3H_2O$ is soluble and crystallises in prisms (Matignon). The *calcium* salts $Ca(C_8H_5O_6N_4)_2,8H_2O$ and $CaC_8H_4O_6N_4,3H_2O$ are crystalline and almost insoluble; the *barium* salt $BaC_8H_4O_6N_4,H_2O$; the *zinc* salts $Zn(C_8H_5O_6N_4)_2$ and

$$ZnC_8H_4O_6N_4,2H_2O$$

are crystalline; the *copper* salt

$$Cu(C_8H_5O_6N_4)_2,8H_2O$$

forms fine yellow needles or prisms, which become red on heating with loss of water. The *silver* salt is unstable; the *ferric* salt is a dark green precipitate, and the formation of a dark green colour with ferric chloride is a characteristic reaction of the salts of hydurilic acid; the *ferrous* salt is white becoming green; the *lead* salt is insoluble in acetic acid.

Dichlorohydurilic acid $C_8H_4Cl_2O_6N_4,2H_2O$ is obtained by the action of potassium chlorate on an intimate mixture of hydurilic and concentrated hydrochloric acids (Baeyer, Annalen, 1863, 127, 26). It is a sparingly soluble powder, soluble in concentrated sulphuric acid and precipitated therefrom by the addition of water, in small rhombic crystals containing $2H_2O$; it is readily decomposed by alkalis yielding the metallic chloride. The *potassium* salt

$$K_2C_8H_2Cl_2O_6N_4,2H_2O$$

is a sparingly crystalline soluble powder.

Tetramethylhydurilic acid (*deoxyamalic acid*) $C_{12}H_{14}O_6N_4$;

$$CO\left\langle\begin{array}{l}NMe\cdot CO\\NMe\cdot CO\end{array}\right\rangle CH\cdot CH\left\langle\begin{array}{l}CO\cdot NMe\\CO\cdot NMe\end{array}\right\rangle CO$$

is obtained by the dry distillation of amalic acid (Fischer and Reese, Annalen, 1883, 221, 339), or more conveniently by heating it in a sealed tube for 3 hours at 180°–185° (Matignon, Compt. rend. 1893, 116, 642); has also been obtained by heating dimethyl*pseudo*uric acid with fused oxalic acid at 170° (Fischer and Ach, Ber. 1895, 28, 2473). Deoxyamalic acid is crystalline, has m.p. 260°, with decomposition and can be distilled, although with partial decomposition. It is almost insoluble in hot or cold water; readily soluble in chloroform or acetic acid; its heat of combustion is 1321·8 Cal. (Matignon, Ann. Chim. Phys. 1893, [vi.] 28, 327). Its chemical properties are similar to those of hydurilic acid, it reduces ammoniacal silver nitrate solution on warming, and gives a beautiful green colouration with ferric chloride; on gentle oxidation it yields a product that gives a blood-red colouration with ferric chloride; but when oxidised by nitric acid it forms dimethylalloxan.

Deoxyamalic acid has only two acidic functions; the *potassium* $K_2C_{12}H_{12}O_6N_4$ and the *sodium* salt $Na_2C_{12}H_{12}O_6N_4$ are sparingly soluble (Matignon, *l.c.*; Fischer and Ach, *l.c.*).

M. A. W.

HYGRINE *v.* VEGETO-ALKALOIDS.

HYOSCYAMINE and **HYOSCYAMUS** *v.* DATURA; HENBANE; and VEGETO-ALKALOIDS.

HYOSEINE *v.* VEGETO-ALKALOIDS.

HYPNAL *v.* SYNTHETIC DRUGS.

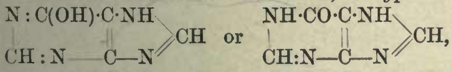
HYPNONE *v.* KETONES; SYNTHETIC DRUGS.

HYPONITRITES *v.* NITROGEN.

HYPOPHOSPHITES *v.* PHOSPHORUS.

HYPOSULPHITES *v.* SULPHUR.

HYPOXANTHINE or **SARCINE**, 6-*oxypurine*

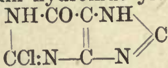


$$\begin{array}{l}N:C(OH)\cdot C\cdot NH\\ \quad\;\; | \qquad\quad \| \qquad\quad \rangle CH\\ CH:N\text{—}C\text{—}N\end{array}\quad\text{or}\quad\begin{array}{l}NH\cdot CO\cdot C\cdot NH\\ \;| \qquad\quad \| \qquad\quad \rangle CH,\\ CH:N\text{—}C\text{—}N\end{array}$$

discovered by Scherer (Annalen, 1850, 73, 328) in milk, spleen, and blood, is widely distributed both in the animal and vegetable kingdoms. Strecker (Phil. Trans. 1858, 10, 121) isolated it from meat juice, and hence called it *sarcine;* it was afterwards found to be identical with Scherer's hypoxanthine. It is a normal constituent of bone marrow (Heymann, Pflüger's Archiv. 6, 184), glands, muscles, liver, brain (Salomon, Ber. 1878, 11, 574; Kossel, Chem. Zentr. 1881, 486), blood (Scherer, *l.c.*; Salomon, Chem. Zentr. 1878, 681) and urine (Strecker, *l.c.*; Salomon, Zeitsch. physiol. Chem. 1887, 11, 410), the amount varying from 0·024 p.c. in the grey matter of the brain (Kossel, *l.c.*) to 0·218 p.c. in the calf's thymus (Schindler, Zeitsch. physiol. Chem. 1889, 13, 432). Piccard found 5–8 p.c. of hypoxanthine and guanine in salmon roe (Ber. 1874, 7, 1714), whilst ox testis and the spermatozoa of carp contain 0·281 and 0·309 p.c. respectively of the former base (Schindler, *l.c.*). In the vegetable kingdom hypoxanthine occurs in beer yeast (Schutzenberger, Chem. Zentr. 1877, 73); potato juice to the extent of 0·0037 gram per 1 c.c. (Schulze, Landw. Versuchs. Stat. 1882, 28, 111); in the leaf buds of plane and maple, bark of plane, in lupines, young grass, red clover, oats, vetch, and in sugar beet (Schulze and Bosshard, Zeitsch. physiol. Chem. 1885, 9, 420; Von Lippmann, Ber. 1896, 29, 2645).

The chief source of hypoxanthine in the animal economy appears to be nucleic acid, which, under the action of certain tissue enzymes; most abundant in the liver and spleen, is decomposed; thus *nuclease* liberates the purine bases adenine and guanine, and these are further changed by the deamidising enzymes *adenase* or *guanase* into hypoxanthine and xanthine respectively, and finally *oxydases* convert hypoxanthine into xanthine and xanthine into uric acid (Halliburton, Chem. Soc. Reports. 1909, 168). Salomon (Ber. 1887, 11, 574; 12, 95) obtained hypoxanthine from blood fibrin by the action of pancreas ferment, by simple decay, or by digestion with dilute hydrochloric acid (8 parts in 1000 parts of water); and Kossel (Zeitsch. physiol. Chem. 1881, 5, 152) found that the nuclein from pus cells and goose blood yielded on prolonged boiling 1·03 and 2·64 p.c. respectively of hypoxanthine. On the other hand, Leathes (J. Physiol. 1906, 35, 125, 205), Leonard and Jones (J. Biol. Chem. 1909, 6, 453), and Vögtlin and Jones (Zeitsch. physiol. Chem. 1910, 66, 250), have shown that uric acid excretion is related in some way to muscular exercise, and the most important purine base which contributes to the endogenous uric acid is muscular preformed hypoxanthine. This is not directly connected with nuclein metabolism, since it may occur in the absence of adenase, an essential factor in the passage from nucleic acid to hypoxanthine.

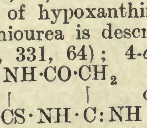
Fischer (Ber. 1897, 30, 2226; D. R. P. 1898, 17673) has synthesised hypoxanthine from trichloropurine by the following reactions: trichloropurine when heated with normal aqueous potassium hydroxide yields 6-*oxy*-2 : 8-*dichloropurine*



$$\begin{array}{l}NH\cdot CO\cdot C\cdot NH\\ \;| \qquad\quad \| \qquad\quad \rangle CCl,\\ CCl:N\text{—}C\text{—}N\end{array}$$

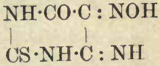
which is reduced to hypoxanthine by the action of hydrogen iodide. Hypoxanthine is also obtained from adenine (6-*aminopurine*) by the action of nitrous acid, or from uric acid by reduction with alkali and chloroform (Sundvik, Zeitsch. physiol. Chem. 1897, 23, 476; 26, 13).

A further synthesis of hypoxanthine from ethylcyanacetate and thiourea is described by Traube (Annalen, 1904, 331, 64); 4-*amino*-6-*hydroxy*-2-*thiopyrimidine*



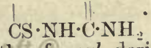
$$\begin{array}{l}NH\cdot CO\cdot CH_2\\ | \qquad\quad\;\; |\\ CS\cdot NH\cdot C:NH\end{array}$$

obtained by the condensation of ethylcyanacetate and thiourea in the presence of sodium ethoxide, forms an *isonitroso derivative*



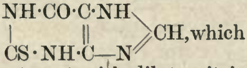
$$\begin{array}{l}NH\cdot CO\cdot C:NOH\\ | \qquad\quad\;\; |\\ CS\cdot NH\cdot C:NH\end{array}$$

which on reduction yields 4 : 5-*diamino*-6-*oxy*-2-*thiopyrimidine*



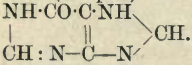
$$\begin{array}{l}NH\cdot CO\cdot C\cdot NH_2\\ | \qquad\quad\;\; \|\\ CS\cdot NH\cdot C\cdot NH_2\end{array}$$

. When the sodium salt of the *formyl* derivative of this compound is heated at 250°–255° it is converted into 6-*oxy*-2-*thiopurine*



$$\begin{array}{l} \mathrm{NH{\cdot}CO{\cdot}C{\cdot}NH}\diagdown \\ \;|\qquad\quad\;\; \| \qquad\quad\; >\mathrm{CH} \\ \mathrm{CS{\cdot}NH{\cdot}C{-}N}\diagup \end{array}$$

, which loses its sulphur on treatment with dilute nitric acid (25 p.c.) at 100°, yielding hypoxanthine



$$\begin{array}{l} \mathrm{NH{\cdot}CO{\cdot}C{\cdot}NH}\diagdown \\ \;|\qquad\quad\;\; \| \qquad >\mathrm{CH.} \\ \mathrm{CH:N{-}C{-}N}\diagup \end{array}$$

Hypoxanthine is a white crystalline powder, crystallising in two modifications, one form consisting of needles containing water of crystallisation, which spontaneously and readily lose their water yielding anhydrous octahedra (Micko, Zeitsch. Nahr. Genussm. 1904, 8, 225); it decomposes without melting at 150°, and dissolves in 69·5 parts of boiling water or 1400 parts at 19° (Fischer, Ber. 1897, 30, 2226).

Hypoxanthine exhibits both acid and basic properties, and combines with one equivalent of an acid, or two equivalents of a base; the following *salts* are described: the *hydrochloride* $C_5H_4N_4O{\cdot}HCl,H_2O$, crystalline plates or needles, yields a sparingly soluble *platinichloride*

$$(C_5H_4N_4O{\cdot}HCl)_2.PtCl_4;$$

and a crystalline *aurichloride*

$$C_5H_4N_4O{\cdot}HCl.AuCl_3$$

the *hydrobromide* $C_5H_4N_4O{\cdot}HBr$ and *nitrate* $C_5H_4N_4O{\cdot}NHO_3$ are crystalline; the *picrate* dissolves in 450–500 parts of water at the ordinary temperature (Krüger and Salomon, Zeitsch. physiol. Chem. 1898, 26, 362). The *barium* derivative $C_5H_4N_4O{\cdot}Ba(OH)_2$ is crystalline, the *silver* salt $C_5H_2N_4OAg_2,H_2O$ loses $\frac{1}{2}H_2O$ at 100°; in the presence of excess of ammonia the salt crystallises with $3H_2O$, and loses $2\frac{1}{2}H_2O$ at 120°.

Hypoxanthine forms characteristic sparingly soluble derivatives with certain metallic salts, and these are used for separating and estimating the base. The *compound* with *mercuric chloride* $C_5H_3N_4O,HgCl_2,H_2O$ is crystalline; the *compound* with *silver nitrate* $C_5H_4N_4O,AgNO_3$ is a flocculent precipitate, crystallising from hot nitric acid (sp.gr. 1·1), 1 part dissolves in 4960 parts cold nitric acid; according to Salkowski (Pflüger's Archiv. 4, 91), the presence of gelatin prevents the precipitation of hypoxanthine by silver nitrate; the *picrate* $AgC_5H_3N_4O,C_6H_3N_3O_7$ is a lemon-yellow crystalline salt, insoluble in cold water, precipitated from a hypoxanthine salt by sodium picrate and silver nitrate (Bruhns, Zeitsch. physiol. Chem. 1890, 14, 555).

Bromohypoxanthine $C_5H_3BrN_4O,2H_2O$ is sparingly soluble in cold water, and is obtained by the action of bromine (1 mol.) on hypoxanthine (1 mol.) at 120°, or by the action of sodium nitrite on a solution of bromadenine at 70°; on heating hypoxanthine for 6 hours at 100°–150° with excess of bromine, *bromohypoxanthine-tetrabromide hydrobromide* $C_5H_3BrN_4O{\cdot}HBr{\cdot}Br_4$ is obtained (Krüger, Zeitsch. physiol. Chem. 1894, 18, 449).

Urethane of hypoxanthine $C_5H_3N_4O{\cdot}COOEt$ prepared by the interaction of ethylchlorocarbonate and hypoxanthine, crystallises in plates, m.p. 185°–190°, and is sparingly soluble (Bruhns and Kossel, Zeitsch. physiol. Chem. 1892, 16, 1). Hypoxanthine combines with adenine to form the crystalline *compound*

$$C_5H_4N_4O{\cdot}C_5H_5N_5,3H_2O$$

(Bruhns, Ber. 1890, 23, 225); and like other purine derivatives containing an imino group in position 7 it yields coloured *derivatives* with diazobenzene salts (Burian, Ber. 1904, 37, 696).

Separation and estimation.—From mixtures of the xanthine bases, adenine and hypoxanthine are separated from xanthine and guanine by means of their sparingly soluble derivatives with silver nitrate in nitric acid solution. The mixed silver compounds are decomposed by hydrochloric acid, the filtrate nearly neutralised with sodium carbonate and the adenine precipitated as picrate. The filtrate is neutralised with ammonia, and the hypoxanthine precipitated with ammoniacal silver nitrate (Bruhns, Ber. 1890, 23, 225; *cp.* also Kossel, Zeitsch. physiol. Chem. 1883, 8, 404; Schindler, *ibid.* 1889, 13, 432: Krüger, *ibid.* 1894, 20, 170). M. A. W.

HYRGOL *v.* SYNTHETIC DRUGS.

HYSTARAZIN *v.* ALIZARIN AND ALLIED COLOURING MATTERS.

I

IBIT *v.* SYNTHETIC DRUGS.

IBOGA. A plant *Tabernanthe iboga* (Baill.), natural order *Acanthaceæ*, found in the Congo, the root of which is chewed by the natives and which is said to possess properties similar to those of coca and kola. It enables persons to withstand fatigue, is used as a remedy for sleeping sickness and acts as an aphrodisiac. According to Dybowski and Landrin, its active principle is an alkaloid, *ibogaïne* $C_{26}H_{33}N_3O$, which readily oxidises on exposure to air. It is lævorotatory and forms well crystallised salts (Compt. rend. 133, 748).

ICACIN *v.* OLEO-RESINS.

ICE BLACK *v.* AZO- COLOURING MATTERS.

ICELAND-SPAR *v.* CALCITE; CALCIUM.

ICE-SPAR *v.* CRYOLITE.

ICHTHARGAN *v.* SYNTHETIC DRUGS.

ICHTHYOL. A pharmaceutical product distilled from fossilised fish remains, found in the Tyrol and on the coasts of the Adriatic.

Crude ichthyol from the Seefeld district between Southern Bavaria and the Tyrol has long been used as an antiseptic remedy. The crude 'rock oil' is obtained by simple distillation from the shale or 'stinkstein,' a bituminous substance of a grey or black colour occurring in the upper dolomites. The amount of oil obtained varies from 1 to 10 p.c. An installation of nine stills yields, on an average, 15 to 20 kilos. of oil per charge. In one works the output of crude oil is over 3000 kilos per annum. As found in pharmacy, the substance consists mainly of the ammonium sulphonate. It is not a simple substance but a mixture of ammonium ichthyol sulphonate with about 1 p.c.

of a powerful-smelling empyreumatic oil, 5 to 7 p.c. of ammonium sulphate, and about 50 p.c. water.

According to Baumann and Schotten, ichthyol-sulphonic acid has the formula

$$C_{28}H_{26}S(SO_2OH)_2.$$

An odourless ichthyol has been prepared by Knorr & Co. which has the therapeutic activity of the original strong-smelling product (J. Soc. Chem. Ind. 1903, 1304; 1910, 44, 174, 264).

For ichthyol preparations *v.* Synthetic drugs.

ICICA and **ICACIN** *v.* Oleo-resins.

ICOSANE $C_{20}H_{42}$. A hydrocarbon found in paraffin. M.p. 36°; b.p. (under 15 mm. pressure) 205°; sp.gr. 0·778 at 37°/4°. Formed by the action of sodium on normal decyl iodide.

ICOSONENE *v.* Resin oil.

IDRYL *v.* Fluoranthene.

IGNOTINE *v.* Carnosine.

ILICIC and **ILICYLIC ALCOHOLS** *v.* Bird-lime.

ILLIPÉ-NUT FAT. Illipé-nuts yield a considerable quantity of a fat which is imported from the Dutch East Indies, and used in conjunction with palm-kernel oil in the manufacture of candles. It is well adapted for the saponification method of stearin manufacture. In the autoclave it yields about 10 p.c. of glycerol of 28°B. (J. Soc. Chem. Ind. 1898, 161, 358); *v.* Bassia oil.

ILMENITE, or titaniferous iron-ore. A common mineral with approximately the formula $FeTiO_3$, but of variable composition. In its rhombohedral crystalline form it shows a close agreement with hæmatite, and it has consequently, until recently, been regarded as an isomorphous mixture of ferric oxide and titanium sesquioxide, the formula being written as an oxide $(Fe,Ti)_2O_3$. The discovery of the rhombohedral titanates of magnesium and manganese, geikielite ($MgTiO_3$) and pyrophanite ($MnTiO_3$), and the frequent presence of magnesium (and manganese) in ilmenite, suggest, however, that the mineral is really a titanate of ferrous iron, $FeTiO_3$ (S. L. Penfield, Amer. J. Sci. 1897, 4, 108). In the variety *picroilmenite* a considerable amount of iron is replaced by magnesium, the formula then being $(Fe,Mg)TiO_3$ (T. Crook and B. M. Jones, Min. Mag. 1906, 14, 165).

Ilmenite is black with a sub-metallic lustre, and often a smooth and lustrous conchoidal fracture, sp.gr. 4·5–5; H. 5–6. The massive mineral in appearance somewhat resembles magnetite, from which it is readily distinguished by its feeble magnetic character. It is of constant occurrence as isolated grains in the more basic igneous rocks (gabbro, diabase, basalt, &c.); and in certain instances it forms rich segregations in such rocks. Enormous deposits of ilmenite are found under these conditions at several places in Norway, Sweden, Canada, and the United States. With the weathering and breaking down of these igneous rocks, grains of ilmenite (*Manaccanite*, from Manaccan in Cornwall) collect in the beds of streams, sometimes forming considerable deposits of 'black iron-sand.'

Although large deposits of ilmenite are available for mining, the mineral has not yet found any important applications. It has been used for the preparation of titanium paints and enamels; and in the future it may be more utilised for the manufacture of titanium-steel, which possesses great ductility and a high limit of elasticity. L. J. S.

IMPERIALINE $C_{35}H_{60}NO_4$. An alkaloid discovered by K. Fragner in *Fritillaria Imperialis* (Linn.). It is a heart-poison, and is probably closely related to the older alkaloid *Tulipine*, discovered by Gerard in *Tulipa Gesneriana* (Linn.).

IMPERIAL GREEN. *Emerald Green v.* Pigments.

IMPERIAL SCARLET *v.* Azo- colouring matters.

IMPERIAL YELLOW *v.* Aurantia.

INACTIVE CAMPHOR *v.* Camphors.

INCANDESCENT MANTLES *v.* Gas mantles.

INCARNATRIN *v.* Glucosides.

INCENSE TREE RESINS *v.* Gum-resins; Oleo-resins.

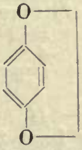
INDALIZARINE *v.* Oxazine colouring matters.

INDAMINES and **INDOPHENOLS.**

Constitution and mode of formation.—The indamines and indophenols are colouring matters most of which are too unstable to be of great practical value, but many of them are interesting as intermediate products in the manufacture of other more important dyestuffs. From a theoretical point of view they can claim great importance, as they form the starting-point of the modern 'quinonoid' structural formulæ now universally adopted for the majority of colouring matters. This is due to the fact that the indamines and indophenols are the simplest real colouring matters derived from the quinones, which are now considered as prototypes of chromogens.

All aromatic hydrocarbons are capable of forming quinonoid derivatives by the displacement of 2 hydrogen atoms by 2 atoms of oxygen. These may stand either in *o*- or in *p*-position to each other, whilst no quinones have ever been discovered which contain the oxygen atoms in *m*- position. The divalent nature of oxygen forces us to consider the quinones either as peroxides of aromatic hydrocarbons or as alicyclic diketones. The first of these possibilities was formerly considered as more probable and was made the basis of this article in the first edition of this dictionary. Since then the diketone formula has come to be generally adopted and it will therefore have to be used in this revision of the article.

The following formulæ represent the two different constitutions which may be given to *p*-quinone, the prototype of all the substances to be mentioned in this article:

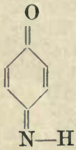


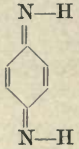
Peroxide formula.

Diketone formula.

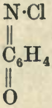
All other quinones, no matter from what aromatic hydrocarbon they are derived and whether they belong to the *o*- or *p*- series, may be similarly formulated and neither of these two different constitutions can be claimed as undoubtedly preferable to the other. It is very probable that the quinones are tautomeric and possessed of both constitutions according to the circumstances under which they react.

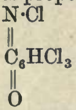
If the oxygen of *p*-quinone be replaced by divalent imino groups =NH, two compounds may be obtained, *p*-quinoneimide and *p*-quinonediimide, which for many years have been considered as hypothetical but have recently been prepared by Willstätter (Ber. 37, 1494, 4605). They are very unstable substances the constitution of which is expressed by the following formulæ (based, as all the subsequent formulæ of this article, on the diketonic constitution of the quinones):

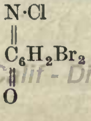

p-Quinoneimide.

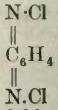

p-Quinonediimide.

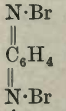
The iminic hydrogen of these compounds may be replaced by halogen atoms, and we thus obtain substances of a comparatively stable nature which have been known for a long time and may be used for the preparation of various derivatives. It was by treating quinonedichlorodiimide, dissolved in ether, absolutely free from moisture, with the theoretical quantity of dry hydrogen chloride that Willstätter first succeeded in preparing *p*-quinonediimide. Later on he found a general method for the production of both these imides in the oxidation of either *p*-phenylenediamine or *p*-aminophenol with dry silver oxide. They are slightly basic substances, capable of forming unstable hydrochlorides. In a free state they are white, but they resemble quinone in their reactions. Their great tendency to polymerisation is the cause why previous attempts at their isolation have failed.

Quinonechloroimide  $\begin{array}{c}N{\cdot}Cl\\ \|\\ C_6H_4\\ \|\\ O\end{array}$ has been obtained by Schmitt and Bennewitz (J. pr. Chem. [ii.] 8, 2). It is prepared by allowing a solution of 43 grams *p*-aminophenol hydrochloride in 500 c.c. water and 100 c.c. concentrated hydrochloric acid to flow into a solution of sodium hypochlorite prepared by introducing 35 grams of chlorine into an ice-cold solution of 45 grams sodium hydroxide. The imide settles out and may be recrystallised from light petroleum (Willstätter, Ber. 37, 1499). It forms yellow crystals, melting at 85°; it is slightly explosive, volatile with aqueous vapour, and resembles quinone in many of its properties.

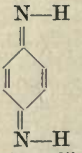
Trichloroquinonechloroimide  $\begin{array}{c}N{\cdot}Cl\\ \|\\ C_6HCl_3\\ \|\\ O\end{array}$ is prepared in the same manner from trichloraminophenol hydrochloride (Schmitt and Andresen, J. pr. Chem. [ii.] 23, 438; 24, 429). Yellow needles, m.p. 118°, similar to quinonechloromide.

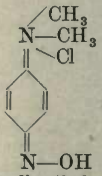
Dibromoquinonechloroimide  $\begin{array}{c}N{\cdot}Cl\\ \|\\ C_6H_2Br_2\\ \|\\ O\end{array}$ is obtained by adding a solution of bleaching-powder to an aqueous acidulated solution of the double salt of dibromaminophenol hydrochloride and tin chloride. It separates in flesh-coloured crystals, melting at 80° (R. Möhlau, Ber. 16, 2845).

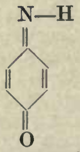
Quinonedichlorodiimide  $\begin{array}{c}N{\cdot}Cl\\ \|\\ C_6H_4\\ \|\\ N.Cl\end{array}$ is formed by acting with a solution of bleaching-powder upon a solution of *p*-phenylenediamine hydrochloride (Krause, Ber. 12, 47). Willstätter (Ber. 37, 1498) prepares it by allowing a solution of 54 grams *p*-phenylenediamine hydrochloride in 120 c.c. hydrochloric acid and 600 c.c. water to flow into a hypochlorite solution prepared by introducing 75 grams of chlorine into the solution of 90 grams sodium hydroxide in 500 c.c. of water. The imide separates in whitish flakes and may be recrystallised from light petroleum. White needles, insoluble in water, soluble in alcohol, benzene, &c., and exploding at 126°.

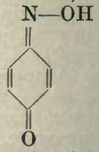
Quinonedibromodiimide  $\begin{array}{c}N{\cdot}Br\\ \|\\ C_6H_4\\ \|\\ N{\cdot}Br\end{array}$ may be prepared by acting with bromine water upon *p*-phenylenediamine hydrochloride (Krause, Ber. 12, 50). It is similar to the chloro derivative, and explodes at 86°.

These substances are not colouring matters, as may be seen from the above description. They cannot be colouring matters, because they are indifferent, whilst every dyestuff must be either an amine or a phenol (Witt, Bau und Bildung färbender Kohlenstoffverbindungen, Ber. 9, 522). Their chromophoric character, however, becomes apparent in those of their derivatives which are endowed with either basic or acid properties. Nitrosodimethylaniline and nitrosophenol, which, as their constitutional formulæ show, are closely related to quinonediimide and quinoneimide:


Quinonediimide.


Quinonedimethylamino-oxime chloride (Nitrosodimethylaniline hydrochloride).

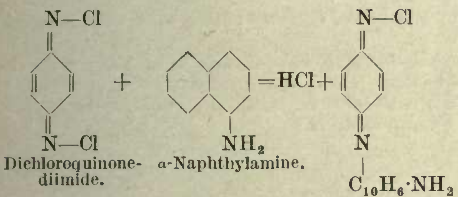

Quinoneimide.


Quinoneoxime (Nitrosophenol).

are by virtue of their basic and phenolic nature, colouring matters possessing some affinity for fibres, although they have no practical value as dyestuffs.

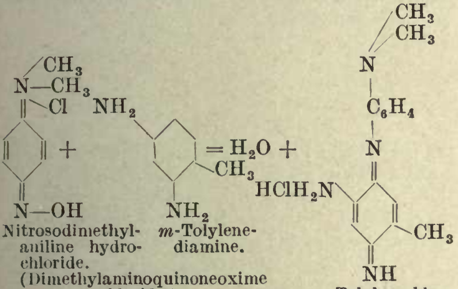
We may, however, obtain real colouring matters, many of which have proved useful and interesting, by preparing substitution products of the quinoneimides in which the substituting radicle is attached to nitrogen. Such products may be prepared by acting with amines or phenols upon quinoneimides, or their equivalents, quinonamidoximes (nitroso bases) and quinoneoximes (nitrosophenols). Various cases may here be cited:

1. By acting with aromatic amines upon quinonedichlorodiimides, indamines are formed, thus:



Dichloroquinonediimide. α-Naphthylamine. Naphthindamine.

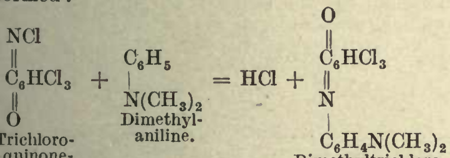
2. By acting with aromatic amines upon quinone-amidoximes (nitroso bases) indamines are formed likewise:



Nitrosodimethylaniline hydrochloride. (Dimethylaminoquinoneoxime chloride.) *m*-Tolylenediamine. Tolylene blue.

In this case, as in many similar ones in this group, the quinonoid character may in the formation of the dyestuff be shifted from one benzene ring to the other. This has been indicated in the formula, although we have no positive proof that such shifting takes place in the formation of tolylene blue.

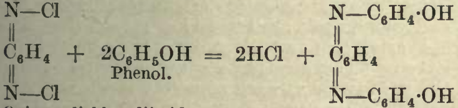
3. By acting with aromatic amines upon quinonechloroimides normal indophenols are formed:



$$\begin{array}{l}NCl\\ \|\\ C_6HCl_3\\ \|\\ O\end{array} + \begin{array}{l}C_6H_5\\ |\\ N(CH_3)_2\end{array} = HCl + \begin{array}{l}O\\ \|\\ C_6HCl_3\\ \|\\ N\\ |\\ C_6H_4N(CH_3)_2\end{array}$$

Trichloroquinonechloroimide. Dimethylaniline. Dimethyltrichlorobenzindophenol.

4. By acting with phenols upon quinonedichlorodiimides indophenols of a more complicated nature may be formed:

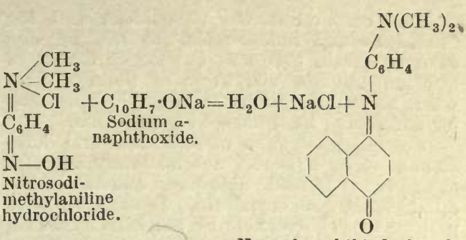


$$\begin{array}{l}N—Cl\\ \|\\ C_6H_4\\ \|\\ N—Cl\end{array} + 2C_6H_5OH = 2HCl + \begin{array}{l}N—C_6H_4{\cdot}OH\\ \|\\ C_6H_4\\ \|\\ N—C_6H_4{\cdot}OH\end{array}$$

Phenol.

Quinonedichlorodiimide. Complex indophenol.

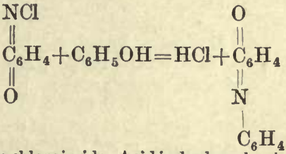
5. By acting with phenols upon quinonamidoximes (nitroso bases) normal indophenols are formed:



Nitrosodimethylaniline hydrochloride. Sodium α-naphthoxide. Normal naphthindophenol.

In this case again, as in No. 2, a migration takes place and the quinonoid nature is shifted from the benzene to the naphthalene nucleus. This can be proved to be the case by the fact that the resulting dyestuff is a weak base but entirely devoid of phenolic properties. It cannot therefore contain an OH group.

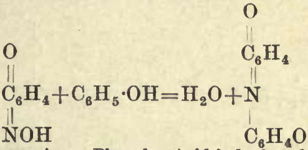
6. By acting with phenols upon quinonechloroimides colouring matters are formed, which although practically belonging to the indophenols are distinguished by the presence of a free hydroxyl group, by which they assume phenolic properties, dissolve in alkalis and have therefore been designated by the name of 'acid indophenols.'



$$\begin{array}{l}NCl\\ \|\\ C_6H_4\\ \|\\ O\end{array} + C_6H_5OH = HCl + \begin{array}{l}O\\ \|\\ C_6H_4\\ \|\\ N\\ |\\ C_6H_4{\cdot}OH\end{array}$$

Quinone chloroimide. Acid indophenol, soluble in alkalis.

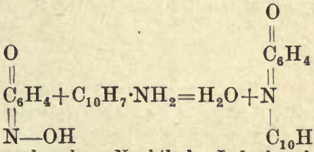
7. The same result takes place if the equivalents of quinoneimide, viz. the quinoneoximes or nitrosophenols be acted upon with phenols:



$$\begin{array}{l}O\\ \|\\ C_6H_4\\ \|\\ NOH\end{array} + C_6H_5{\cdot}OH = H_2O + \begin{array}{l}O\\ \|\\ C_6H_4\\ \|\\ N\\ |\\ C_6H_4OH\end{array}$$

Quinoneoxime (nitrosophenol). Phenol. Acid indophenol, soluble in alkalis.

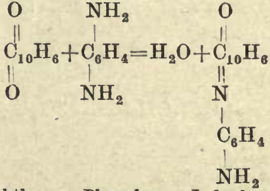
8. If, however, amines be acted upon with nitrosophenols, a normal indophenol is the result:



$$\begin{array}{l}O\\ \|\\ C_6H_4\\ \|\\ N—OH\end{array} + C_{10}H_7{\cdot}NH_2 = H_2O + \begin{array}{l}O\\ \|\\ C_6H_4\\ \|\\ N\\ |\\ C_{10}H_6{\cdot}NH_2\end{array}$$

Nitrosophenol. α-Naphthylamine. Indophenol, insoluble in alkali.

9. The quinones themselves may be utilised for the production of these dyestuffs by being acted upon with suitable diamines or aminophenols:



$$\begin{array}{l}O\\ \|\\ C_{10}H_6\\ \|\\ O\end{array} + \begin{array}{l}NH_2\\ |\\ C_6H_4\\ |\\ NH_2\end{array} = H_2O + \begin{array}{l}O\\ \|\\ C_{10}H_6\\ \|\\ N\\ |\\ C_6H_4\\ |\\ NH_2\end{array}$$

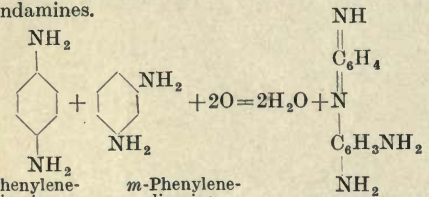
Naphthaquinone. *p*-Phenylenediamine. Indophenol.

This reaction makes it evident that the indamines and indophenols are nothing else than a certain group of the larger family of quinone anilides, viz. those of these anilides which contain the auxochromic groups necessary for developing their nature as dyestuffs.

For the production of indamines and indophenols it is, however, not necessary to start from ready-formed quinones, quinoneimides, diimides, or quinoneoximes. It is possible to prepare these substances by the joint oxidation of amines or phenols with compounds which are capable of producing a quinoneimide or diimide.

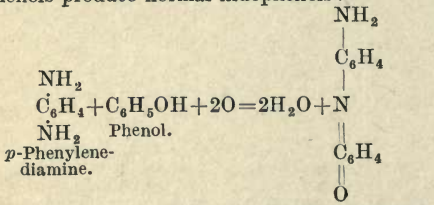
In this process we may assume that the hypothetical quinoneimides and -diimides are formed as intermediate products which immediately react upon the amines or phenols present in the mixture, forming indamines or indophenols, as the case may be. Every p-aminophenol or p-diamine is capable of being used for this reaction, and a large variety of colouring-matters may thus be produced. The following combinations may take place:

10. p-Diamines simultaneously oxidised with aromatic amines give rise to the formation of indamines.



p-Phenylene-diamine. m-Phenylene-diamine. Indamine (phenylene-violet).

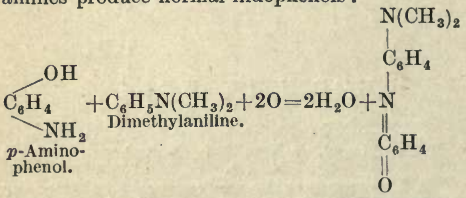
11. p-Diamines oxidised with aromatic phenols produce normal indophenols:



$$\begin{array}{c} NH_2 \\ C_6H_4 \\ NH_2 \end{array} + C_6H_5OH + 2O = 2H_2O + \begin{array}{c} NH_2 \\ | \\ C_6H_4 \\ | \\ N \\ \| \\ C_6H_4 \\ \| \\ O \end{array}$$

p-Phenylene-diamine. Phenol. Typical indophenol.

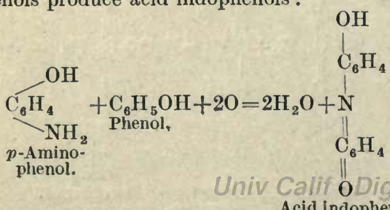
12. p-Aminophenols oxidised with aromatic amines produce normal indophenols:



$$C_6H_4\begin{array}{l} \diagup OH \\ \diagdown NH_2 \end{array} + C_6H_5N(CH_3)_2 + 2O = 2H_2O + \begin{array}{c} N(CH_3)_2 \\ | \\ C_6H_4 \\ | \\ N \\ \| \\ C_6H_4 \\ \| \\ O \end{array}$$

p-Amino-phenol. Dimethylaniline. Indophenol.

13. p-Aminophenols oxidised with aromatic phenols produce acid indophenols:



$$C_6H_4\begin{array}{l} \diagup OH \\ \diagdown NH_2 \end{array} + C_6H_5OH + 2O = 2H_2O + \begin{array}{c} OH \\ | \\ C_6H_4 \\ | \\ N \\ \| \\ C_6H_4 \\ \| \\ O \end{array}$$

p-Amino-phenol. Phenol. Acid indophenol.

From the above it will be seen that all the various colouring matters prepared by these reactions and built up on the quinone type may be subdivided into three varieties:—

a. True *indamines* containing no oxygen, and having the generic formula:

$$\begin{array}{l} R^{II} = NH \\ \| \\ N \\ | \\ R^{II} - NH_2 \end{array}$$

strong bases, forming stable salts with mineral acids.

b. Normal indophenols, containing oxygen in their chromophoric group, being amino derivatives of substituted quinoneimides of the generic formula:

$$\begin{array}{l} R^{II} = O \\ \| \\ N \\ | \\ R^{II} - NH_2 \end{array}$$

very weak bases, incapable of forming stable salts. With these the hydroxy derivatives of quinonediimides:

$$\begin{array}{l} R^{II} - OH \\ | \\ N \\ \| \\ R^{II} = NH \end{array}$$

are practically identical, being transformed into normal indophenols *in statu nascendi* by the shifting or migrating process already mentioned.

c. Acid indophenols, hydroxyl derivatives of quinonimides of the generic formula:

$$\begin{array}{l} R^{II} = O \\ \| \\ N \\ | \\ R^{II} - OH \end{array}$$

distinct phenols, dissolving in caustic alkali solutions with intense colourations.

Like all colouring matters the indamines and indophenols are capable of being reduced by the action of nascent hydrogen, of which two atoms are taken up. Colourless 'leuco-' compounds are formed which stand in the same relation to the original dyestuff as hydroquinone stands to quinone:

$$\begin{array}{ccc} R^{II}\cdot NH_2 & R^{II}\cdot NH_2 & R^{II}\cdot OH \\ | & | & | \\ NH & NH & NH \\ | & | & | \\ R^{II}\cdot NH_2 & R^{II}\cdot OH & R^{II}\cdot OH \end{array}$$

Leuco-indamine. Normal leuco-indophenol. Acid leuco-indophenol.

It will be clearly seen that these formulæ of the leuco derivatives are identical with the formulæ of paradiamino, aminohydroxy, and p-dihydroxy derivatives of secondary aromatic bases. Now as the leuco derivatives of indamines and indophenols are capable of reoxidation into the original dyestuff, it is apparent that we have by this means three additional methods for the production of such colouring matters:

14. Di-p-amino derivatives of secondary aromatic bases may be oxidised into indamines.

15. p-Amino-p-hydroxy derivatives of secondary aromatic bases may be oxidised into normal indophenols.

16. Di-*p*-hydroxy derivatives of secondary aromatic bases may be oxidised into acid indophenols.

The conditions under which these various reactions should be performed are stated below.

The remarkable relations existing between dyestuffs and their leuco compounds were recognised and studied by chemists at an early period. In no group are they so clearly defined as in that of the indamines and indophenols. Their complete elucidation in this group very naturally sheds light upon analogous phenomena observed in other colouring matters and thus the study of this class of substances greatly facilitated the introduction of the modern views of the 'quinonoid' constitution of colouring matters.

Literature on the Constitution of Indamines and Indophenols, Otto N. Witt, J. Soc. Chem. Ind. 1882, 255; R. Möhlau, Ber. 16, 2843; Otto N. Witt, British Association, 1887; Journ. Soc. Dy. Col. 1887; R. Nietzki, Organische Farbstoffe, 5th ed. 1906, 197 *et seq.*

History.—The first indamine observed was the intermediate product obtained in the production of safranine, of which, however, no account was published. In 1879, Otto N. Witt prepared the first indamine in a state of purity by acting with nitrosodimethylaniline hydrochloride upon *m*-tolylenediamine (Ber. 12, 931; Chem. Soc. Trans. 1879, 1, 356). In 1881, Otto N. Witt and Horace Köchlin obtained patents for the production of normal indophenols. The production of 'acid indophenols' by the reaction of quinonechloroimide upon phenol was first mentioned by Hirsch (Ber. 13, 1909), and discussed by Möhlau (*ibid.* 16, 2845). The normal indophenols only have found a practical application in dyeing and calico-printing. Owing, however, to their insufficient resistance to the action of acids and to the difficulties in their application, they did not make very rapid progress in the favour of practical dyers and colourists. A change for the better took place, when it was shown that the typical indophenol is a good vat-dye and capable of being used in combination with indigo. The consumption of indophenol became considerable for a while, but went down again as rapidly as it had gone up when the introduction of synthetic indigo lowered the prices of this 'king of dyestuffs' and the invention of many indigoid colouring matters overwhelmed the dyer with dyes suitable for the vat-process.

In later years some of the indophenols have become important as raw materials for the production of some valuable sulphur dyes, which are prepared from them by the well-known process of boiling or melting with alkaline sulphides. This new application of the indophenols had been first indicated in D. R. P. 132212 of the Gesellschaft für Chemische Industrie, in Basle (14 Dec. 1898), and the corresponding Fr. Pat. 284387 and Amer. Pat. 665547.

Properties.—The properties of the indamines and indophenols are more uniform than those of other classes of colouring matters. It has consequently been necessary to prepare only a small number from the host of possible members of this group in order to obtain a fair notion of the properties of the whole group. With very few exceptions their shade is blue or violet; in some cases a bluish-green. The shade of the dyestuff is exhibited:

a. In the indamine group by the normal salts of the indamine bases.

b. In the group of normal indophenols by the free bases.

c. In the group of acid indophenols by the alkaline salts of the dyestuffs.

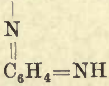
All the indamines and indophenols possess the generic character of the quinone group. They are therefore capable of acting as oxidising agents if brought together with oxidisable substances. In such reactions they take up hydrogen and are transformed into their leuco derivatives. So considerable is their tendency to act as oxidising agents that, under suitable conditions, an indamine or indophenol will attack its own molecules, when a mixture of its oxidation products and its leuco compounds is the result (*v. Safranines*, art. AZINES). The conditions under which such reactions take place are, an elevated temperature and the presence of mineral acids. The indamines and indophenols are consequently unstable in the presence of acids, whilst in alkaline and neutral solution they display but little tendency to decompose. A similar decomposition is caused, especially in the indamines, by the action of sunlight; the normal indophenols may, on the contrary, be called rather fast.

The following is an account of those members of this group of dyestuffs which have been more closely examined or proved important from a technical point of view:—

I. INDAMINES.

Phenylene-blue $C_{12}H_{11}N_3$

Constitution



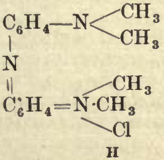
$$\begin{array}{l} C_6H_4-NH_2 \\ \vert \\ N \\ \Vert \\ C_6H_4=NH \end{array}$$

This compound is best prepared by oxidising a mixture of *p*-phenylenediamine and aniline hydrochloride in equal molecules in the cold, with the theoretical quantity of potassium dichromate. A greenish-blue liquid is formed, from which the iodide of phenylene-blue may be precipitated by the addition of potassium iodide solution. This salt forms long needles with a green metallic lustre. It is soluble in water with a greenish-blue colour, which turns into green on the addition of mineral acids. Acid solutions decompose very rapidly, a considerable quantity of *p*-quinone being formed in this decomposition. On reduction phenylene-blue yields di-*p*-aminodiphenylamine, from which phenylene-blue may be regenerated by simple oxidation. Phenylene-blue is transformed into safranine on being boiled in a neutral solution with aniline hydrochloride (*v. Safranine*).

Literature.—R. Nietzki, Ber. 1883, 16, 464; R. Nietzki, Organ. Farbstoffe, 5th ed. 1906, 200.

Tetramethyl derivative of Phenylene-blue (*Dimethylphenylene-green*).

$C_{16}H_{20}N_3Cl$. Constitution



$$\begin{array}{l} C_6H_4-N\!<\!\begin{array}{l}CH_3\\CH_3\end{array} \\ \vert \\ N \\ \Vert \\ C_6H_4=N\begin{array}{l}\diagup CH_3\\ \cdot CH_3\\ \diagdown Cl\end{array} \end{array}$$

This interesting compound, which is the completely methylated derivative of the preceding one, is formed by the joint oxidation of *asym*-dimethyl-*p*-phenylenediamine with dimethylaniline, in equal molecules, with potassium dichromate in the presence of zinc chloride (Bindschedler, Ber. 13, 207). The zinc double salt is at once deposited from the liquid. According to the quantity of zinc chloride present the crystals are either of a copper colour or have a metallic green lustre. These crystals are freely soluble in pure water, with a fine green colouration. Potassium iodide precipitates from this solution the phenylene-green iodide $C_{16}H_{20}N_3I$ in beautiful green needles, which are easily soluble in pure water, very insoluble in the presence of an excess of potassium iodide. The platinum double chloride has the composition $(C_{16}H_{20}N_3Cl)_2PtCl_4$; dimethylphenylene-green is more stable than the majority of indamines. On reduction it yields tetramethyldiaminodiphenylamine from which the green may be regenerated by oxidation.

Dimethylphenylene-green dyes silk and other fibres a yellowish shade of green. It has, however, found no application as a colouring matter, being rather unstable to light.

Its solution, on being boiled with the solution of an equal molecule of the hydrochloride of a primary amine, yields the corresponding safranine. (Also *Safranine.*)

Literature.—Bindschedler, Ber. 13, 207; R. Nietzki, *ibid.* 16, 464; Bindschedler, *ibid.* 16, 865.

Diethylphenylene-green $C_{20}H_{28}N_3Cl$ is obtained by oxidising diethyl-*p*-phenylenediamine with diethylaniline in the presence of mercuric chloride. Very similar to the methyl derivative, but less stable.

Literature.—Bindschedler, Ber. 16, 867.

Homologues of phenylene-blue. These are formed by the joint oxidation of *p*-phenylenediamine and the homologues of aniline or of *p*-tolylenediamine with aniline and its homologues. They play an important part in the manufacture of the commercial safranines, in which they are obtained as intermediate products.

Literature.—O. N. Witt, J. Soc. Chem. Ind. 1882, 256.

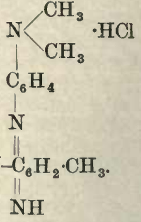
Witt's phenylene-violet $C_{12}H_{12}N_4{\cdot}HCl$. This substance is obtained by the joint oxidation of *p*-phenylenediamine with *m*-phenylenediamine. Its aqueous solution, which exhibits a fine purple shade, is decomposed on boiling, when a corresponding diamino-azine or eurhodine is formed. Similar compounds are obtained by the joint oxidation of other *p*-diamines with *m*-phenylenediamine. This reaction is, therefore, applicable as a test for both *p*- and *m*-diamines.

Witt's phenylene-blue $C_{14}H_{16}N_4{\cdot}HCl$. The dimethyl derivative of the preceding substance is formed either by the joint oxidation of dimethyl-*p*-phenylenediamine and *m*-phenylenediamine hydrochloride, or by mixing together lukewarm solutions of nitrosodimethylaniline hydrochloride and *m*-phenylenediamine, both dissolved in glacial acetic acid. It forms bronze-coloured crystals, readily soluble in water, with a purplish-blue shade. On the addition of mineral acids unstable diacid salts of a yellowish-brown colour are formed. The aqueous solution is decomposed by prolonged boiling, yielding neutral violet, a colouring matter of the eurhodine group (*v. Safranine*).

Literature.—Otto N. Witt, D. R. P. 15272, 1880; Eng. Pat. 4846, 1880.

Tolylene-blue $C_{15}H_{18}N_4{\cdot}HCl$

Constitution



This is the most thoroughly investigated member of the group. It is formed by the action of oxidising agents upon a mixture of dimethyl-*p*-phenylenediamine and *m*-tolylenediamine, or by the direct combination of nitrosodimethylaniline hydrochloride and free *m*-tolylenediamine. It is best prepared by the latter method. On mixing lukewarm aqueous solutions of the two ingredients in the proportion of equal molecules the blue is formed at once, and on cooling settles out in the shape of glistening bronze-coloured crystals which have the composition $C_{15}H_{18}N_4{\cdot}HCl$. On adding hydrochloric acid to an aqueous solution of this compound a much more soluble diacid salt

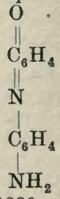
$$C_{15}H_{18}N_4{\cdot}2HCl,$$

of a reddish-brown colour, is formed. By the action of reducing agents, especially stannous chloride, the leuco derivative of tolylene-blue, dimethyltriaminotolylphenylamine $C_{15}H_{20}N_4$ is formed. An aqueous solution of the blue is decomposed by prolonged ebullition. The products of this decomposition are leucotolylene-blue and dimethyldiaminotoluphenazine (*Tolylene red, v.* Azines).

Literature.—Otto N. Witt (Ber. 12, 931; Chem. Soc. Trans. 1879, 356; D. R. P. 15272, 1880; J. Soc. Chem. Ind. 1882, 256). R. Nietzki (Ber. 16, 1883, 475).

II. Indophenols.

The simplest *indophenol* $C_{12}H_{10}N_2O$



$$\begin{array}{c} O \\ \| \\ C_6H_4 \\ \| \\ N \\ | \\ C_6H_4 \\ | \\ NH_2 \end{array}$$

was prepared in 1880 and described by the inventors, Horace Köchlin and Otto N. Witt in their fundamental patents: D. R. P. 15915, Amer. Pat. 261518, Fr. Pat. 141843, Eng. Pat. 1373, 5249, 1881. It may be obtained by any of the processes indicated for the purpose by theory (see above, modes of formation). The best method for its preparation is the joint oxidation of *p*-phenylenediamine and phenol dissolved in water in equimolecular proportions with oxidising agents, which act in a neutral or alkaline solution, such as sodium ferricyanide, potassium persulphate, or hypochlorites. The last-named are exclusively used in industrial work. The dyestuff, which is of a reddish-blue shade, settles out at once. It is, however, very impure and contains other colouring matters which are formed by the condensation of part of the indophenol formed into more complicated indophenols of a higher molecular weight. According to the D. R. PP. 179294 and 179295, this is not the case if lead or manganese peroxides be used as an oxidising agent. Another method, indicated in the D. R. PP. 160710 and 168229 consists in oxidising a mixture of phenol with the monoacetyl or the monoaryl sulphonic derivatives of *p*-phenylenediamine and subsequent decomposition with alkali.

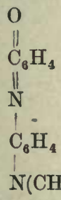
This dyestuff is insoluble in water, easily soluble in alcohol, ether, or benzene. Acids dissolve it readily with a yellow colour. The solution is quickly decomposed on standing.

A very similar dyestuff of a bluer shade may be obtained by the joint oxidation of a mixture of *p*-phenylenediamine and *p*-xylenol in molecular proportions.

Other nearly allied indophenols are prepared by the joint oxidation of *o*-toluidine and *p*-aminophenol (Cassella and Co., D. R. P. 199963, 1901); and by the action of nitrosophenol upon *p*-chloro-*o*-nitrodiphenylamine (Kalle & Co., D. R. P. 205391, 1907).

All these indophenols are extremely similar in their properties. Notwithstanding the intensity and beauty of their blue colouration they have not acquired any importance as practical dyestuffs, probably because they are so easily attacked and decomposed by mineral acids. But in later years they have assumed great importance as raw materials for the manufacture of very fast blue sulphur dyes and this has caused the appearance of numerous patents for the production of such indophenols, the more important of which only can be mentioned in this article.

Dimethyl derivative of simplest indophenol, $C_{14}H_{14}N_2O$,

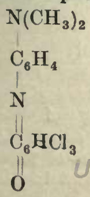


$$O=C_6H_4=N-C_6H_4-N(CH_3)_2$$

is obtained like the preceding compounds by joint oxidation from a mixture of phenol and dimethyl-*p*-phenylenediamine or by oxidising a mixture of dimethylaniline and *p*-aminophenol; it crystallises from alcohol in glistening green needles. Its alcoholic solution is of a brilliant greenish blue colour.

Literature.—Horace Köchlin and Otto N. Witt, D. R. P. 15915, 1881. Leop. Cassella & Co., second addition to D. R. P. 15915.

Dimethyl-trichloroindophenol $C_{14}H_{11}Cl_3N_2O$,



$$(CH_3)_2N-C_6H_4-N=C_6HCl_3=O$$

is obtained by mixing alcoholic solutions of trichloroquinonechloroimide (1 mol.) and dimethylaniline (2 mol.), according to the equation:

$$C_6HCl_3(NCl)O+2C_6H_5{\cdot}N(CH_3)_2$$
$$=C_{14}H_{11}Cl_3N_2O+C_6H_5N(CH_3)_2HCl.$$

Recrystallised from alcohol, it forms long green glistening needles, which have the general character of the indophenols and are comparatively stable. On reduction it yields the corresponding leuco compound, dimethylaminohydroxytrichlorodiphenylamine, $C_{14}H_{13}Cl_3N_2O$.

Literature.—Schmitt and Andresen (J. pr. Chem. [ii.] 24, 435).

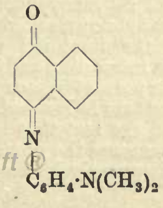
Carbazole indophenol. This curious substance, which has been obtained by Cassella & Co. according to mode of formation No. 8 from carbazole and nitrosophenol has evidently the constitution:

It is of great importance because on being heated with polysulphides it yields *hydron blue*, a sulphur dye insoluble in sodium sulphide solution, but capable of being used in the vat in exactly the same way as indigo and giving deep blue shades which are quite as fine and fast as those obtained with indigo itself. It is therefore expected to become a serious competitor of indigo blue. (*See* INDIGO, ARTIFICIAL, and INDIGOID DYESTUFFS; VAT DYES, MODERN.)

All the indophenols mentioned so far have this in common, that they are derivatives of *p*-quinone, and this accounts for the similarity of their properties and chemical behaviour.

A marked difference in this respect is shown by the indophenols which are derived from naphthaquinone which is itself less reactive and consequently more stable than the benzene derivative. This stability also shows itself in the naphthindophenols which can therefore claim to be applicable and even valuable dyestuffs.

Although a large number of these substances is foreseen by theory, the only well-known member of the group is the one first discovered, the *typical indophenol of commerce* $C_{18}H_{16}N_2O$ (vat blue, Küpenblau), the structure of which is expressed by the constitutional formula



It was discovered in 1880 by Horace Köchlin and Otto N. Witt and described in their fundamental indophenol patents already mentioned.

It is prepared from an alkaline mixture of dimethyl-*p*-phenylenediamine and α-naphthol in molecular proportions by oxidation. On a small scale potassium ferricyanide or ammonium persulphate is the most convenient oxidising agent, whilst on the manufacturing scale air is blown through the liquid, or a solution of sodium hypochlorite is employed. It may also be prepared by adding potassium chromate to the alkaline mixture of the ingredients and acidifying with acetic acid. Another process consists in simply heating on the water-bath an alcoholic solution of free nitrosodimethylaniline and sodium α-naphthoxide; or in bringing together, in an aqueous solution, α-naphthol, nitrosodimethylaniline, and caustic soda; this mixture is rapidly transformed into indophenol if a small quantity of a reducing agent, such as sodium stannite or glucose, be added.

Indophenol forms a dark-blue microcrystalline powder with a coppery metallic lustre, exactly resembling indigo. It is quite insoluble in water, sparingly soluble in spirit, ether, or benzene. It dissolves in dilute mineral acids, forming salts of a yellow colour, which are, however, quickly decomposed. In this decomposition α-naphthaquinone is formed as one of the products. Indophenol is slightly volatile; on being strongly heated it forms a sublimate resembling sublimed indigo. By reducing agents it is transformed into its leuco derivative

$$C_{18}H_{18}N_2O,$$

dimethylaminophenylhydroxynaphthylamine. This has been an article of commerce under the name of indophenol-white. It is quite stable in an acid state, but in the presence of alkalis it rapidly absorbs the oxygen of the air, indophenol being regenerated.

The application of indophenol to dyeing and calico-printing is based either on the formation of the dyestuff on the fibre, or on the oxidation of its ready-formed leuco derivative after fixing the latter on the fibre. The first method is rarely employed. As an example the following description, taken from the patent specification, may serve. Bleached calico is printed with a thickened mixture of aminodimethylaniline and sodium α-naphthoxide; after drying and steaming it is passed through a solution of potassium dichromate, when the blue is instantaneously developed. As a rule ready-formed indophenol is employed for printing, reduced by being mixed with a solution of stannous acetate, then thickened with starch paste and printed on the fibre. The colour is developed by steaming and exposure to the air. Indophenol-blue on calico is very fast to the action of soap, fairly so to the action of light, but rather susceptible to acids.

In spite of its many good qualities, indophenol at first did not meet with an enthusiastic reception in the tinctorial world. This was changed by an interesting and for its time (about 1885–1895) important discovery of the Swiss manufacturing firm L. Durand, Huguenin & Co. It is based on the fact that indophenol, mixed with indigo, assumes the properties of the latter and may consequently be used in the vat process, especially with hydrosulphite as a reducing agent.

It is more than probable that the two leuco compounds of indigo and indophenol are capable of combining chemically and that the resulting substance is endowed with strong affinities for the fibre, especially cotton. It is thus easily taken up from the vat and, on being reoxidised on the fibre, deposits in the molecular interstices of the latter an intimate mixture or even a chemical combination of the two dyestuffs, indigo and indophenol.

An intimate mixture of indigo and indophenol, ground together into an impalpable powder is the 'vat blue' or 'küpenblau' of commerce, which may still occasionally be met with, although it has lost many of its advantages by the great reduction in the price of indigo and by the introduction of the cheap and excellent dark-blue sulphur dyes, many of which are also capable of being applied in the vat.

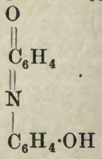
Literature.—Otto N. Witt and Horace Köchlin, D. R. P. 15915, 1881, with several additions; and corresponding patents in England, France, the United States, Sweden, Belgium, and Austria; Otto N. Witt, J. Soc. Chem. Ind. 1882, 144, 225, 405; R. Möhlau, Ber. 16, 2845.

III. Acid Indophenols.

It has already been mentioned that these substances are not true acids, containing no carboxyl groups in their molecule. They owe their name to the fact that, containing no amino and several hydroxyl groups, they readily combine and form stable salts with metallic oxides. Of these only the alkali salts are known. In a solid state they form crystalline powders with a green or copper-coloured metallic lustre. They are easily soluble in water with an intense blue colouration. By the addition of acids the free indophenols are deposited in the shape of brown or reddish flakes, which are soluble with a dark red colour in spirit, ether, benzene, and analogous solvents.

The acid indophenols show in even a higher degree the tendency of the whole group to polymerise into colouring matters of a more complex molecule. It is therefore extremely difficult to prepare them in a state of purity. On the other hand, they do not show the susceptibility to acids so characteristic of the indamines and typical indophenols. It is therefore possible to prepare them not only in alkaline but also in acid solutions and by means of oxidising agents which act in such. Their modes of formation are given above under methods 4, 6, 7, 12, and 15.

Typical acid indophenol $C_{12}H_9NO_2$,

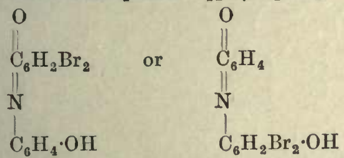


$$\begin{array}{c} O \\ \| \\ C_6H_4 \\ \| \\ N \\ | \\ C_6H_4{\cdot}OH \end{array}$$

The possibility of preparing this compound by the joint oxidation of *p*-aminophenol and phenol is mentioned in Köchlin and Witt's fundamental indophenol patents, but its manufacture seemed at first to offer no interest It is formed if quinoneimide is brought into contact with phenol, and R. Hirsch observed it on adding caustic potash to a solution of quinonechloroimide in phenol, but did not succeed in isolating it (Ber. 13, 1909). The cause of these difficulties was revealed by the D. R. P. 157288 of the Actiengesellschaft für Anilinfabrikation of Berlin. The formation of the dyestuff must take place at unusually low temperatures if its tendency for polymerisation in a nascent state is to be overcome. According to this patent, the product may be prepared with a good yield if an equimolecular mixture of phenol and *p*-aminophenol be oxidised with sodium hypochlorite at a temperature of −15° to −18°, preferably in solutions saturated with sodium chloride so that the sodium salt of the dyestuff is at once salted out of the liquid. It is thus obtained in the shape of glistening metallic green needles.

These dyestuffs become more stable and are therefore more easily prepared if their molecule be weighted by the introduction of various substituents:

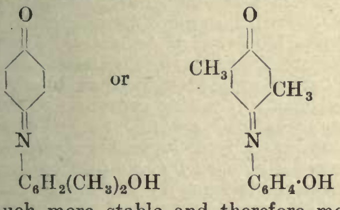
Acid dibromoindophenol $C_{12}H_7Br_2NO_2$,



$$\begin{array}{c} O \\ \| \\ C_6H_2Br_2 \\ \| \\ N \\ | \\ C_6H_4{\cdot}OH \end{array} \quad \text{or} \quad \begin{array}{c} O \\ \| \\ C_6H_4 \\ \| \\ N \\ | \\ C_6H_2Br_2{\cdot}OH \end{array}$$

(See remarks on migration under 2 and 5.) has been prepared in various ways by R. Möhlau (Ber. 16, 2843). It may either be obtained by the joint oxidation of a mixture of dibromoaminophenol and phenol in molecular proportions, or by adding dibromo-quinonechloroimide, suspended in alcohol, to an alkaline solution of phenol. The sodium salt of the indophenol separates out in green glistening needles, which are soluble in water and alcohol with a pure blue colour. On adding acetic acid to the solution the free indophenol settles out in dark-red, almost black prisms with a metallic lustre. It is soluble in alcohol with a magenta colour. Mineral acids decompose this compound into dibromo-aminophenol and *p*-quinone. If a current of sulphur dioxide be introduced into the solution of the sodium indophenolate, the corresponding leuco compound $C_{12}H_9Br_2NO_2$, dihydroxydibromodiphenylamine, is formed. It crystallises in white glistening needles, melting at 170°.

Acid dimethylindophenol $C_{14}H_{13}NO_2$,



is also much more stable and therefore more easily prepared than the typical acid indophenol. This was shown in 1902 by L. Cassella & Co. in their D. R. P. 191863 and the corresponding Eng. Pat. 4653, 1902; 2617, 1902. According to these patents, 1:4:5-(*p*-) xylenol and *p*-aminophenol give a good yield of this dyestuff if subjected to joint oxydation in equimolecular proportions.

All these acid indophenols have assumed a new interest and are being largely investigated, since it has been shown that they are valuable raw materials for the manufacture of the sulphur dyes which have come so much to the front in these later years. O. N. W.

INDANE *v.* INDENE.

INDANTHRENE. Within recent years, considerable advances have been made in the discovery and commercial production of certain compounds belonging to the class of the vat dyes. By the term 'vat dye' is understood an insoluble pigment which, when reduced by an alkaline reducing agent, passes into a hydro derivative soluble in the alkaline reducing solution. The hydro derivative is absorbed by fabrics steeped in this solution and is then reconverted into the pigment when the material is exposed to the oxidising action of the air. Indigo, the most important of all colouring matters, is a typical vat dye, and it is apparent that the process entailed by the use of these colours not only produces the shades fastest to light and washing but is also one of the simplest with which the dyer has to deal.

For many years research on the formation of new vat dyes was confined to the indigo group, but in the year 1901 it was demonstrated by R. Bohn that certain derivatives of anthraquinone could be applied for this purpose. The vat dyes of this series possess, however, one important property which distinguishes them from all other members of the class, that is, the vat formed by the alkaline reduction of the pigment is always strongly coloured. The hydro derivatives are, therefore, themselves coloured substances, whereas the hydro derivatives from other vat dyes, for example indigo white, are colourless or at most faintly yellow.

The vat dyes of the indanthrene series may be conveniently divided into five groups:—

(1) Indanthrene.
(2) Flavanthrene.
(3) Benzanthrone colours.
(4) Anthraquinoneimide colours.
(5) Acyl derivatives of aminoanthraquinone.

Indanthrene: *Preparation* (R. Bohn, D. R. P. 129845; Zusatze, 129846, 129847, 129848, 135407, 135408, 138167, 155415, 210223, and 216891; Scholl and Berblinger, Ber. 1903, 36, 3427).

The colouring matter is prepared by fusing β-aminoanthraquinone with caustic potash at 200°–300° and is found in the melt as the soluble potassium salt of the blue hydro derivative of indanthrene which, when dissolved in water with free access of air, is converted into the insoluble blue colouring matter. At a lower temperature (150°–200°) alizarin is formed at the same time as indanthrene, but at the higher temperature this is transformed into a brown substance soluble in alkali; the separation of the blue colouring matter is, therefore, simple owing to its insolubility in the alkaline liquid. Whether produced at the higher or lower temperature, the indanthrene is not a homogeneous substance but consists of two compounds, indanthrene A and indanthrene B, the latter being worthless as a colouring matter. It is possible so to regulate the conditions as to cause indanthrene A to be the chief product; thus, when the fusion is carried out in the presence of potassium nitrate the product consists almost entirely of indanthrene A, and indanthrene B is only formed in small amount. By fusing β-aminoanthraquinone with caustic potash at a still higher temperature, that is at 330°–350°, the product is a yellow vat dye, flavanthrene (*v. infra*).

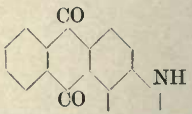
500 grams of caustic potash together with a little water are placed in a nickel basin which is heated by means of an anthracene bath. The melt is then heated to 200° and mixed with 20 grams of potassium nitrate; 100 grams of β-aminoanthraquinone are now gradually added with constant stirring. The temperature is raised to 250° and maintained at this point for half an hour when the melt is poured into water, the solution boiled, and the precipitated colour filtered and washed. The small quantity of indanthrene B present in the product is separated by taking advantage of the greater solubility of its hydro derivative in dilute alkali. 100 grams of the crude indanthrene in the form of paste are diluted with 10 litres of water and warmed to 60°–70°; 200 grams of a 25 p.c. caustic soda solution and 1500 grams of sodium hydrosulphite solution (sp.gr. 1·074) are then added and the temperature of the mixture maintained at 60°–70° for 1 hour. By this time the colour will have completely dissolved, and the solution, when cooled, will slowly deposit the sodium salt of the hydro derivative of indanthrene A as well-defined glistening needles with marked copper reflex. The salt is collected by filtration, washed with a little dilute caustic soda solution to which a small quantity of hydrosulphite solution has been added, and is then converted into pure indanthrene A by dissolving in hot water and allowing free access of air. The brown-red mother liquor contains the more soluble salt of the hydro derivative of indanthrene B from which the colour separates as blueish-green flocks when air is led into the solution.

Indanthrene prepared in this manner is a dark blue powder with strong metallic reflex, and is practically insoluble in all the usual solvents. It dissolves with great difficulty in boiling aniline and in nitrobenzene, in the latter case to the extent of one part in 5000, forming a greenish blue solution. It dissolves to the extent of 1 part in 500 in boiling quinoline, forming a blue solution from which the colour separates as characteristic curved needles resembling pure indigo in appearance; the solutions are without fluorescence. When heated it partly sublimes in the form of its characteristic needles and then decomposes with charring between 470° and 500°.

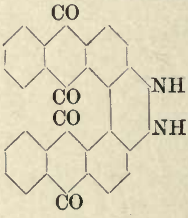
Constitution of indanthrene (Scholl, Ber. 1903, 36, 3410). Indanthrene as shown by its elementary analysis and molecular weight determination by the ebullioscopic method in quinoline has the molecular formula $C_{28}H_{14}O_4N_2$ and is therefore formed by the condensation of two molecules of β-aminoanthraquinone with loss of 4 atoms of hydrogen.

$$2C_{14}H_9O_2N - 4H \rightarrow C_{28}H_{14}O_4N_2.$$

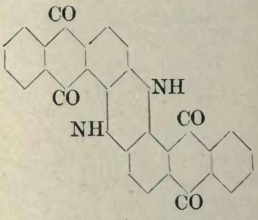
That these 4 hydrogen atoms are not removed from the amino groups alone—in other words, that an azo compound is not formed—is shown by the fact that indanthrene when reduced does not yield β-aminoanthraquinone or a reduction product of this base. Moreover, as indanthrene no longer contains a free amino group, it is probable that two of these hydrogen atoms are supplied by the two amino groups and that the other two belong to the rings bearing the amino groups in the two molecules of β-aminoanthraquinone taking part in the reaction. From the fact that 1:2-dihydroxyanthraquinone (alizarin) is always a product of the fusion in its earlier stages, it is reasonable to assume that the hydrogen atoms removed from the two rings are those in the ortho position to the two amino groups. This leads to two formulæ for indanthrene, namely—



β-Aminoanthraquinone residue.



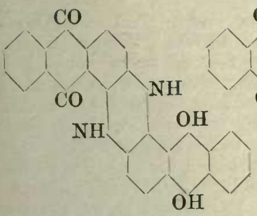
(1)



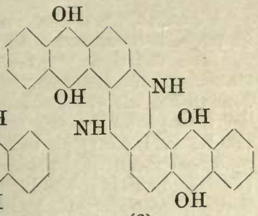
(2)

Since indanthrene is not reduced to a diamine, which would be the case if it possessed an ortho diazine formula represented by (1), it follows that it must be a dihydro paradiazine represented by formula (2), or in other words, that it is *N*-dihydro-1:2:2′:1′-anthraquinoneazine. This view of the structure of indanthrene is completely upheld by its chemical behaviour. It has been suggested by Nietzki (Chemie der Organ. Farbstoffe, 5 Aufl. S. 121, 1906) that the formation of indanthrene is due to the intermediate production of 1-hydroxy-2-aminoanthrahydroquinone, two molecules of which combine to form tetrahydroindanthrene. This has, however, been disproved by Scholl, Berblinger, and Mansfield (Ber. 1907, 40, 320), who find that neither 1-hydroxy-2-aminoanthrahydroquinone nor 1-hydroxy-2-aminoanthraquinone yields indanthrene when fused with potash.

Properties of indanthrene.—When indanthrene in dilute alkaline solution is heated at 40°–50° with sodium hydrosulphite, it passes into a blue hydro derivative, dihydroindanthrene. This substance possesses the property of dyeing unmordanted cotton blue, and when the fibre so dyed is exposed to the oxidising action of the air the hydro derivative is reconverted into indanthrene. When indanthrene is reduced by zinc dust, a brown hydro derivative is formed; this hydro derivative is also converted into indanthrene on exposure to the air. Scholl, Steinkopf, and Kabacznik (Ber. 1907, 40, 390) have shown that the blue substance is *N*-dihydro-1:2:2′:1′-anthraquinoneanthrahydroquinoneazine (1), and that the brown solution contains *N*-dihydro-1:2:2′:1′-anthrahydroquinoneazine (2)



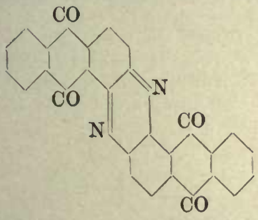
(1)
Blue hydro derivative.



(2)
Brown hydro derivative.

The compound commercially known as indanthrene S is the disodium salt of formula 2, and this is the substance which is always formed in the indanthrene vat.

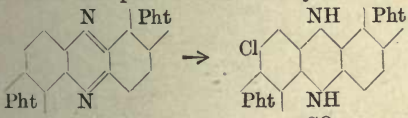
When indanthrene is oxidised by nitric acid (sp.gr. 1·24), it is converted into the yellow 1 : 2 : 2′ : 1′-anthraquinoneazine (Scholl and Berblinger, Ber. 1903, 36, 3427; *cp.* Scholl, Berblinger, and Mansfield, *ibid.* 1907, 40, 321).

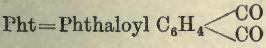


This substance is reconverted into indanthrene on reduction, a reaction which may be effected by means of direct sunlight.

Indanthrene is one of the most stable substances known; sodium hypochlorite, which destroys most colouring matters such as the alizarins, indigos, &c., merely converts indanthrene into the above yellow azine, which can be readily reconverted into indanthrene by means of sodium hydrosulphite.

When halogen atoms enter the molecule of indanthrene, the shade becomes greener. Indanthrene blue GC (D. R. P. 138167) is a bromindanthrene; indanthrene blue GCD and CE are chloro derivatives (D. R. P. 155415). Monochlorindanthrene is prepared by the action of boiling concentrated hydrochloric acid on anthraquinoneazine whereby chlorination and reduction take place simultaneously—





$$\text{Pht}=\text{Phthaloyl } C_6H_4{<}\begin{matrix}CO\\CO\end{matrix}$$

The reaction is analogous to the formation of chlorhydroquinone from quinone and hydrochloric acid. Owing to the alkali required in the preparation of the indanthrene vat, this substance cannot be used for the dyeing of wool. The sulphonic acid (D. R. P. 216891) can be employed, however, for this purpose. The blue produced on cotton by the aid of indanthrene is one of the fastest known. (For the method of dyeing compare D. R. P. 139834; for printing, compare D. R. P. 132402, 140573.)

Flavanthrene (indanthrene yellow). As already mentioned, flavanthrene was discovered by R. Bohn (D. R. P. 138119), in the products formed by the fusion of β-aminoanthraquinone with potash. At the present time it is prepared by treating β-aminoanthraquinone with antimony pentachloride in boiling nitrobenzene. (*V.* art. FLAVANTHRENE.)

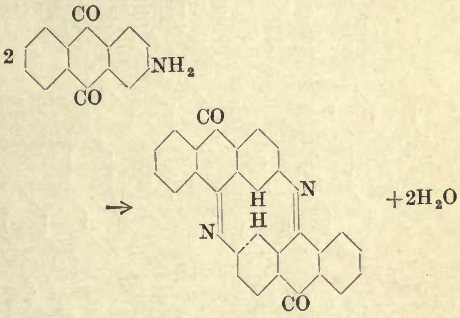
When reduced by alkaline hydrosulphite, flavanthrene yields a violet-blue vat in which cotton is dyed a deep blue; when exposed to the oxidising action of the air the colour changes, in the course of a few minutes, to the light yellow of flavanthrene.

Preparation.—Ten grams of β-aminoanthraquinone are gradually added to a solution of 35 grams anhydrous antimony pentachloride in 100 grams nitrobenzene, heated at 60°–80°. The mixture is then heated to the boiling-point and maintained at this temperature for one hour, the containing flask being without a condenser. The yellow-brown solution deposits, on cooling, chemically pure flavanthrene as brownish-yellow needles.

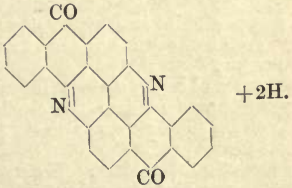
The constitution of flavanthrene has been determined by Scholl (Ber. 1907, 40, 1691). The molecular formula is $C_{28}H_{12}O_2N_2$, and it must therefore be formed from β-aminoanthraquinone in accordance with the equation

$$2C_{14}H_9O_2N \rightarrow C_{28}H_{12}O_2N_2+2H+2H_2O.$$

The two molecules of water formed in the reaction at once suggest the interaction of the hydrogen atoms of the amino groups with the carbonyl oxygens, an assumption which leads to the following formula:—

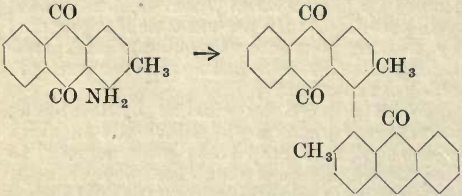


The ring then closes thus:



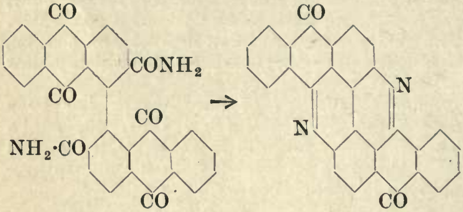
The hydrogen thus formed is not eliminated in the free condition, but reduces the colour to the dihydro base, the state in which it always occurs in the melt.

This view of the constitution of flavanthrene has been confirmed by Scholl by the actual synthesis of this substance in the following way: 2-methyl-1-aminoanthraquinone (1) is converted into 2 : 2′-dimethyl-1 : 1′-dianthraquinonyl (2) either by heating the corresponding iodide with copper powder or by the action of copper powder and acetic anhydride on the diazonium sulphate:



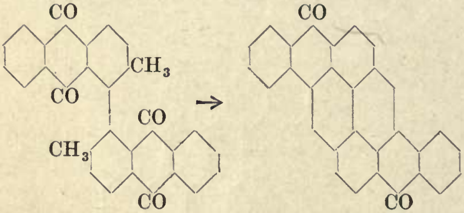
(1) (2)

This substance is then oxidised to the dicarboxylic acid which is converted, through the acid chloride, into the acid amide (3). An attempt to prepare the amino compound from this by the action of bromine and potash led to the formation of flavanthrene :



(3)

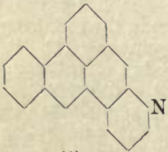
Pyranthrene (indanthrene golden orange) (D. R. P. 175067 ; Ber. 1910, 43, 346 ; R. Scholl). This substance is a valuable orange vat dye which is formed by the elimination of two molecules of water from 2:2′-dimethyl-1:1′-dianthraquinonyl (formula (2) above). It differs from flavanthrene in having two methin groups in place of the azine nitrogen atoms :



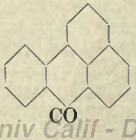
The condensation proceeds readily in the presence of a dehydrating agent such as zinc chloride or by merely heating alone at 350°–380°. Pyranthrene forms a magenta red vat with alkaline hydrosulphite in which cotton is dyed a deep red ; on exposure to the air this oxidises to a fast orange.

The entrance of halogen atoms into the molecule of pyranthrene reddens the shade and of these derivatives dibromopyranthrene (D. R. P. 218162) is the most red.

The benzanthrone colours. The vat colours of this class were discovered by O. Bally (Ber. 1905, 38, 194 ; D. R. P. 176018), who found that when the Skraup quinoline synthesis was applied to 2-aminoanthraquinone, two glycerol residues entered into the molecule, forming benzanthronquinoline (1) :



(1)



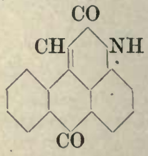
(2)

When this reaction was applied to anthraquinone, benzanthrone (2) was formed.

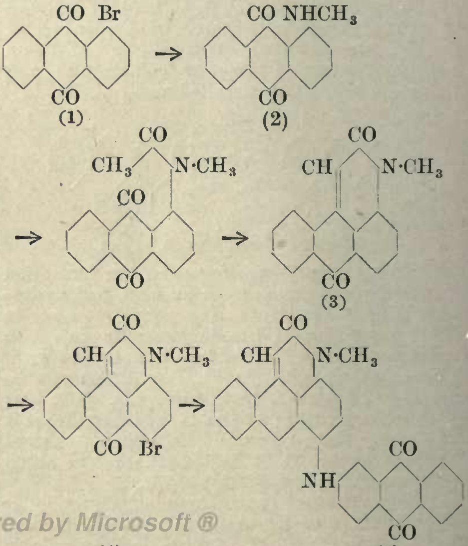
Blue vat dyes are formed from these substances on fusion with potash, two molecules condensing with loss of four atoms of hydrogen. To this group belong indanthrene dark blue (D. R. P. 185221) as well as its isomeride and halogen substitution product, indanthrene violet (D. R. PP. 177574, 194252, 217570); indanthrene green (D. R. P. 185222) is an amino-derivative of indanthrene dark blue ; if the last-named colour is strongly chlorinated a deep, very fast black is formed. Cyananthrene and violanthrene also belong to this group.

Colours derived from anthraquinoneimide. These colours consist of several anthraquinone residues joined together in much the same manner as in flavanthrene. They are, for the most part, trianthraquinonediimides and their substitution products which are formed by the condensation of aminoanthraquinones and halogenanthraquinones. Indanthrene Bordeaux (D. R. PP. 184905 and 206717) and indanthrene red (D. R. P. 197554) belong to this group.

Acyl derivatives of aminoanthraquinone. Colours of this group are derived from anthraquinonepyridone :



by the replacement of the hydrogen atom in the para- position to the imino group by arylamino residues. Thus algol red is formed when 1-bromanthraquinone (1) is converted into methyl-1-aminoanthraquinone (2) by means of methylamine. This is acetylated and condensed to *N*-methylanthraquinonepyridone (3), which is then brominated, yielding 4-brom-*N*-methylanthraquinonepyridone (4), and this, on condensation with 2-aminoanthraquinone, yields algol red (5) :



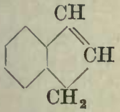
(1) (2) (3) (4) (5)

Other members of this class are algol yellow, algol rose, algol scarlet, algol green, algol blue, and algol brown. They all yield coloured vats with sodium hydrosulphite in which cotton is dyed the colour of the dihydro derivative; on exposure to the air the colour on the fibre is quickly oxidised to the algol dye.

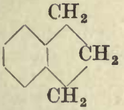
The following indanthrene colours are formed from anthraquinone derivatives by the aid of various reactions, but have not as yet had a definite constitution assigned to them. Indanthrene maroon (D. R. P. 160814) and indanthrene grey (D. R. P. 157685) are derived from diaminoanthraquinones. Indanthrene orange and indanthrene copper (D. R. P. 198048) are prepared from the acetyl derivatives of aminoanthraquinone by means of phosphorus oxychloride. Cibanon yellow, cibanon orange, and cibanon brown, are derived from methylanthraquinone and its derivatives. J. F. T.

INDAZINE *v.* AZINES.

INDENE. The compounds of the indene group are derived from the hydrocarbons indene and hydrindene



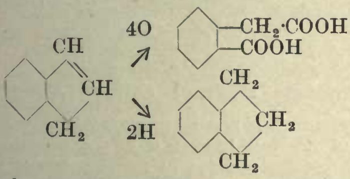
Indene.



Hydrindene.

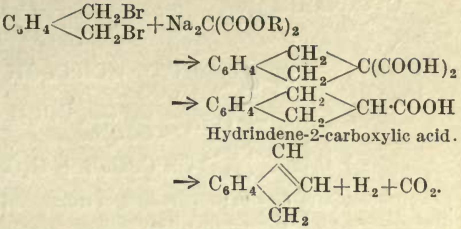
by the replacement of the hydrogen atoms either in the five-membered ring or in the aromatic nucleus. They therefore yield two classes of derivatives: (1) Those of aromatic character which are formed when the hydrogen atoms of the benzene ring are substituted. (2) Those of aliphatic character which are produced by the replacement of the hydrogen atoms attached to the five-membered ring.

Constitution.—The constitution of indene follows from its conversion into homophthalic acid by oxidation with permanganate:



and the structure of hydrindene is shown by the production of this substance from indene by reduction with sodium and alcohol.

Occurrence and preparation of indene and indene derivatives. Indene was isolated from coal-tar by Krämer and Spilker (Ber. 1890, 23, 3276) who obtained it from the higher boiling fraction of the light oil in which it occurs to the extent of about 30 p.c. It is formed, accompanied by hydrindene, in the dry distillation of paraindene $(C_9H_8)x$, a white substance which is formed when benzene containing indene is treated with concentrated sulphuric acid (Ber. 1900, 33, 2261). It has, moreover, been prepared synthetically by Perkin and Revay (Chem. Soc. Trans. 1894, 65, 228; *cp.* Kipping and Hall, *ibid.* 1900, 77, 469), by the distillation of barium hydrindenecarboxylate, a substance which can be prepared from *o*-xylylene dibromide by the following series of reactions.



$$C_6H_4\left<\begin{matrix}CH_2Br\\CH_2Br\end{matrix}\right. + Na_2C(COOR)_2$$

$$\rightarrow C_6H_4\left<\begin{matrix}CH_2\\CH_2\end{matrix}\right>C(COOH)_2$$

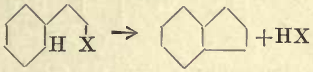
$$\rightarrow C_6H_4\left<\begin{matrix}CH_2\\CH_2\end{matrix}\right>CH{\cdot}COOH$$

Hydrindene-2-carboxylic acid.

Owing to the ease with which the five-membered ring is usually formed, derivatives of indene and of hydrindene are readily produced from the corresponding benzene derivatives, having a side chain containing the requisite number of carbon atoms. The benzene derivatives which lend themselves to this change may therefore be divided into two classes: (1) those having one side chain of three carbon atoms; (2) those having two side chains, attached in the ortho position to the benzene nucleus, one of these side chains being composed of one carbon atom the other of two carbon atoms.

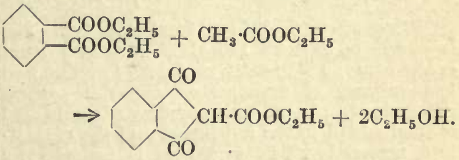
The derivatives of hydrocinnamic acid fall within the first class and a large number of indene compounds have been prepared from this substance and its derivatives (*v.* Miller and Rohde, Ber. 1902, 35, 1762).

The general character of this reaction may be expressed by the scheme

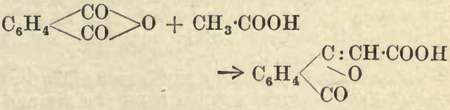


(X=halogen).

As an illustration of the formation of hydrindene derivatives by the method indicated under class (2), the formation of 1:3-diketohydrindene can be given. The ethyl salt of the carboxylic acid of this substance is formed when ethyl phthalate is condensed with ethyl acetate in the presence of sodium or sodium ethoxide (W. Wislicenus, Ber. 1887, 20, 593).



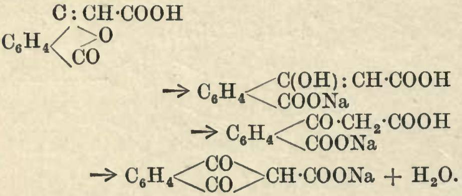
A curious molecular rearrangement, leading to the formation of hydrindene derivatives, has been discovered by Gabriel and Neumann (Ber. 1893, 26, 951). The condensation of phthalic anhydride and sodium acetate in the presence of acetic anhydride leads to the formation of phthalylacetic acid:



$$C_6H_4\left<\begin{matrix}CO\\CO\end{matrix}\right>O + CH_3{\cdot}COOH$$

$$\rightarrow C_6H_4\left<\begin{matrix}C{:}CH{\cdot}COOH\\ \quad >O\\ CO\end{matrix}\right.$$

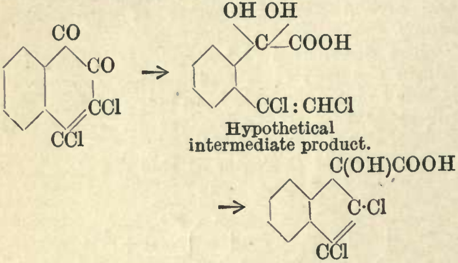
and this substance, when treated with sodium methoxide, passes into a derivative of 1:3-diketohydrindene. The reaction may be explained as follows:—



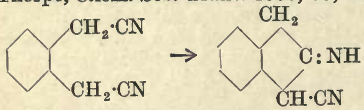
$$C_6H_4\!<\!\begin{matrix}C:CH\cdot COOH\\ \quad >O\\ CO\end{matrix} \rightarrow C_6H_4\!<\!\begin{matrix}C(OH):CH\cdot COOH\\ COONa\end{matrix} \rightarrow C_6H_4\!<\!\begin{matrix}CO\cdot CH_2\cdot COOH\\ COONa\end{matrix} \rightarrow C_6H_4\!<\!\begin{matrix}CO\\ CO\end{matrix}\!>\!CH\cdot COONa + H_2O.$$

It can be applied to the preparation of numerous derivatives of 1:3-diketohydrindene.

The formation of indene derivatives from compounds containing the naphthalene nucleus in which the stability of the ring is weakened by the presence of strongly negative groups has been investigated by Zincke and his pupils (Ber. 1886, 19, 2500; 1887, 20, 1265, 2894, 3216; 1888, 21, 491, 2381, 2379; 1894, 27, 744; Annalen, 1892, 267, 319; 1894, 283, 341; 1898, 300, 197). This type of reaction may be illustrated by the transformation of dichloro-β-naphthaquinone into dichlorohydroxyindene carboxylic acid by the action of caustic alkali.



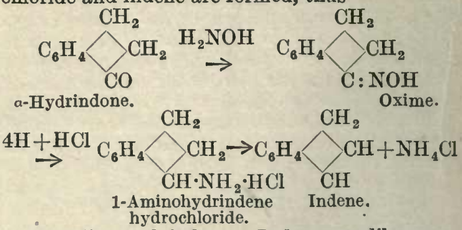
Derivatives of hydrindene can also be formed from ortho benzenoid dinitriles. Thus *o*-phenylenediacetonitrile passes into β-imino-α-cyanohydrindene when its solution in alcohol, containing a trace of sodium ethoxide, is warmed (Moore and Thorpe, Chem. Soc. Trans. 1908, 93, 165).

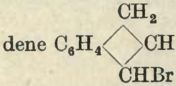


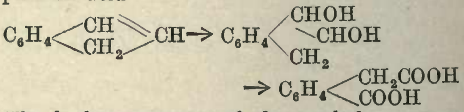
Preparation of indene from coal-tar. The fraction boiling at 176°–182° obtained from crude benzene is first titrated with bromine and the amount of unsaturated material present determined. A sufficient quantity of picric acid is then added to the hot liquid and the crystalline material which separates is isolated by filtration. The impure picrate is then distilled with steam, under which conditions the naphthalene picrate contained in it is only slowly decomposed whereas the indene picrate is readily transformed into indene which passes over with the steam. The crude hydrocarbon is then again converted into the picrate and the operation repeated until pure indene is obtained. Indene picrate forms golden yellow needles which melt at 98°.

Indene is a clear mobile liquid boiling at 179·5°–180·5° (corr.).

It is obtained pure only with great difficulty, as it rapidly absorbs oxygen from the air and when kept in a sealed vessel polymerises to a resin. The most convenient synthetic method for the preparation of indene is from α-hydrindone, the oxime of which passes on reduction into 1-aminohydrindene, and when the hydrochloride of this base is distilled, ammonium chloride and indene are formed, thus—

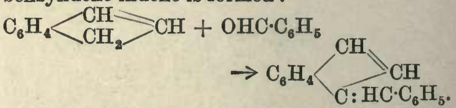


Reactions of indene. Indene readily combines with bromine, forming 1:2-dibromohydrindene  and when oxidised passes first into hydrindene glycol and then into homophthalic acid



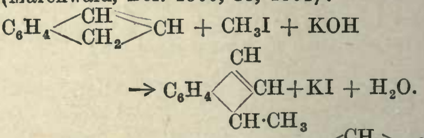
$$C_6H_4\!<\!\begin{matrix}CH\\ CH_2\end{matrix}\!>\!CH \rightarrow C_6H_4\!<\!\begin{matrix}CHOH\\ \quad CHOH\\ CH_2\end{matrix} \rightarrow C_6H_4\!<\!\begin{matrix}CH_2COOH\\ COOH\end{matrix}$$

The hydrogen atoms of the methylene group present in indene are reactive; thus, when the hydrocarbon is condensed with benzaldehyde, benzylidene indene is formed:



$$C_6H_4\!<\!\begin{matrix}CH\\ CH_2\end{matrix}\!>\!CH + OHC\cdot C_6H_5 \rightarrow C_6H_4\!<\!\begin{matrix}CH\\ \quad CH\\ C:HC\cdot C_6H_5.\end{matrix}$$

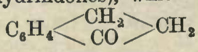
In fact, this grouping behaves in much the same manner as the corresponding complex in ethyl malonate and analogous compounds; thus, when indene is treated with methyl iodide and powdered alkali, methyl indene is formed (Marckwald, Ber. 1900, 33, 1504):



Hydrindene (Indane) $C_6H_4\!<\!\begin{matrix}CH_2\\ CH_2\end{matrix}\!>\!CH_2$.

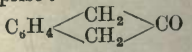
This hydrocarbon can be prepared by dissolving 1 part of indene in 10 parts of 90 p.c. alcohol and adding metallic sodium in small portions until the product is no longer converted into a resin by concentrated sulphuric acid. It is a mobile oil boiling at 176°–176·5° (corr.).

The ketones derived from hydrindene. The ketones derived from this substance may be classified as follows: (1) The mono-ketones (hydrindones), which comprise:



$$C_6H_4\!<\!\begin{matrix}CH_2\\ CO\end{matrix}\!>\!CH_2$$

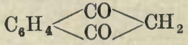
α-Hydrindone.



$$C_6H_4\!<\!\begin{matrix}CH_2\\ CH_2\end{matrix}\!>\!CO$$

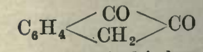
β-Hydrindone.

(2) **The di-ketones** (di-ketohydrindenes), which are



$$C_6H_4\!<\!\begin{matrix}CO\\ CO\end{matrix}\!>\!CH_2$$

1:3-Diketohydrindene.

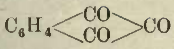


$$C_6H_4\!<\!\begin{matrix}CO\\ CH_2\end{matrix}\!>\!CO$$

1:2-Diketohydrindene.[1]

[1] This substance has been prepared by Perkin, Roberts and Robinson (Chem. Soc. Trans. 1912, 101, 232) from isonitroso-α-hydrindone (Kipping, *ibid.* 1894, 65, 492). It crystallises from benzene as golden yellow plates, m.p. 95°–115°, and gives a semicarbazone (m.p. 230°–233° with decomposition), an osazone (m.p. 230°–235°), and an indenoquinoxaline (m.p. 164°–165°).

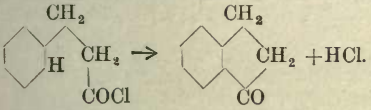
(3) The tri-ketone is



$$C_6H_4\left<\substack{CO\\CO}\right>CO$$

1 : 2 : 3-Triketohydrindene.

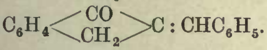
α-Hydrindone $C_6H_4\left<\substack{CH_2\\CO}\right>CH_2$. This substance is best prepared by the action of aluminium chloride on the chloride of hydrocinnamic acid in accordance with the following equation:—



It forms rhombic plates from dilute alcohol, melts at 40° and boils at 243°–245°. The oxime melts at 146° and the phenyl hydrazone at 130°–131°. The methylene group adjacent to the carbonyl group in α-hydrindone is reactive and derivatives of the ketone can be formed by the usual reagents. Thus amyl nitrite gives the oxime of 1 : 2-diketohydrindene

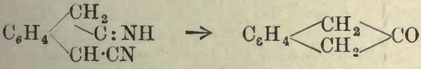
$$C_6H_4\left<\substack{CO\\CH_2}\right>C : NOH,$$

and the action of benzaldehyde leads to the formation of the benzylidene derivative



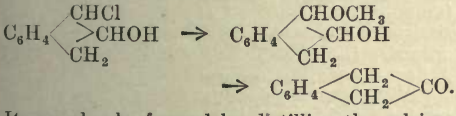
$$C_6H_4\left<\substack{CO\\CH_2}\right>C : CHC_6H_5.$$

β-Hydrindone $C_6H_4\left<\substack{CH_2\\CH_2}\right>CO$. This ketone is best prepared from β-imino-α-cyanohydrindene by distilling with dilute sulphuric acid (Moore and Thorpe, Chem. Soc. Trans. 1908, 93; *cf.* also Chem. Soc. Proc. 1911, 27, 128).



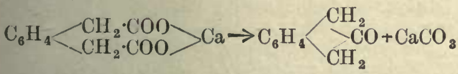
$$C_6H_4\left<\substack{CH_2\\ >C : NH\\ CH\cdot CN}\right. \rightarrow C_6H_4\left<\substack{CH_2\\CH_2}\right>CO$$

It can also be prepared from the indene of coal-tar (Heusler and Schieffer, Ber. 1899, 32, 28). The method most convenient for this purpose is to convert indene into the oxychloride by the method of Krämer and Spilker (Ber. 1890, 23, 3280) and then to transform this into the methoxy derivative which, with dilute sulphuric acid, yields β-hydrindone:



$$C_6H_4\left<\substack{CHCl\\ >CHOH\\ CH_2}\right. \rightarrow C_6H_4\left<\substack{CHOCH_3\\ >CHOH\\ CH_2}\right. \rightarrow C_6H_4\left<\substack{CH_2\\CH_2}\right>CO.$$

It can also be formed by distilling the calcium salt of *o*-phenylenediacetic acid (Benedikt, Annalen, 1893, 275, 353; Schad, Ber. 1893, 26, 222):

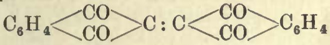


$$C_6H_4\left<\substack{CH_2\cdot COO\\CH_2\cdot COO}\right>Ca \rightarrow C_6H_4\left<\substack{CH_2\\ >CO\\ CH_2}\right. + CaCO_3$$

β-Hydrindone crystallises from dilute alcohol as long needles, melts at 61° and boils with partial decomposition at 220°–225°. The oxime melts at 155°, the phenylhydrazone at 120° and the semi-carbazone at 210°.

1 : 3-Diketohydrindene $C_6H_4\left<\substack{CO\\CO}\right>CH_2$, is probably the best known derivative of indene and is formed by the method of W. Wislicenus already described. It may be isolated (Kaufmann, Ber. 1897, 30, 385) by dissolving the sodium compound of ethyl diketohydrindene-carboxylate, prepared from ethyl phthalate and ethyl acetate, in as little boiling water as possible, cooling to 70°–75° and adding dilute sulphuric acid. A vigorous evolution of carbon dioxide then ensues and the diketone separates in the crystalline form. 1:3-diketohydrindene melts and decomposes at 129°–131°.

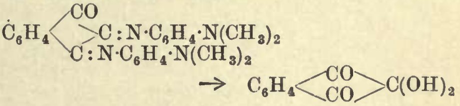
As is to be expected, the methylene group between the two carbonyl complexes of 1 : 3-diketohydrindene is exceedingly reactive and this substance shows all the reactions of the β-diketones. When oxidised by hydrogen peroxide or potassium persulphate, it is converted into the oxygen analogue of indigo, having the formula



$$C_6H_4\left<\substack{CO\\CO}\right>C : C\left<\substack{CO\\CO}\right>C_6H_4$$

This substance crystallises from aniline as glistening red needles.

1 : 2 : 3-Triketohydrindene $C_6H_4\left<\substack{CO\\CO}\right>CO$. A substance of this formula was prepared in small quantity by Kaufmann (Ber. 1897, 30, 387) by the oxidation of 1 : 3-diketohydrindene with hydrogen peroxide. The compound prepared in this way crystallised from glacial acetic acid as brown leaflets which melted and decomposed at 190°–206°. It is probable that the substance obtained by Kaufmann possesses another structure and that the true triketohydrindene is the compound prepared by Ruhemann, in the form of a hydrate, by the action of dilute sulphuric acid on the compound formed by the condensation of α-hydrindone with *p*-nitrosodimethylaniline



$$C_6H_4\left<\substack{CO\\ >C : N\cdot C_6H_4\cdot N(CH_3)_2\\ C : N\cdot C_6H_4\cdot N(CH_3)_2}\right. \rightarrow C_6H_4\left<\substack{CO\\CO}\right>C(OH)_2$$

This reaction can also be applied to 1 : 3-diketohydrindene and to β-hydrindone (Chem. Soc. Trans. 1910, 97, 1438, 2025; 1911, 99, 792).

Triketohydrindene hydrate forms prisms from water which redden at 125°, give off gas at 139° and melt with decomposition at 239°–240°. The hydrate colours the skin red and reduces Fehling's solution. The diphenylhydrazone melts at 207°–208° and the disemicarbazone darkens at 175° and melts with evolution of gas at 208°.

Triketohydrindene hydrate may be used as a reagent for proteins and their hydrolytic products (*cp.* Chem. Soc. Trans. 1911, 99, 798).

J. F. T.

INDIAN FIRE is a light used in pyrotechnical displays and for purposes of signalling. It is usually composed of 7 parts of sulphur, 2 of realgar, and 24 of nitre.

INDIAN HEMP RESIN *v.* Resins.

INDIAN INK or **CHINESE INK.** This substance, used for writing or drawing, consists of lamp-black held together with animal or fish glue and dried in the form of cakes or sticks of paint. According to Chinese writers, the invention of ink is due to one Tien-Tchen who lived between 2697 and 2597 B.C. It is said by them that at that time the ink used was a kind of lacquer; later some kind of black stone rubbed in water came into use; lastly, about 250 years B.C., balls of lamp-black from the burning of lacquer and firewood, afterwards mixed with size, became the customary material. It is probable, however, that the Chinese became acquainted with the substance from the Coreans, to whom they are indebted for other useful arts. The material used for producing the lamp-black is in most instances fir timber, although many other media, such as rice treated with a decoction of *Hibiscus mutabilis* (Linn.), the bark of the pomegranate tree infused with vinegar, and rock-oil are employed. The glue or size appears at the present day to be always obtained either from oxen or fish; the points of difference between various makers being (1) the mode of its preparation; (2) the method of incorporation; and (3) the quantity relative to the amount of soot. Sometimes perfumed essences, as of musk or camphor, are added, especially in the choicest qualities. After baking, the sticks or other moulded forms are laid in a cool, dry place, and are said to improve with long keeping.

The manufacture of Indian ink is also carried on in Japan, the following description, from a native source, indicating the method followed in that country. ‘The body of the ink is soot obtained from pine-wood or resin, and lamp-black from sesamum oil for the finest sort. This is mixed with liquid glue made of ox-skin. This operation is effected in a large, round, copper bowl formed of two spherical calottes placed 1 inch apart, so that the space between can be filled up with hot water to prevent the glue from hardening during the time it is being mixed by hand with the lamp-black. The cakes are formed in wooden moulds, and dried between paper and ashes. Camphor, or a peculiar mixture of scents which come from China, and a small quantity of carthamine (the red colouring substance of safflower) are added to the best kinds for improving the colour as well as for scenting the ink.’

M. Merimée (De la Peinture à l’Huile) asserted that the Chinese do not use an animal but a vegetable size; but apparently without warrant. For a curious monograph compiled from native Chinese sources *v.* L’Encre de Chine, son Histoire et sa Fabrication d’après documents chinois traduits, par Maurice Jametel, Paris, 1882.

INDIAN RED. A mineral pigment from the Persian Gulf. In appearance it is a coarse powder of a purplish-red colour.

Howe’s analysis of (1) the entire mineral, and of (2) that portion soluble in hydrochloric acid, gave

	SiO_2	Fe_2O_3	Al_2O_3	CaO	MgO	SO_3	CO_2	H_2O	
(1)	30·17	56·59	3·79	2·65	1·43	2·28	1·73	1·62	=100·26
(2)	—	3·19	2·22	2·65	0·87	2·28	1·73	—	=12·94

(Edin. New Phil. Jour. New Series, 2, 306.)

The portion insoluble in hydrochloric acid is a ferric silicate $Fe_2O_3{\cdot}SiO_2$. A pseudo-Indian red is composed principally of sesquioxide of iron.

INDIAN YELLOW, PIURI, PURREE, or **PIOURY,** is a pigment mainly used in India for colouring walls, doors, and lattice work, and by artists for water-colour work. On account of its disagreeable smell it is but rarely employed as a dyestuff. It is made almost exclusively at Monghyr in Bengal, and is obtained from the urine of cows which have been fed upon mango leaves. On heating the urine, usually in an earthen pot, the colouring matter separates out; this is pressed into a ball and dried partly over a charcoal fire and finally in the sun. It sells on the spot at about 1 rupee per lb., and is mainly sent to Calcutta and Patna. One cow produces, on the average, 3·4 litres of urine per diem yielding 2 oz. (56 grams) of piuri. The yearly production is stated to be from 100 to 150 cwts., which is probably over-estimated (*v.* Journ. Soc. Arts, 1883, [v.] 32, 16, and Annalen, 254, 268).

Piuri occurs in commerce in the form of round balls, which internally are of a brilliant yellow colour, whereas the outer layers are either brown or of a dirty green colour. The substance has a characteristic urinous smell. The undecomposed part consists only of *euxanthic acid* ($C_{19}H_{18}O_{11}$) in the form of a magnesium or calcium salt; the outer and decomposed portion contains in addition *euxanthone* both free and combined. The composition of piuri seems to be variable: a fine sample, according to Graebe, contained

Euxanthic acid . . .	51·0
Silicic acid and alumina . .	1·5
Magnesium	4·2
Calcium	3·4
Water and volatile matter .	39·0
	99·1

Euxanthic acid is easily obtained by digesting piuri of good quality with dilute hydrochloric acid and treating the residue with a solution of ammonium carbonate. On the addition of hydrochloric acid to the filtered solution euxanthic acid crystallises out with $1H_2O$ in glistening straw-yellow needles, melting at 162°.

Euxanthic acid is, according to Spiegel, decomposed by hydrochloric acid into glycuronic acid and euxanthone:

$$C_{19}H_{18}O_{11}=C_{13}H_8O_4+C_6H_{10}O_7.$$

Külz, in order to prove the animal origin of euxanthic acid, gave euxanthone to rabbits and dogs, and was able to detect euxanthic acid in the urine. Külz’s experiments did not corroborate Schmid’s statement that mangostin (obtained from *Garcinia Mangostana* [Linn.]) is similarly converted into euxanthic acid by animals (E. Külz, Zeitsch. Biol. 33, 475; J. Soc. Chem. Ind. 6, 507).

Although the potassium and sodium salts of euxanthic acid are of the type $C_{19}H_{17}O_{11}M$, the silver salt obtained from the potassium salt by silver nitrate has the composition $C_{19}H_{15}O_{10}Ag$, and is derived from an anhydride of the acid (*Anhydroeuxanthic acid*); the methyl and ethyl esters prepared from the silver salt are of the same type (Graebe, Ber. 1900, 53, 3360).

Potassium euxanthate $C_{19}H_{17}O_{11}K,H_2O$ crystallises readily from water, and is prepared by neutralising euxanthic acid with potassium carbonate.

Magnesium euxanthate $C_{19}H_{16}O_{11}Mg,5H_2O$ is the main constituent of Indian yellow (Graebe, Annalen, 254, 268).

Barium euxanthate $Ba(C_{19}H_{17}O_{11})_2,9H_2O$ is soluble in boiling water, and on cooling separates in the gelatinous condition.

Silver anhydroeuxanthate $C_{19}H_{15}O_{10}Ag$ behaves similarly.

Ethyl anhydroeuxanthate $C_{19}H_{15}O_{10}C_2H_5$, yellow-coloured needles, melts at 198°.

Tetra-acetylethylanhydroeuxanthate

$$C_{19}H_{11}O_{10}C_2H_5(C_2H_3O)_4$$

colourless needles, melts at 216°.

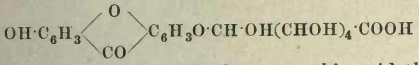
Methyl anhydroeuxanthate $C_{19}H_{15}O_{10}CH_3$, melts at 218°, and closely resembles the ethyl derivative.

Benzoyl anhydroeuxanthate

$$C_{19}H_{11}O_{10}(CO{\cdot}C_6H_5)_5$$

melts at 194°, but has not yet been crystallised.

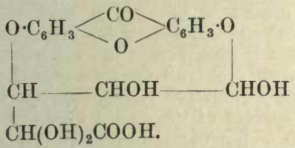
The constitution of euxanthic acid is expressed by Graebe (Annalen, 254, 267) as



whereas for that of anhydro-euxanthic acid the following two formulæ are given:

I.

II.

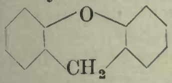


Euxanthone, Purrenone, Purrone $C_{13}H_8O_4$ was first obtained by Stenhouse (Annalen, 51, 425), and soon afterwards by Erdmann (*ibid.* 52, 365) from euxanthic acid. It crystallises in pale yellow needles or laminæ, melting at 240° (corr.), which sublime with little decomposition on gentle heating.

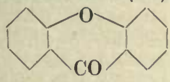
Diacetyl euxanthone, pale yellow prisms (Salzmann and Wichelhaus, Ber. 1877, 10, 1397), melts at 185°.

By distillation with zinc dust (Salzmann and Wichelhaus; Graebe and Ebrard, Ber. 16, 75) euxanthone gives *methylenediphenylene oxide* (I.), which by oxidation is converted into *xanthone* (II.)

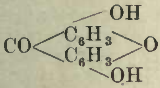
I.



II.

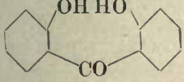


indicating that euxanthone possesses the constitutional formula



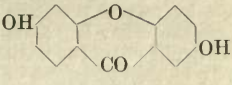
of a *dihydroxyxanthone* (S. and W.).

When fused with alkali euxanthone yields *euxanthonic acid*,

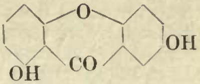


hydroquinone (*v.* Baeyer, Annalen, 155, 257), and *resorcinol* (Graebe, *ibid.* 254, 265).

The first synthesis of euxanthone is due to Graebe (*l.c.*), who accomplished this by distilling a mixture of β-resorcylic acid, and hydroquinonecarboxylic acid, and it was shown later by Kostanecki and Nessler (Ber. 1891, 24, 3983) that if in this reaction the β-resorcylic acid is replaced by resorcinol the same product is obtained. As the result of these syntheses two constitutional formulæ for euxanthone were possible:



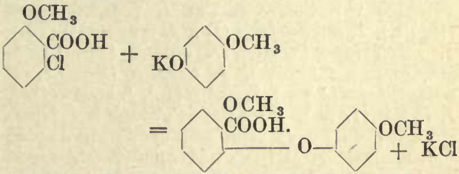
I.



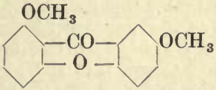
II.

When methylated by means of methyl iodide in the usual manner (Kostanecki, Ber. 1894, 27, 1992), euxanthone yields only a *monomethyl ether* $C_{13}H_7O_3(OCH_3)$ (yellow plates; m.p. 129°), and this on treatment with strong sodium hydroxide solution gives an insoluble yellow sodium salt. The latter, by washing with water, is decomposed with regeneration of the free monomethyl ether. These reactions indicate that euxanthone contains an hydroxyl in the ortho position to a carboxyl group (*cp.* also Herzig, Monatsh. 12, 161), and that, therefore, its constitution is represented by formula II. The final proof of this formula is afforded by a later synthesis of euxanthone (Ullmann and Panchaud, Annalen, 350, 108).

2-Chloro-6-methoxybenzoic acid is condensed with the potassium derivative of hydroquinone monomethyl ether, employing copper powder as a catalyst.



The resulting 4-*methoxy*-2-*phenoxy*-6-*methoxybenzoic acid* when treated with concentrated sulphuric acid is converted into *euxanthone dimethyl ether*



and this by treatment with aluminium chloride in the presence of benzene gives euxanthone.

Disazobenzene euxanthone $C_{13}H_6O_4(C_6H_5N_2)_2$ A. G. Perkin, Chem. Soc. Trans. 73, 666), red needles; m.p. 249°–250° (decomp.) is readily prepared by adding diazobenzene sulphate to a weak alkaline solution of euxanthone.

Acetyldisazobenzene euxanthone ochre-yellow needles, melts at 197°–199°. Euxanthone possesses only feeble tinctorial properties; the respective shades obtained with woollen cloth mordanted with chromium, aluminium and tin being dull brown-yellow, pale bright yellow, and very pale bright yellow (Perkin and Hummel, Chem. Soc. Trans. 1896, 69, 1290). A. G. P.

INDIA RUBBER or **CAOUTCHOUC** *v.* RUBBER.

INDICAN *v.* GLUCOSIDES; INDIGO, NATURAL.

INDICANURIA *v.* INDOXYL COMPOUNDS.

INDICATORS *v.* ACIDIMETRY AND ALKALIMETRY; also art. ANALYSIS.

INDIGO, NATURAL. Indigo has been known in Asia from a remote period of antiquity, and there exist very ancient records in Sanskrit describing its methods of preparation. The Romans appear to have only recognised it as a pigment (*indicum*), but evidence as to its use as a dye by the ancient Egyptians has been abundantly proved from the examination of mummy cloths. Its employment in Europe was very limited, until in 1516 it began to be imported from India by way of the Cape of Good Hope, though, on the other hand, its introduction in large quantity did not occur until about 1602. Owing chiefly to the opposition of the growers of woad, its European rival, its use as a dyeware met with much opposition, and various laws were enacted both on the Continent and in England prohibiting its use. It was, moreover, called a 'devilish drug,' and was said to be injurious to fabrics. In 1737 its employment was legally permitted in France, and from this period its valuable properties appear to have become gradually recognised throughout Europe.

The most important plants which yield indigo are those of the genus *Indigofera* belonging to the natural order of the *Leguminosæ*; these have been cultivated in India, China, Egypt, the Philippines, Caracas, and Brazil.

For the purpose of indigo manufacture the *Indigofera tinctoria* (L.), *I. sumatrana* (Garrtn.) (the Indian plant), *I. disperma* (L.), *I. argentea* (L.), and *I. arrecta* (Hochst.) (the Natal plant), the *I. paucifolia* (Delile) (Madagascar plant), and *I. secundiflora* (Poir.) (Guatemala plant), have been mainly used, though certain less valuable varieties, viz. the *I. pseudotinctoria* (R. Br.), *I. angustifolia* (L.), *I. arcuata* (Willd.), *I. caroliniana* (Walt.), *I. cinerea* (Willd.), *I. longeracemosa* (Boiv.), *I. cœrulea* (Roxb.), *I. endecaphylla* (Jacq.), *I. glabra* (L.), *I. hirsuta* (L.), *I. indica* (Lam.), *I. mexicana* (Benth.), *I. leptostachya* (DC.), have been employed. In Japan, China, and Russia the plant usually cultivated has been the *Polygonum tinctorium* (Ait.), but the *Isatis tinctoria* (L.), or woad plant, at one time very largely grown in Europe, is now used in very limited quantity as an adjunct in the dyeing of indigo (woad vat). The native source of indigo in Western Africa appears to consist almost entirely of the *Lonchocarpus cyanescens* (Benth.) (Perkin, J. Soc. Chem. Ind. 1907, 26).

Other indigo-yielding plants are the *Nerium tinctorium*, *Gymnema tingens* (Spreng.), *Eupatorium laeve* (DC.), *Tephrosia tinctoria* (Pers.), *Marsdenia tinctoria* (R. Br.), and certain species of orchids such as the *Phaius grandiflorus* (Reich.), and *Calanthe veratrifolia* (R. Br.).

In addition to these various plants of which the *Mercurialis perennis* (Linn.), *Fagopyrum esculentum* (Moench), *Fraxinus excelsior* (Linn.), *Baptisia tinctoria* (R. Br.), and *Rhamnus Alaternus* (L.) (Georgievics, Der. Indigo, 1892) may be given as examples, are stated to yield indigo, or a very similar colouring matter, but this requires confirmation.

The production of indigo from the indigo plant is of a simple character and consists mainly of two processes, viz. a steeping of the plant with water (fermentation), followed by the oxidation of the solution with air in a separate vessel. Until very recently but little modification appears to have been introduced into this ancient process, and there is also but little variation to be found in the main features as described by Bancroft (Philosophy of Permanent Colours, 1813), Crookes (Manual of Dyeing and Calico Printing, 1874), Bridges-Lee (Indigo Manufacture, 1892), Georgievics (*l.c.* 1892), and Rawson (The Cultivation and Manufacture of Indigo, J. Soc. Dyers. 1899).

Directly the plants are cut down they are tied in bundles and brought to the factory without delay, because it is necessary that the material should be operated on at once. The tanks for the extraction (steeping vats) and precipitation of the indigo by oxidation (beating vats) are sometimes of stone, but more usually of brick-work lined inside with cement, and are respectively ranged in two rows one above the other, so that the former can be drained into the latter. The steeping vats may have a capacity of about 1000 cub. ft., and are usually of much smaller dimensions than the beating vats, of which less are consequently required. According to Rawson (*l.c.*), who describes a small indigo factory, each range of beating vats runs the whole length of six steeping vats, and has a width of 13 feet 6 inches.

Into each of the upper tanks the bundles of the plant are tightly packed (preferably in a horizontal position, Bridges-Lee, *l.c.*), on the top of this is laid a horizontal trellis of bamboo, and the whole is wedged down into the tanks by means of timber, so that the material is unable to float during the fermentation process. Water is then run in in such quantity that the bundles are entirely submerged. After about 2 hours an active fermentation is observed, and the surface of the liquid becomes covered with froth owing to evolution of a mixture of carbon dioxide, oxygen, and nitrogen (Georgievics, *l.c.*); in the later stages (Rawson, *l.c.*) either marsh gas or hydrogen or a mixture of the two is freely produced. After 10–15 hours, according to the prevailing temperature of the water, the straw-yellow, orange, or olive-green coloured liquid is drawn off into the tanks below, and submitted to oxidation with air.

This is accomplished by 'hand beating,' by machinery (the beating wheel), by blowing air through the liquid, or by the shower-bath method. During this operation the colour of the liquid gradually changes, becoming first dark-green and then blue, and considerable frothing is produced. When it is observed that the indigo precipitate or 'fecula' readily settles, the beating is discontinued and the mixture allowed to rest for some 2 hours. The supernatant liquid or 'seet water,' having been drained off as completely as possible, the indigo sludge or 'mal' is led into a reservoir inside the factory, from which it is subsequently elevated by means of a hand pump or steam injector into a large cauldron known as the 'mal boiler.' It is here heated by direct fire or by the admission of steam, and this has for its object the prevention of a further fermentation, the solution of certain brown impurities, and a more complete granulation of the 'mal.'

The product is then run on to a filter known as a 'table,' consisting of stout cotton or linen cloth stretched over a shallow rectangular basin of stone or cement, with a drainage opening at one corner, and allowed to remain until it has the consistency of a stiff paste. In order to remove excess of moisture the indigo is transferred to perforated wooden boxes lined with sail cloth and cautiously pressed. Finally, the resulting slab is cut into cakes by means of a guillotine or metal wires and allowed to dry at the ordinary temperature on trellis-work shelves in a specially constructed drying house.

The Plant.

Until the last few years the *I. sumatrana* appears to have been exclusively employed in the best-conducted factories in India. According to Leake (Report of the Dalsingh Serai Research Station, 1903–1904) this is a mixture of several sub-varieties of different values. In this, as in apparently all other indigo plants, the indican exists exclusively in the leaf, though Bloxam and Leake (*l.c.*) point out that the midrib or rachis also contains the glucoside. For the manufacture of indigo the main points in connection with the plant are the weight of plant yielded per acre, the percentage of leaf given by the plant, and the indigotin producing value of the leaf. According to Rawson (Cultivation and Manufacture of Indigo, *l.c.*) the good plant contains 40 p.c. of leaf, though occasionally, but not often, the proportion of leaf rises to as much as 60 p.c. Bloxam and Leake have found, however, much higher values, 51·7–61·6 on ordinary Indian plant, and 65 p.c. given by twelve experimental plots, figures which include the rachis. Bergtheil (Report of the Indigo Research Station, Sirsiah, 1906, 8) finds the percentage of leaf to be 40 p.c., and never higher than 45 p.c.; but, on the other hand, in a redetermination, Leake (J. Soc. Chem. Ind. 1907, 26, 1174) records the value as 62·2 p.c. Rawson, who conducted numerous analyses of the leaf by his persulphate process (*l.c.*), shows that the indican content as expressed by indigo yielding capacity varies at different periods of the year. Thus, whereas in one instance on May 28 the figure was 0·20 p.c., on August 25 this had risen to 0·76 p.c. of indigotin. Though the leaf on young plant gives but a small percentage of colouring matter, yet as the plant grows, the new leaf contains more colouring principle than the old on the same plant. As an example, on one occasion the percentages of indigotin recorded with new and old leaf were respectively 0·71 and 0·35 p.c. Finally, there is a gradual increase in colouring matter given by leaves from the bottom of the plant upwards as represented by the figures 0·30, 0·44, and 0·62 p.c. respectively. According to Bergtheil (Report of the Indigo Research Station, 1907, 3) the 'indigotin content' of the plant is rarely so high as 0·3 p.c. Though the leaf, as a rule, contains a maximum of colouring matter from about the middle to the end of August, it does not necessarily follow that this is the best period for manufacture, as by this time the plant will usually have lost a considerable portion of leaf (Rawson). The manufacture, indeed, usually commences about the middle of June. Gaunt, Thomas, and Bloxam (J. Soc. Chem. Ind. 1907, 26, 1174) refer to a sample of the air-dried leaves of the *I. sumatrana*, which, in comparison with other dry samples of the same variety (0·6 approx.) and of the Java plant *I. arrecta* (1·81 p.c.) yielded indigotin to the value of 3·53 p.c., and consider that this indicates that by selection and suitable methods of cultivation it should be possible to obtain an average plant of greater indigo producing power than has hitherto been the case.

The plant formerly employed by the Java planters was the *Indigofera secundiflora* 'Guatemala plant,' but for several years past this has been replaced by the *I. arrecta* or 'Natal plant.' The latter, it is stated, contains not only more leaf than the ordinary Indian plant, but, as a rule, the leaf yields also a considerably larger percentage of indigo. More recently the Indian planters have recognised the value of the *I. arrecta*, and accounts are given by Coventry (Indigo Improvements Syndicate Report, 1901) of experiments in connection with its introduction. Leake (Dalsingh Serai Report, 1905) discusses the difficulties of the germination of the seed of the Natal-Java plant, which is due to the impermeable character of the seed coat. This defect, it is pointed out, can be overcome by a process of scratching, and a practicable method for this purpose is described. Bergtheil (*l.c.*), in conjunction with D. L. Day, treats the seed with strong sulphuric acid, which leads either to a swelling of the seed coat and its eventual rupture or converts it into a body akin to cellulose and permeable to water. Analyses of the indigo-yielding power of this leaf by Rawson (*l.c.*) gave figures up to 0·96 p.c., whereas Bergtheil (*l.c.* 1906) finds in comparison to the *I. sumatrana* (0·585) that the *I. arrecta* produced 1·05 p.c. of colouring matter. The percentage of leaf given by the latter averages 52·2 p.c. Again in 1909 the yield from 100 maunds of the *I. arrecta* was 15 seers 10 chittacks, as against 11 seers 14 chittacks from the same quantity of the *I. sumatrana.* The Natal plant is now established in India, and its superiority over the Indian plant is fully recognised. According to Bergtheil (1907) the indigo made from the Java plant has generally been of a high indigotin content, and (1906) that whereas the yield of indigo per acre was 12·6 'seers,' that given by the *I. sumatrana* was by comparison only 8 seers.

A full account of much detailed work on the cultivation of the indigo plants by Rawson, Bloxam and Leake, and Bergtheil is given in the reports above enumerated (c.p. also Bergtheil, *ibid.* 1908–1911).

The Chemistry of Natural Indigo Manufacture.

According to the early researches of Chevreul (Ann. Chim. Phys. 1808, 66, 8, and 1808, 68, 284) and of Geradin and Preisser (J. Pharm. Chim. 1840, 26, 344) the colouring principle of indigotin present in indigo-yielding plants was considered to consist of indigo white, and this theory remained uncontradicted until Schunck (Phil. Mag. 1855, [iv.] 17, 74, and 1858, 15, 127) isolated from the *Isatis tinctoria* (woad), *Polygonum tinctorium* and *Indigofera tinctoria* (Schunck and Roemer, Ber. 1879, 12, 2311), a glucoside, which was named indican.

To prepare this substance from woad the leaves were extracted with cold alcohol, the solution treated with a little water, and concentrated at the ordinary temperature by blowing air over it. The waxy matter which thus separated was removed by filtration, and the filtrate shaken up with freshly precipitated cupric hydroxide. The mixture was filtered, the liquid freed from dissolved copper by means of sulphuretted hydrogen, and then evaporated at the ordinary temperature. The residue was extracted with cold alcohol, the extract treated with ether to precipitate certain impurities, and the solution evaporated.

Thus obtained it consisted of a yellow or yellowish-brown syrup, which was of an exceedingly unstable nature, and could not be dried without decomposition. With alcoholic lead acetate it gave a yellow precipitate, whereas in aqueous solution it could only be precipitated by means of basic lead acetate. Analyses of the lead compound indicated that it possessed the formula $C_{26}H_{31}NO_{17}$. Schunck found that this compound was a glucoside, and that by the action of dilute acids, alkalis and of a ferment present in the plant, it was readily hydrolysed with the formation of indigotin, and a sugar indiglucin

$$2C_{26}H_{31}O_{17}{\cdot}N+4H_2O=C_{16}H_{10}O_2N_2+6C_6H_{10}O_6$$

For the production of indigotin the presence of air or other suitable oxidising agent was however necessary, and it appeared, therefore, that during the reaction the indigotin at first formed was reduced to indigo white.

Later, however, Schunck and Roemer showed (*l.c.*) that indican, when hydrolysed in the absence of air, gave a product which, on subsequent treatment with oxidising agents, did not yield indigotin. Schunck further obtained by the action of cold dilute acids on his indican a brown powder, from which he isolated six distinct substances, viz. *indihumin, indifuscin,* and *indiretin,* soluble in warm sodium hydroxide solution, and *α*- and *β-indifulvins* and *indirubin,* insoluble in alkalis.

When aqueous solutions of the indican were boiled or heated for some time a decomposition ensued, and the product, on treatment with acid, gave indiglucin, but no indigotin, this being replaced by *indiretin* and *indihumin* brown amorphous substances. The latter closely resembled, and was probably identical with, indigo brown. By the action of alkalis or alkaline earths at the ordinary temperature, indican was converted into a new glucoside *indicanin* $C_{20}H_{23}NO_{12}$, which on treatment with acid gave indiglucin and indirubin.

Oxyindicanin, a brown gummy substance, insoluble in alcohol, was isolated during the preparation of indican, and yielded, under the influence of acids, indiglucin and a brown substance similar to indifuscin.

Marchlewski and Radcliffe (J. Soc. Chem. Ind. 1898, 17, 434), in a theoretical discussion of the subject, suggested that indican $C_{14}H_{17}O_6N$ was a glucoside of indoxyl the hydrolysis of which could be represented by the following equation:

$$C_{14}H_{17}O_6N+H_2O=C_8H_7ON+C_6H_{12}O_6.$$

As a result of the communication of Marchlewski and Radcliffe, Hazewinkel, the director of the experimental station for indigo, Klaten, Java (Proc. K. Akad. Wetensch. Amsterdam, 1900, 2, 512), gave an account of a research, concluded in 1898, which he had hitherto considered to be to the interest of the Java planters to keep secret. In this important paper he gives proof for the first time that indican is an indoxyl glucoside, and that the sugar obtained from it is dextrose.

The elaborate researches of Beyerinck, van Romburgh, and other Dutch chemists, proved that the indican present in the various *Indigoferæ* and in the *Polygonum tinctorium* was far more stable than Schunck supposed, and the experiments of these authors eventually led to the isolation of this glucoside in a crystalline condition from the *Indigofera leptostachya* and *Polygonum tinctorium* by Hoogewerff and ter Meulen (Proc. K. Akad. Wetensch. Amsterdam, 1900, 2, 520).

The leaves were immersed in two and a half times their weight of boiling water, boiled for a few minutes, and further systematically exhausted. Without any sensible decomposition the decoction could be evaporated *in vacuô* if care was taken to keep the reaction alkaline. The dry residue was extracted with methyl alcohol, and to the solution ether was added as long as a precipitate was formed. This was removed, the clear liquid evaporated, the residue completely dried *in vacuô,* and then dissolved in water. The filtered and concentrated solution deposited on cooling well-defined crystals of indican. This process may be modified by treating the decoction of the leaves with baryta water before concentration, by which means a large proportion of the impurities are precipitated. 17 kilos. of the leaves of *Polygonum tinctorium* yielded 5 grams of pure indican.

Thus obtained indican $C_{14}H_{17}O_6N$ crystallises from water in spear-shaped crystals, which contain 3 molecules of water of crystallisation. Heated in a test tube, or on platinum foil, purple-coloured fumes are given off, but this does not take place in an atmosphere of carbon dioxide. By passing a current of air through a hot solution of indican in dilute hydrochloric acid containing a little ferric chloride, 91 p.c. of the indican was converted into indigotin according to the equation

$$2C_{14}H_{17}NO_6+O_2=C_{16}H_{10}N_2O_2+2C_6H_{12}O_6.$$

There was no difference between the indican prepared from the *I. leptostachya* and that obtained from the *P. tinctorium.*

In a paper by Beyerinck (Proc. K. Akad. Wetensch. Amsterdam, 1900, 3, 101), 'On the Formation of Indigo from Woad,' this chemist discusses Schunck's well-known work on the same subject, and points out that the indigo-yielding substance contained in this plant is not as Schunck regarded it, identical with the indican present in the *Polygonum tinctorium.* The colouring principle of woad Beyerinck names *isatan,* and shows that this compound, unlike indican, is decomposed in feebly alkaline solutions, whereas indican is stable even in concentrated alkaline liquids. In presence of acids both isatan and indican are hydrolysed, but indican with greater difficulty. Isatase, the specific enzyme of woad, does not act on indican, and isatan, on the other hand, is unaffected both by the indigo enzyme or by common bacteria.

Schunck (Chem. News, 1900, 82, 176) considered that the crystalline indican of Hoogewerff and ter Meulen was not the substance obtained by him, and should not be considered as a pure variety of it, but was rather derived from it, by extracting the plant with a hot solvent and the use of chemicals. He preferred to name his compound *a*-indican and theirs *b*-indican.

Bergtheil (Chem. Soc. Trans. 1904, 85, 877), who experimented with the *I. sumatrana* and *I. arrecta,* did not find it possible to prepare indican from the leaves of these plants in the manner described by Hoogewerff and ter Meulen.

It was, however, shown by Perkin and Bloxam (Chem. Soc. Trans. 1907, 91, 1715) that crystalline indican can be isolated from both of these plants by such a method, and is in reality the source of the natural indigo which is derived from them.

In a further communication ter Meulen (Rec. trav. chim. 1905, 29, 444) describes a modification of the method previously given for the isolation of indican from the *Polygonum tinctorium*, which consists in treating a cold solution of the partially purified substance with sulphuric acid, by which means certain impurities are precipitated. The acid is then removed with barium carbonate. The main object of the investigation was, however, the determination of the sugar that this glucoside yields when hydrolysed by its specific enzyme, and this proved to be dextrose, as already indicated by Hazewinkel (*l.c.*).

As a result of the study of the behaviour of indican with solvents, Perkin and Bloxam (*l.c.*) devised a very simple process for the isolation of this glucoside, by the aid of which large quantities of the pure substance could be readily prepared.

The leaves and stems of the *I. sumatrana* (1000 grams) were treated with 4 litres of cold acetone, the mixture being occasionally shaken during 7 days, and the green-coloured extract was evaporated on the steam bath to a very small bulk. To the residue light petroleum was added, causing the deposition of a brown viscous precipitate of crude indican, and this was repeatedly agitated with small quantities of light petroleum. The product on treatment with water gave a pale yellow liquid, containing resinous matter in suspension, and the latter was removed by shaking with ether. The clear aqueous solution, treated with 10 c.c. *N*/2 sodium carbonate, on gradual evaporation *in vacuô* deposited crystals, and eventually a semi-solid mass was obtained. It was collected, drained, and allowed to dry at the ordinary temperature. When exhaustively extracted, 1000 grams of leaf gave 31·66 grams of indican, and by a continuous system of working more than 500 grams of crystalline indican were prepared. The preparation of this glucoside from the leaves of *I. arrecta* is more troublesome, owing partly to the presence of kæmpferitrin, but more especially of a colourless sugar-like compound $C_6H_{12}O_5$; m.p. 186°–187°; possibly a modification of quercitol. The fact that indican can be so readily isolated without the aid of heat, and merely with the use of acetone, light petroleum and ether, is not in harmony with the contention of Schunck (*l.c.*) that the crystalline glucoside is an alteration product of his amorphous substance, and consequently the terms α- and β-indican suggested by him should disappear.

Indican crystallised from water

$$C_{14}H_{17}O_6N,3H_2O$$

melts at 57°–58°, but in the anhydrous condition as obtained by the addition of boiling benzene to its hot alcoholic solution, at 176°–178°. Owing to its somewhat ready solubility in water it can be more economically purified by the latter process, and, according to Perkin and Thomas (Chem. Soc. Trans. 1909, 95, 793), crystallisation from absolute alcohol gives excellent results.

It has been shown by Baeyer (Ber. 1881, 14, 1745) that indoxyl readily condenses with aldehydes and ketones to form the so-called *indogenides*, and Hazewinkel (*l.c.*), in the valuable communication which demonstrated for the first time that indican is an indoxyl glucoside, partly identified this substance by means of its condensation products with isatin, benzaldehyde, and pyruvic acid, relying, however, on their qualitative reactions, as he did not prepare these compounds in a pure enough condition for analysis. Almost simultaneously Beyerinck (Proc. K. Akad. Wetensch. Amsterdam, 1899, 2, 120) prepared indirubin by hydrolysing crude indican in the presence of isatin.

Perkin and Bloxam (*l.c.*), and Gaunt, Thomas, and Bloxam (J. Soc. Chem. Ind. 1907, 26, 1174), who experimented with the pure substance, found that when indican dissolved in water is added to a boiling solution of isatin, acidified with a little hydrochloric acid, and the operation is carried out in an atmosphere of hydrogen or carbon dioxide, the yield of indirubin is quantitative according to the following equations:—

$$C_{14}H_{17}O_6N+H_2O = C_8H_7NO+C_6H_{12}O_6.$$
$$C_8H_7NO+C_8H_5NO_2 = C_{16}H_{10}N_2O_2+H_2O.$$

This 'isatin' method, for full details of which the original papers must be consulted, affords a ready means, not only for the analysis of the crystalline glucoside, but also for the estimation of the amount which is present in aqueous infusions of the leaf (*v. infra*).

More recently Perkin and Thomas (Chem. Soc. Trans. 1909, 95, 795), who studied in a similar way the condensation of indoxyl derived from indican with *p*-nitrobenzaldehyde, found that the *p*-nitrobenzaldehydeindogenide is deposited in quantitative amount, and that this reaction could also be employed for the analysis, both of crystalline indican and that present in the leaf extract. The reaction takes place with extreme readiness, for with indican solution at a dilution of 1 in 1000, the above compound quickly separates, and even at 1 in 10,000 the condensation can be observed to take place. Piperonal and indican in the presence of dilute acid yield the analogous compound $C_{16}H_{11}O_3N$, orange-coloured needles; m.p. 223°–224°, but this process, under analytical conditions, gave only approximately satisfactory results. As a side issue, *p*-hydroxybenzaldehydeindogenide $C_{15}H_{11}O_2N$ orange-red needles, m.p. 267°–269°, and dihydroxybenzaldehydeindogenide $C_{15}H_{11}O_3H$ orange-red needles, m.p. 264°–265°, were prepared from indican. The latter compound derived from protocatechuic aldehyde dissolves in concentrated sodium hydroxide, with a bluish-violet colouration, and dyes with mordanted woollen cloth well-defined shades.

On the other hand, when indican is hydrolysed with acid in the presence of an oxidising agent it does not appear possible to obtain a quantitative yield of indigotin. Hazewinkel (*l.c.*) states, in regard to this point, that acid oxidising agents convert indican into indigo, and this in turn is oxidised by an excess of the reagent. By the use of ferric chloride and hydrochloric acid, Hoogewerff and ter Meulen obtained from the pure glucoside only 91 p.c. of the theoretical quantity of colouring matter, which appeared to contain indirubin, and was of doubtful purity. Gaunt, Thomas, and Bloxam (*l.c.*), who examined the behaviour of ammonium persulphate, a reagent suggested by Rawson for the analysis of the plant extract (Report on the Cultivation and Manufacture of Indigo, Mozzufferpore, 1904; *cp.* also Bloxam and Leake, Dalsingh, Serai Report, 1904), found that the process was far from quantitative with pure indican, and that the yield of colouring matter averaged but 82 p.c. of the theoretical. Perkin and Thomas (*l.c.*) studied the effect of the hydrolysis of solutions of indican with acid during the aspiration of air through the liquid, under varying conditions of temperature and concentration. The most satisfactory yield of pure colouring matter (93·5 p.c.) was produced when air was passed during 8 hours through a solution of 0·5 gram of the glucoside in 850 c.c. of water acidified with 15 c.c. of 33 p.c. hydrochloric acid, and the temperature maintained at 60°.

When, however, the operation was carried out at 70° less colouring matter was obtained (87·6 p.c.), and, curiously enough, replacement of the hydrochloric acid by an equivalent amount of sulphuric acid, gave under similar conditions, a much lower result. The deficiency in the yields given by these air oxidation processes was due to the fact that a portion of the indoxyl had been converted into substances other than indigotin, and it was observed that whereas in the case of hydrochloric acid the filtrate possessed a pale yellow colour, that containing sulphuric acid had a browner and darker tint. Indirubin was also present in these indigo preparations.

Whereas Schunck (*l.c.*) had described the production of various brown substances by the action of dilute acids on his indican, and Schunck and Roemer (*l.c.*) had obtained a brown-yellow compound by means of hydrochloric acid in absence of air, the behaviour of the pure crystalline glucoside in this respect was studied by Perkin and Bloxam. When 100 c.c. of a 4 p.c. solution of indican was treated with 3 c.c. of sulphuric acid, and digested at a boiling temperature, the liquid, at first yellow, became brown, a brown resinous substance, together with a little indigotin, quickly separated, and the presence of indole was observed. The product of the reaction was almost identical in weight with that required by the amount of indoxyl which the glucoside would yield on hydrolysis, and consisted chiefly of a dark reddish-brown powder (*a*), sparingly soluble in alcohol, together with a small quantity of a similar, though more readily soluble substance (*b*). Analyses of (*a*), which is termed *indoxyl brown*, gave $C=68{\cdot}10$; $H=4{\cdot}10$; $N=9{\cdot}34$, figures almost identical with those found by the same authors for the main constituent of indigo brown, and though these two products differ from one another in certain minor respects, there could be no doubt that they were closely allied. The more readily soluble substance (*b*) also closely resembled the indoxyl brown, and gave on analysis $N=9{\cdot}65$ p.c. Indican, when treated with cold hydrochloric acid in the absence of air, for 90 hours, gave indoxyl brown and a soluble brown substance similar to that described above (Perkin and Thomas). The acid filtrates from the indoxyl brown preparations contained dextrose, and this was identified by means of its osazone, and also by the preparation of its acetyl derivative.

The indigo enzyme discovered by Schunck (*l.c.*) has been elaborately investigated by the Dutch chemists. Beyerinck (Proc. K. Akad. Wetensch. Amsterdam, 1899, 1, 120) extracts the finely divided leaves of the plant, first with cold 96 p.c. alcohol, and subsequently with more dilute alcohol, which removes chlorophyll, indican, wax, &c., and leaves a snow-white highly active powder. From such preparations the enzyme itself was only imperfectly removed, for in water it is almost insoluble, only sparingly so in glycerol, and rather more readily in 10 p.c. solutions of sodium and calcium chlorides respectively. The residue which remains after extraction in this way is not perceptibly less active than before treatment. A minute study of these leaf preparations was carried out by Beyerinck in regard to their behaviour with partly purified indican solutions, and he indicates the effect of temperature on the intensity of the hydrolysis by means of curves. Among numerous points of interest it was observed that ammonia quickly destroys the enzyme, and also that emulsin slowly hydrolyses indican, although the intensity of its action was only one twentieth of that of *Indigofera* enzyme preparations.

Hazewinkel (*ibid.* 1900, 2, 513), who investigated the subject in 1898, arrived independently at Beyerinck's conclusions. By means of his enzyme preparation he proved for the first time that indican is a glucoside of indoxyl. Finding that emulsin also acted on indican solutions he called the indican enzyme *indimulsin*, and considered that a 10 p.c. solution of sodium chloride is the best medium for dissolving it. A very interesting point which he mentions is that during fermentation no indican passes from the leaf into the surrounding liquid.

In the paper of van Romburgh (*ibid.* 1899, 2, 344) allusion is made to the insoluble character of the enzyme, and to the activity of emulsin with solutions of indican. Finally, Beyerinck (*ibid.* 1900, 3, 101) demonstrated that the ferment present in woad, *Isatis tinctoria*, is not capable of hydrolysing indican, though it reacts with isatan, the peculiar indigotin yielding principle of this plant. Bergtheil (Chem. Soc. Trans. 1904, 85, 877), whose paper covers ground already traversed by Hazewinkel, Beyerinck, and van Romburgh, considers that the difficulty which occurs in extracting the enzyme is due to the presence of tannin in the leaves (*cp.* Brown and Morris, Chem. Soc. Trans. 1893, 63, 604). By pounding the leaves with hide powder the tannin becomes fixed, and a very active solution of the enzyme can be obtained.

Ter Meulen (Rec. trav. chim. 1905, 24, 444) is, however, in agreement with the other Dutch work referred to above, as is evident from his statement 'L'enzyme de l'indigo est insoluble dans l'eau.' According to Gaunt, Thomas, and Bloxam (*l.c.*), Bergtheil's product is not a true solution, as the enzyme is entirely removed from it by means of a Berkfeld filter. Thomas, Perkin, and Bloxam (Chem. Soc. Trans. 1909, 95, 829) again point out that there is no certainty of the presence of tannin in the leaves of the *I. sumatrana* and *I. arrecta*, and that any tannin matter if originally present would be eliminated during the repeated extraction of the material with alcohol. As the result of their experiments the insolubility of the enzyme was confirmed.

A study of the hydrolysis of pure indican by means of the enzyme and subsequent oxidation of the indoxyl solution with air under varied conditions has been made by Thomas, Perkin, and Bloxam (*l.c.*). The fermentation was carried out in an atmosphere of purified hydrogen, and the temperature and dilution of the solution in both this and the subsequent oxidation process were so arranged as to fairly approximate the ordinary factory routine. For full details of apparatus and the analytical precautions adopted the original paper must be consulted.

The results of this investigation show that the hydrolytic action of the enzyme proceeds somewhat rapidly, and that by employing 2 grams of the enzyme and 1 gram of indican under the conditions of dilution stated, the reaction was complete after 2 hours' digestion at 50°. The solution, though free from indican, contains, however, less than the theoretical amount of indoxyl (93 p.c.). This is due to the fact that some quantity of the indoxyl (4 p.c.) is occluded by the enzyme powder, and it was found that by increasing the quantity of this latter a correspondingly greater loss occurs. The residual deficiency (3 p.c. approx.) arises from the instability of indoxyl itself, which even in an atmosphere of hydrogen at 50° is slowly converted into a product which is incapable of giving indigotin on oxidation. This property, which is referred to as the 'decay' of indoxyl, is much more evident when the digestion with the ferment is prolonged for several hours, and the experiments of these authors indicate that by such a treatment for 30 hours, at least 20 p.c. of the indoxyl undergoes this transformation. On the other hand, at 15°, in an atmosphere of hydrogen, the indoxyl solution is comparatively stable, and on standing for 24 hours, had experienced a loss of only 3 p.c.

According to Beyerinck (*l.c.*) great attention should be paid to the degree of the acidity of indican solutions which are undergoing fermentation, and this is corroborated by Thomas, Perkin, and Bloxam. Thus, by the presence of a trace of sulphuric acid during the fermentation, the decay of the indoxyl is practically inhibited, and, moreover, by the addition of a further quantity of the acid at the close of the operation, the occlusion of the indoxyl by the enzyme powder is also prevented. As a result of this procedure the solution contained 99·5 p.c. of the theoretical quantity of indoxyl.

When a dilute aqueous solution of indoxyl is oxidised by air the reaction is more complex than has usually been considered the case, and a quantitative yield of indigotin is not produced. Thomas, Perkin, and Bloxam have, for instance, found that the indoxyl solutions produced by the enzyme hydrolysis of indican, when treated with air at 60°, gave only 88 p.c. of the theoretical quantity of indigotin, admixed with a little indirubin. It thus appears evident that in addition to the oxidation of indoxyl to indigotin some secondary reaction occurs, but of the chemical nature of this change there is as yet no certain evidence. The isolation from the indigo thus produced of traces of substances resembling indoxyl brown or indigo brown indicates the effect, at least in part, of a condensation similar in character to that which is involved in the production of the former product. Moreover, the filtrate from the indigo, which is prepared in this manner, was invariably of a dull yellow colour, and yielded, by extraction with ether, a small quantity of a yellowish-brown resin.

This secondary change of indoxyl is facilitated by the presence of potassium acetate in the liquid during the oxidation, for by this means the yield of indigotin was decreased to 81 p.c., and the filtrate obtained from it possessed a rich dichromate colour. It has long been known that the oxidation of indoxyl solutions, in so far as the crude fermented factory liquid is concerned, is facilitated by the presence of ammonia or lime water, and the subject has been discussed by Rawson and by Beyerinck (*l.c.*). According to Thomas, Perkin, and Bloxam, the employment of a small quantity of either of these reagents during the oxidation of the indoxyl derived from pure indican was beneficial, and an increase of about 5 p.c. in the yield of indigo thus took place. On the other hand, the addition of only a trace of these compounds is advisable, because should an excess be present the amount of indigo produced is rather decreased than increased thereby.

But whilst both ammonia and lime water in suitable amount partially inhibit the secondary change of the indoxyl referred to above, a third factor, well known to manufacturers, comes into play, which is represented by the production of notable amounts of indirubin. For the formation of this colouring matter isatin is necessary, and it is likely that, in the presence of a large amount of the above reagents, an excessive production of this substance occurs, and occasions the decreased yield of indigo which, under these circumstances, has been shown to take place. It has, in fact, been pointed out by Perkin (Chem. Soc. Proc. 1907, 23, 30) that traces of isatin exist in Java indigos, which are rich in indirubin.

Curiously enough the presence of a trace of hydrochloric acid during the oxidation acts in the same manner as ammonia, though to a less extent, in increasing the yield of colouring matter, but in this case the reaction proceeds much less rapidly. The employment of pure oxygen with neutral solutions of indoxyl gives 3–4 p.c. less colouring matter than is obtained when air alone is employed, whereas in presence of ammonia the yield is but little affected. The addition of Chile saltpetre to the fermentation vat has been a custom of Indian planters for some time, and Rawson (Report on the Cultivation and Manufacture of Indigo, 2nd ed., 1907) states that although no increase of colouring matter is thus produced in the oxidation vat, the precipitate settles better. The laboratory experiments of Thomas, Bloxam, and Perkin with pure indican corroborate this statement. Finally, there is but little difference in the yield of colouring matter experienced when the solution of indoxyl is oxidised by air at either

30° or 60°, although, if anything, the advantage is in the case of the higher temperature.

As a result, therefore, of the employment of acid during the enzyme hydrolysis of indican, and oxidation of the resulting indoxyl solution under feebly alkaline conditions, the best yields of colouring matter have been obtained. On the other hand, it has not been found possible either with synthetical indoxyl or indoxyl derived from indican to obtain a quantitative yield of pure indigotin or of an admixture of this colouring matter with indirubin. In regard to the bearing of this work on the commercial process, Thomas, Perkin, and Bloxam suggest that the effect of the addition of a small quantity of sulphuric or oxalic acid to the fermentation vat should be studied. They consider, however, that the most satisfactory laboratory results on the preparation of indigotin from the plant extract, or from pure indican, are given when the solution is hydrolysed by hydrochloric acid, with simultaneous oxidation by air. The cost of hot water extraction of the plant is, however, considered by Rawson to be prohibitive.

Bacterial fermentation. Though in the manufacture of indigo, hydrolysis of the indican is mainly due to the action of its specific enzyme indimulsin, it is well known that the bacteria which are present exert a similar although minor effect.

In 1887 Alvarez (Compt. rend. 115, 286) isolated from an extract of the indigo plant, an organism *Bacillus indigogenus*, which was capable of producing this fermentation. Beyerinck (*l.c.*), who studied the matter in considerable detail, points out that a similar effect is produced by infecting indigo plant infusions with garden soil, and that in this case the common gas-producing bacteria perform the chief part. Alvarez, he suggests, went too far in insisting on the existence of a specific bacterium in indigo fermentation. On the other hand, Bergtheil (*l.c.*) considers that at least one organism capable of producing indigo fermentation is invariably found in large quantities in an infusion of the plant. This corresponds very closely with the description given by Alvarez of his *Bacillus indigogenus*, and is no doubt identical with it.

MANUFACTURE OF INDIGO.

Water. Pure water in large quantity is necessary for the manufacture of natural indigo (Crookes, Handbook of Dyeing and Calico-Printing, 1874; Indigo Manufacture, Bridges-Lee, 1892; Rawson, Report on the Cultivation and Manufacture of Indigo, 1902). When such is not available, Bridges-Lee recommends its purification, if hard, by treatment with lime water, and should much organic matter be present by the use of permanganate. Rawson also lays stress on this point, and recommends a similar method of procedure. In special circumstances the employment of aluminoferric is advisable (Bergtheil, 1909). As the duration of the fermentation varies with the temperature of the water, Rawson recommends, in case this should be lower than 90°F., a preliminary heating in the reservoir.

Fermentation. The duration of this process is given by Crookes (*l.c.*) as 9–14 hours, according to the prevailing temperature of the water, whereas Georgievics (Der Indigo, 1892) suggests 18 hours when the external temperature is 35·6°C. In very hot weather the fermentation is completed in 6 hours. According to Rawson (*l.c.*), when the temperature of the fermentation vat is from 90°–92°F., a 12 hours' steeping gives the best result in the case of the *I. sumatrana*; whereas Bergtheil (Indigo Research Station, Sirsiah, 1906) is of opinion that a 10 hours' fermentation is sufficient. With the *I. arrecta* the steeping should vary from 13 to 15 hours at 90°, according to the indican content of the plant. In other respects, according to Rawson and Bergtheil, there is practically no improvement necessary in the steeping operation as carried out in well-managed factories. The addition of such chemicals as mercuric chloride, sodium and potassium carbonates, lime, carbolic acid, formaldehyde, and sugar are not of advantage, although sodium nitrate, which has been employed by planters for many years past, may facilitate the deposition of the indigo in the oxidising vat. On the other hand, the work of Thomas, Bloxam, and Perkin indicates as beneficial the curtailment, as far as possible, of the steeping operation, and the addition of sulphuric or oxalic acid in small quantity to the vat as advantageous.

Hot-water extraction. The extraction of the indigo plant with hot water has been employed for many years, and in Bancroft's Philosophy of Permanent Colours, an account is given by Dr. Roxburgh, dated 1797, of such a method:—'The hot water process begins to be used over these provinces; . . . with it they can make indigo when the weather is too cold for the usual process of fermentation, and it gives a more beautiful and lighter indigo. . . . A more complete and certain extraction of the basis of indigo is effected by subjecting the plant to the action of water heated to about 150°–160°F.' Bridges-Lee (*l.c.*) claims an advantage by the employment of hot water, and heats the contents of the steeping vat gradually either by direct fire or steam pipes. It is also well known that the Java planters who have employed the *I. arrecta*, for several years past have favoured a hot-water process, and although the exact details of their methods have not been disclosed, it is certain that sulphuric acid is also employed in the manufacture. Perkin (Chem. Soc. Trans. 1907, 91, 435) refers to samples of Java indigo prepared by three distinct methods, viz. 'the new process with hot water,' 'the new process with cold water,' and 'the old process in which no chemicals are used.' There can be no doubt that by these hot water processes the indican is very rapidly hydrolysed by the ferment, and that the indigo eventually produced is of a superior quality. During this hot extraction it appears preferable, as far as possible, to exclude air from the vat by means of a cover, and the necessity in this case is easy to understand, because the evolution of carbon dioxide and other gases which act as a protection to the indoxyl during the ordinary process of fermentation, is greatly decreased when operating in this manner (Roxburgh, *l.c.*). Rawson (*l.c.*), who refers to a patent No. 157, 1892, granted to A. Schulte in Hofe, for manufacturing indigo on these lines, and also to Henly's 'heating process of 1888,' carried out numerous experiments on this subject with the *I. sumatrana.* In order to economise fuel the indigo plant was, in the first instance, extracted by the accumulative method; but, contrary to expectation, this did not give such good results as a simple extraction in ordinary vats fitted with perforated steam pipes. He finally concludes, however, that except in wet or cold weather the hot water system offers no advantage over ordinary steeping carried out under favourable conditions. The indigo made by this method was, however, of better quality (75–77 p.c.) than that made in the ordinary way (50–55 p.c.). In regard to extraction of the plant by means of boiling water, or extraction by steaming, Rawson considers that the cost would be prohibitive.

When the fermented liquid is run off into the oxidising vat, the residual plant still contains a small quantity of indoxyl. The question of a second steeping in order to recover this is referred to by Roxburgh as early as about 1797; he considers that a considerable economy would probably be effected thereby; but Rawson's (*l.c.*) experiments in this direction gave an unsuccessful result. Thomas, Perkin, and Bloxam (*l.c.*) suggest that the employment of a slightly acid water for this purpose should be advantageous, and that the amount of indoxyl retained by the plant residue is probably greater than the 5 p.c. (on the total colouring matter) as believed by Rawson to be the case. The extracted plant, known as 'seet,' is a valuable manure.

The oxidation vat. Although the oxidation of the fermented liquid was until very recently carried out to some extent by 'hand beating,' a method practised over a century ago, according to Bancroft (*l.c.*), this operation is commonly effected by machinery. The apparatus is identical with, or very similar to the 'beating wheel,' a rimless wheel, the spokes of which are paddles, and which is now very generally employed in India. Geneste in 1888 patented the pumping in of air, and Bridges-Lee (*l.c.*) in 1891 a shower-bath arrangement, as improvements in the method of oxidation. Rawson again (1902, Eng. Pat. 173) proposed to treat the liquid with acid and an alkaline persulphate; but although excellent results were obtained in the laboratory, these were not satisfactory on the manufacturing scale. As the outcome of an elaborate investigation, Rawson considers that the oxidation of the fermented liquid by blowers and compressors is superior to wheel beating, the yield being thereby increased about 20 p.c.

It has long been the custom to facilitate the deposition of the indigo by what were termed 'precipitants,' and experiments are recorded by Roxburgh, who employed for this purpose ammonia, stale urine, caustic lye, lime water, and potassium ferrocyanide. That such chemicals must be considered to have assisted in the more rapid oxidation of the indoxyl is certain, and their effect is not to be confused with the mere settlement of the indigo by the use of slaked lime, as adopted by the Chinese.

In 1894 Coventry patented a process which was based on the employment of lime under certain conditions. The invention consisted in the employment of a special vat intermediate between the steeping and oxidising vats, in which the fermented liquor was treated with lime. A copious precipitate of calcium and magnesium carbonates was thus produced, which on settling carried down various impurities. The supernatant liquid was then oxidised in the usual manner. The indigo thus produced is somewhat contaminated with lime, and the removal of this is subsequently effected by the addition of a certain amount of acid to the 'mal' in the boiler. Indigo prepared in this manner is of superior quality, and although not equal to the Java product resembles the latter in containing some quantity of indirubin. According to Rawson a substantially increased yield of colouring matter is given by this process.

Caustic soda added to indigo liquor before oxidising behaves very similarly to lime, and on the large scale gave an increase of 43 p.c. of dry indigo as weighed. Sodium peroxide also gave an average increase of 33 p.c., but on the whole was not so serviceable as caustic soda (Rawson).

The oxidation of the fermented plant extract in the presence of ammonia, first mentioned by Roxburgh (*l.c.*), was patented by Michea in 1876, whereas Geneste in 1889 suggested the use of caustic soda and ammonium sulphate instead of liquid ammonia itself. The use of ammonia is mentioned as beneficial by Georgievics (*l.c.*), and there appears to be no doubt that it is superior to the other reagents which have been employed for this purpose. In its presence the indoxyl is rapidly oxidised to indigotin, and the precipitated colouring matter settles well. The more general employment of ammonia in India has resulted from the work of Rawson, and its use in conjunction with the steam injector blower constitutes the most important improvement which he has recommended to the notice of the indigo planters. The procedure adopted by Rawson consists briefly in connecting the outlet of an ammonia still (containing lime and ammonium sulphate) loosely with the steam blower, so that when in action, ammonia, air, and steam are injected into the vat by means of perforated pipes laid at the bottom of the receptacle. During the operation the temperature rises 10°–15°F., and the oxidation is rapidly completed. The employment of ammonia gas and steam in connection with the beating wheel gives also satisfactory results. By these methods Rawson describes increases in the yields of dry indigo, varying from 37 to 63·8 p.c., and considers that the average increase of colouring matter is about 34 p.c. as compared with that given by the ordinary oxidising process.

On the other hand, Bergtheil (Report of the Indigo Research Station, Sirsiah, 1906, 6) states that the ammonia process effects very little, if any, improvement over ordinary oxidising when this is carried out under optimum conditions of speed, weather, water, &c.

After the indigo has settled in the vat, the supernatant liquid, or 'seet' water, is run off as completely as possible. This seet water, as a rule, contains more or less colouring matter in suspension, and it is during this operation that a considerable loss of indigo occurs, which may reach as much as 20 p.c. (Rawson). This, as a rule, is much reduced by using an alkali in oxidising, on account of the readier settlement of the precipitate. Rawson found that filter pressing cannot be adopted in this respect, but suggests treating the 'seet' water with an alkali by which the suspended indigo more readily subsides. On the other hand, Bergtheil (1909) recommends the employment of alumino-ferric as an aid to the deposition of the indigo precipitate in the oxidation vat.

Final treatment of indigo. According to Bancroft (*l.c.*) it was the practice of some manufacturers in the East Indies to purify their indigo by boiling it with water and fossil alkali (soda), whereas Roxburgh, as well as de Cosigny, recommended also the action of a diluted sulphuric acid. The more general practice, until very recently, in India has consisted in merely boiling the semi-fluid indigo paste in a large cauldron, but the use of a dilute sulphuric acid appears now to be very generally adopted. According to Rawson the quality of the indigo may be in this way improved 5–10 p.c. At the close of the operation the indigo is allowed to settle, the acid liquid run off, and the precipitate treated with fresh water and again boiled.

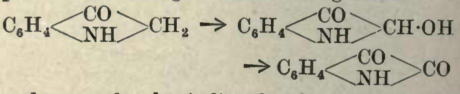
The subsequent filtering, pressing, and drying operations call for no special comment. The slow drying of the product appears to be most advantageous, and in this way an indigo of slightly higher percentage than when the mass is dried artificially is produced. This is accounted for by the fact that certain impurities of the indigo in the presence of moisture undergo gradual decomposition with evolution of ammonia and other gases.

Briggs (Pat. Spec. 292, 1906) has devised an apparatus for drying the indigo paste, and simultaneously converting it into powder. An illustration of this machine, essentially a revolving drum, appears in Bergtheil's Report, 1906, 12. Attempts, moreover, are being made to place natural indigo on the market in the paste form (*ibid.* 1910).

Constituents of Natural Indigo.

In addition to indigotin natural indigo contains varying proportions of indirubin, indigo brown, indigo gluten, and mineral matter. Indigo yellow or kæmpferol is also present as a rule when the *I. arrecta* has been employed for the manufacture.

Indirubin. The identity of the natural indirubin or indigo red, with the artificial product prepared according to Baeyer's method (*l.c.*) about which there was formerly some controversy, appears now to be fully established (Marchlewski and Radcliffe, J. Soc. Chem. Ind. 1898, 17, 434). Bloxam at one time (Chem. Soc. Trans. 1905, 87, 979) considered that a red substance other than indirubin was present in some quantity in natural indigo, whereas Bergtheil (Report of the indigo Research Station, Sirsiah, 1906) has stated that 'decisively there is more than one red body in most commercial indigos.' The investigation of numerous samples of the dyestuff by Perkin and Bloxam (Chem. Soc. Trans. 1907, 91, 279, and 1910, 97, 1461) indicate, however, that this is not the case. Whereas certain varieties of natural indigo, notably Java and Coventry process indigos, contain notable amounts of indirubin, it is probable that a trace occurs in all samples of the natural dyestuff. That the indirubin originates from the indican existing in the leaves of the various species of *Indigofera*, and is due to no second constituent of the plant, is now certain, and its production is to be explained in all cases as due to the condensation of isatin with indoxyl. Thus it has been shown by Thomas, Bloxam, and Perkin (*l.c.*) that indigo containing indirubin can be readily produced from indican by a repetition of the factory method, and again isatin itself has been isolated from natural indigo rich in indirubin (Perkin, Chem. Soc. Proc. 1907, 23, 30). The formation of the isatin is favoured by special circumstances such as the oxidation of the indoxyl by air in the presence of alkali or acid, and may also be affected to some extent by temperature. That indoxyl can be converted into isatin without an intermediate formation of indigotin has been shown by the Badische Anilin und Soda-Fabrik (D. R. P. 107719, 1898), and it has been found by Perkin (Chem. Soc. Trans. 1909, 85, 847) that indoxylic acid, on standing in the presence of moist air, is converted chiefly into indirubin, although some quantity of indigotin together with a substance, probably indigo brown, and traces of isatin are simultaneously produced. Again it has been pointed out (T. B. & P.) that the indican present in air-dried leaves of the indigo plant slowly disappears and, according to Perkin (private communication), this is accompanied in most cases by a development in the leaf of considerable quantities of indirubin. It appears probable that this so-called 'secondary' oxidation of the indoxyl proceeds according to the following scheme:



$$C_6H_4\left<\begin{matrix}CO\\NH\end{matrix}\right>CH_2 \rightarrow C_6H_4\left<\begin{matrix}CO\\NH\end{matrix}\right>CH{\cdot}OH \rightarrow C_6H_4\left<\begin{matrix}CO\\NH\end{matrix}\right>CO$$

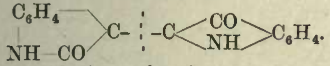
and may also be indirectly the cause of the production of indigo brown. The following are the results of analyses illustrating the percentages of indirubin and indigotin in certain indigos (B. and P.):—

Sample.	Total colouring matter.	Indigotin.	Indirubin.
Java Indigo.—New process with hot water.			
1.	75·20	67·76	7·43
2.	73·60	63·86	9·51
6.	62·91	57·35	5·01
Java indigo.—New process with cold water.			
7.	72·88	69·23	3·06
8.	71·02	66·35	4·04
9.	58·30	55·61	2·15
Java indigo.—Old process without chemicals.			
13.	74·96	72·89	1·74
15.	69·54	68·26	0·99
Coventry.—Process indigo.			
	61·76	56·63	5·23

Finally, Bloxam and Perkin refer to an abnormal sample of laboratory indigo prepared from pure indican, which contained 88·9 p.c. of colouring matter, and of this 25·83 p.c. was indirubin.

Though indirubin was at one time considered to be a valuable constituent of natural indigo (*cp.* Rawson and Knecht, J. Soc. Dyers, 1888, 4; Hummel, *ibid.*; and Bergtheil, Report Indigo Research Station, Sirsiah, 1907, 7) it is now known that such is not the case.

Fasal (Mitt. K. Tech. Gew-Mus. Wien. 1895, 11, 307) found that the shade of colour given by an indirubin vat became bluer from day to day, and that this was due to the formation of indoxyl by the further reduction of the leuco-indirubin. More recently Perkin (Chem. Soc. Proc. 1909, 25, 127) has shown that in addition to indoxyl oxindole is simultaneously produced, and this is in harmony with the formula assigned by Baeyer (*l.c.*) to this substance.



In vat dyeing, therefore, indirubin may produce not more than one-half its weight of indigotin. Matthews (J. Soc. Chem. Ind. 1902, 21, 22), again, points out that indirubin requires for reduction a much stronger reagent than indigotin, and as a result the greater part of this dyestuff is not attacked, but settles to the bottom of the vat.

On the other hand, indirubin disulphonic acid is, according to Fasal (*l.c.*), and also to Rawson and Knecht (*l.c.*), a useful dyestuff, and gives colours much faster to light than sodium indigotin disulphonate, the 'indigo extract' of commerce.

Indigo brown. An important impurity of natural indigo is the so-called indigo brown, a product isolated and cursorily examined by both Chevreul (Gmelin, Handbook of Chem. 1859, 13, 48) and Berzelius (*ibid.*). In order to isolate this product, the latter chemist digested indigo with boiling dilute sulphuric acid to remove indigo gluten, and subsequently with potassium hydroxide to dissolve the brown. The alkaline liquid was neutralised with acetic acid, evaporated to dryness, the residue digested with alcohol, and the solution evaporated. Thus obtained the indigo brown consisted of a dark-coloured resin, soluble in alkaline solutions. According to Schunck (Phil. Mag. 1855, [iv.] 10, 74, and *ibid.* 1858, 15, 127) the indihumin $C_{10}H_9O_3N$ produced in conjunction with other brown amorphous products by the action of dilute acids on his indican was, perhaps, identical with indigo brown.

Perkin and Bloxam (Chem. Soc. Trans. 1907, 91, 279) extracted Bengal indigo, which had been already digested with boiling dilute hydrochloric acid to remove the gluten, with boiling pyridine. In addition to a little indirubin the product contained three substances: (*a*) the main constituent, $C_{16}H_{12}O_3N_2$ (?) insoluble in alcohol and acetic acid, (*b*) $C_{24}H_{22}O_5N_3$ (?) soluble in acetic acid, and (*c*) $C_{16}H_{14}O_4N_2$ (?) soluble in alcohol. These compounds, the molecular weight of which is uncertain, consist of brown amorphous powders, closely resembling one another in general property, and are readily reduced by zinc dust in alkaline solution with formation of pale brown liquids. When digested with boiling 50 p.c. potassium hydroxide solution they give some quantity of *anthranilic acid*, a point which indicates that they are derived from indoxyl. At the same time a brown resinous substance is also produced, and this studied in the case of the main constituent (*a*) $C_{16}H_{12}O_3N_2$ contained C=71·39; H=4·05; N=7·94. Natural indigo further contains a small quantity of a brown substance (*α*), insoluble in pyridine, but soluble in boiling dilute alkali (Chem. Soc. Trans. 1910, 97, 1473), and is distinguished from the substances above enumerated by the fact that it is not susceptible to sulphonation (with 96 per cent. sulphuric acid) or conversion by this means into a product soluble in water. In the analytical method described by Rawson (J. Soc. Chem. Ind. 1899, 18, 251) this brown material, at least in part, consists of the impurity which is carried down by a precipitation of barium sulphate in the liquid. There is now considerable evidence in favour of the view that the constituents of indigo brown are derived from indoxyl during the manufacture of indigo from the plant. The fact that indican itself, when boiled with dilute acids, produces the very similar indoxyl brown, and the isolation of brown substances, although in trifling amount, from indigo prepared by the hydrolysis of pure indican in the laboratory, harmonises with this suggestion.

Beyerinck (Proc. Roy. Akad. Scien. Amsterdam, 1899, 120) observed that the disappearance of indoxyl in a dying woad (*Isatis tinctoria*) leaf is accompanied by the appearance of brown substances. Again, he states that 'strong acids, just as alkalis . . . favour the formation of indigo from indoxyl, but then part of this substance constantly changes into a brownish-black matter.' It has also been noted by Thomas, Perkin, and Bloxam that the disappearance of indican in the leaves of the *I. sumatrana* on keeping is accompanied by the formation of brown extractive matter. Rawson, again (Report on the Cultivation and Manufacture of Indigo, Mozzufferpore, 1904), says, 'The blower . . . by quickly getting rid of CO_2 gas . . . prevents decomposition of a portion of the colouring matter into worthless brown substances, which takes place to a greater extent under other conditions.' All indigos, moreover, appear to contain indigo brown so that this property is irrespective of their origin, which may have been due to such distinct plants as the *Indigoferæ*, the *Polygonum tinctorium*, or the *Lonchocarpus cyanescens* of West Africa. Finally, it has been shown by Perkin (*l.c.*) that among the decomposition products of commercial indoxylic acid which has been kept for a long time, a brown compound exists, which has a very similar percentage composition, and is probably identical with the main constituent of indigo brown. It is quite possible that indoxylic acid is produced during the fermentation process (Perkin). The percentage of indigo brown, soluble in pyridine in natural indigos is very variable, and appears to depend upon the details of manufacture. Analyses made by Bloxam and Perkin (Chem. Soc. Trans. 1910, 97, 1472) gave the following result:—

Java indigo, new process, hot water.	*Java indigo, new process, cold water.*	*Java indigo, ordinary process.*	*Coventry process indigo.*	*New Bengal indigo.*
5·4	5·2	4·15	8·7	9·60

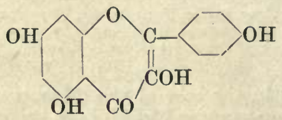
Except in the case of the Coventry process indigo, these samples had all been derived from the *I. arrecta*. The average amount of crude indigo brown—containing, however, some mineral matter—in numerous samples of Bengal indigo was 14 p.c. (Chem. Soc. Trans. 1907, 297).

Indigo brown dissolved in alkaline hydrosulphite solution does not colour fabrics, and appears to be entirely devoid of tinctorial property. The frequently asserted superiority of the natural over the artificial variety of indigo cannot therefore be accounted for in this manner.

Indigo gluten. Indigo gluten was first isolated from crude indigo by Berzelius (Berz. Jahresb. 7, 26), who extracted it with dilute acid, neutralised the extract with chalk, evaporated to dryness and dissolved out the gluten with alcohol. It was subsequently prepared by Orchardson, Wood, and Bloxam (J. Soc. Chem. Ind. 1907, 26, 4), who describe it as a horny mass, which on grinding gives a light biscuit-coloured powder, and when heated evolves ammonia. In cake indigo it appears to exist in combination with mineral matter, possibly as a calcium compound, for though itself readily soluble in water it can only be removed from the dyestuff by means of dilute mineral acid. A considerable quantity of this substance is frequently present in indigo, and Perkin and Bloxam (*l.c.*) found that when the crude Bengal variety containing approximately 62 p.c. of indigotin was digested with dilute hydrochloric acid, it lost 21·5 p.c. of its weight. This figure naturally includes some quantity of mineral matter simultaneously removed by the acid. It has been suggested that this compound plays an important rôle in the dyeing operation, and accounts in part for the alleged superiority of natural over artificial indigo. This point, however, has not been scientifically investigated.

Indigo yellow. The first application of the term 'indigo yellow' to a substance existing in natural indigos is due to Bolley and Crinsoz (J. 1866, 573), who state that it is to be found in the Bengal variety, and can be isolated by sublimation. It is described as golden-yellow needles, subliming at 130°, and soluble in soda lye. Crude Bengal indigo, however, gives no sublimate of this character (Perkin, Chem. Soc. Proc. 1906, 22, 198), but by submitting refined indigo, or the commercial synthetical variety to sublimation with limited access of air, a trace of a yellow compound $C_{15}H_8O_2N_2$ is produced. This substance, however, is insoluble in alkaline solutions, and cannot, therefore, be the indigo yellow of Bolley and Crinsoz.

Rawson (J. Soc. Chem. Ind. 1899, 18, 251) detected in Java indigos a yellow compound, present usually to the extent of 2–3 p.c., although in one special sample as much as about 20 p.c. occurred. This substance was soluble in alkalis with a yellow colour; on heating it partially sublimed, and had the properties of an adjective yellow dyestuff. A more recent investigation (Perkin, Chem. Soc. Proc. 1904, 20, 172) has indicated that this in reality is *kæmpferol*



a trihydroxy flavonol known to exist (Chem. Soc. Trans. 1902, 81, 587) in the flowers of the *Delphinium consolida* (Linn.) and other plants. Ultimately it was shown that the leaves of the *I. arrecta*, from which Java indigo is prepared, contain sometimes as much as 4 p.c. of a glucoside *kæmpferitrin* $C_{27}H_{30}O_{14}$, almost colourless needles, m.p. 201°–203°, which when digested with acid gives kæmpferol and rhamnose

$$C_{27}H_{30}O_{14}+4H_2O=C_{15}H_{10}O_6+2C_6H_{12}O_5,H_2O.$$

This compound is not hydrolysed by the indigo enzyme, and no enzyme has as yet been isolated from the plant possessing such a property. It is likely (Chem. Soc. Trans. 1907, 91, 435) that the use of sulphuric acid, when manufacturing Java indigo, may result in the contamination of the dyestuff with kæmpferol. When the wet indigo sludge or 'mal' is boiled in the 'mal' boiler with addition of a little of the acid, the kæmpferitrin present in the adhering water will be hydrolysed, and the insoluble colouring matter remain with the indigo. Samples of Java indigo more recently obtained contained only a trace (0·2 p.c. approx.) of kæmpferol, whereas in a sample of the new Bengal indigo manufactured from the *I. arrecta* approximately the same quantity was detected (Perkin, private communication). If indigo mixed with kæmpferol is cautiously sublimed the sublimate then contains appreciable quantities of this yellow colouring matter, and it seems likely, therefore, that this is in reality the indigo yellow of Bolley and Crinsoz, but that the indigo experimented with by these authors did not, as they supposed, originate from Bengal. The leaves of the *I. sumatrana*, the Indian indigo plant, contain but the merest trace of a yellow dyestuff resembling kæmpferol, but according to Henry (Gmelin's Handbook of Chem. 1846, 13, 50) the *Polygonum tinctorium*, or Chinese indigo plant, contains appreciable quantities of a yellow colouring matter.

THE ANALYSIS OF INDIGO.

The methods which have been proposed for the analysis of indigo are of a varied character, and the literature upon the subject is extremely voluminous.

These may be classified as follows: methods (*a*) involving the extraction of impurities with volatile solvents (Schützenberger, Die Farbstoffe, ii. 526); (*b*) the extraction of indigotin with coal tar oil (Stein, Die Prüfing der Zeugfarben); with aniline (Hönig, Zeitsch. angew. Chem. 1899, 280); with phenol (Brandt, J. Soc. Dyers. 1898, 34); with naphthalene (Schneider, *ibid.* 1895, 194); with nitrobenzene (Gerland, J. Soc. Chem. Ind. 1897, 108); with aceto-sulphuric acid (Möhlau and Zimmermann, Zeitsch. farb. text. Chem. 1903, 10, 189); (*c*) the extraction of indigotin by sublimation (Lee, Chem. News, 1884); (*d*) the extraction of indigotin by processes of reduction, lime, and ferrous sulphate (Berzelius), stannous chloride and caustic soda (Dana, Jahres. f. prakt. Chem. 26, 398), zinc and caustic soda (Owen, J. Amer. Chem. Soc. 10, 178), grape sugar, alcohol, and alkali (Fritzsche, Dingl. poly. J. 1842, 86, 306), and hydrosulphite and lime (Rawson, *l.c.*); (*e*) estimation of nitrogen (Voeller, Zeitsch. angew. Chem. 1891, 110).

More important, however, are the methods based upon the titration of a solution of the sulphonated indigo by oxidising agents (*f*) chlorine water (Berzelius), chloride of lime (Chevreul, Lecons. d. chem. appliq. de la teinture, ii.), potassium chlorate and hydrochloric acid (Bolley, Dingl. poly. J. 119, 114), potassium dichromate and hydrochloric acid (J. pr. Chem.

1851, 18, and Schlumberger, Bull. de la Soc. Mullhouse, 1863, 210, 284) potassium dichromate and oxalic acid (Kinley, Chem. News, 1863, 210, 284), potassium ferricyanide (Ullgren, Annalen, 136, 96), and potassium permanganate (Mohr, Dingl. poly. J. 132, 363), and by reducing agents, (*g*) sodium hydrosulphite (Müller, Ber. 1880, 13, 2283), and titanous chloride (Knecht, J. Soc. Dyers. 1904, 97, and *ibid.* 1905, 292).

Finally (*h*) colorimetric methods (Dingl. poly. J. 27, 54, and 40, 448); (*i*) spectrum analysis (Wolff, Zeitsch. anal. Chem. 17, 65, and *ibid.* 23, 92); and (*k*) dye trial methods (Chevreul, *l.c.*, and Grossmann, J. Soc. Dyers. 1897, 124) have been proposed.

Of these methods of indigo analysis, modifications of Mohr's permanganate process are most generally employed, although others involving the reduction of sulphonated indigo with titanous chloride and sodium hydrosulphite are to some extent in vogue.

The permanganate methods. In order to eliminate the error due to the oxidising action of permanganate upon substances other than indigotin which are present in natural indigo, Rawson, who has been the pioneer in this respect, has devised two processes.

Salting out method. 0·5 gram of finely powdered indigo mixed with its own weight of ground glass is sulphonated in a porcelain crucible by means of 20 c.c. of concentrated sulphuric acid at 70° for $\frac{3}{4}$-1 hour; the product is diluted with water to 500 c.c., and the liquid filtered to remove insoluble impurities. 50 c.c. of this solution are mixed with 50 c.c. of water and 32 grams of common salt, and after standing for 1 hour the precipitated sodium indigotin sulphonate is collected and freed from certain soluble impurities by washing with about 50 c.c. of salt solution (sp.gr. 1·2). The precipitate is dissolved in hot water, treated with 1 c.c. of sulphuric acid, diluted to 300 c.c., and titrated with a solution of $N/50$ potassium permanganate. The liquid gradually takes a greenish tint, and the final disappearance of this constitutes the end point of the reaction. According to Rawson, 1 c.c. of the $N/50$ permanganate corresponds to 0·0015 of pure indigotin (J. Soc. Dyers., 1885, 74 and 201; A Manual of Dyeing, Knecht, Rawson, and Löwenthal, 1910, 817).

Barium chloride precipitation process. 0·5 gram of indigo is sulphonated as before, and after diluting with water, but before making up to 500 c.c., 10 c.c. of a 20 p.c. solution of barium chloride are added. The barium sulphate formed carries down with it the suspended impurities of the indigo, and the clear liquid can be pipetted off and titrated as before. The results are practically identical with those given by the 'salting out' method (Rawson, J. Soc. Chem. Ind. 1899, 251).

Bloxam (*ibid.* 1906, 735) notes that the barium precipitate thus produced is always coloured blue, and this is confirmed by Bergtheil and Briggs (*ibid.* 1906, 729). The latter authors contend that the results given by this modification of Rawson, are therefore too low, and consider that this defect is obviated by adding instead of barium chloride freshly precipitated barium sulphate to the indigo mixture.

Grossmann (*ibid.* 1905, 308) throws down the impurities from the indigo solution with calcium carbonate. Bergtheil and Briggs (*l.c.*), and also Bloxam (*l.c.*), find that some quantity of the colouring matter is also precipitated in this way. Knecht, however, recommends its successful use even in larger quantity (J. Soc. Dyers. 1904, 97, and 1905, 292) in connection with his titanous chloride method; but Bloxam (*l.c.*) points out that such being the case this can only be due to the observance of conditions which are not stated in Knecht's paper.

Hydrosulphite method. This process, devised by Müller (Ber. 1880, 13, 2283), depends upon the fact that sodium hydrosulphite ($Na_2S_2O_4$) quantitatively reduces pure indigotin sulphonic acids to their corresponding leuco compounds. The solution of the hydrosulphite contained in a stone bottle, is covered with a layer of petroleum to prevent oxidation and connected with a supply of hydrogen gas. By means of a siphon, or other convenient arrangement, the liquid can be drawn into a burette. The solution should be equivalent to about 1 c.c. = 0·0025 gram of indigotin, and the titrations are performed in an atmosphere of hydrogen or coal gas.

Titanous chloride method. This reagent is much more stable than sodium hydrosulphite, and Knecht (J. Soc. Dyers. 1904, 97, and 1905, 292) was the first to recommend its use for the analysis of indigo. The apparatus employed is similar in character to that required for the hydrosulphite process, and the titration is carried out in an atmosphere of carbon dioxide. If the reduction of the indigotin is effected by the titanium chloride in the presence of mineral acid, no definite end-point can be observed (Knecht), but by the addition of salts of tartaric acid this end-point is rendered quite definite.

In working with natural indigo, Knecht (Manual of Dyeing; Knecht, Rawson, and Löwenthal, 822) sulphonates 1 gram of indigo with 5 c.c. of 100 p.c. sulphuric acid at 90° for 1 hour. The solution diluted to 300 c.c. is warmed and slowly treated with 12 grams of chalk, cooled, made up to 500 c.c., and 50 c.c. of the clear liquid to which 25 c.c. of a 20 p.c., solution of Rochelle salt has been added, is titrated whilst boiling with titanium chloride.

On account of the sparing solubility of Rochelle salt, Bloxam (*l.c.*) recommends the use of sodium tartrate, but states that the presence of excess of this or of Rochelle salt (as advocated by Knecht) is to be avoided, or otherwise too high percentages of indigotin are indicated. In the case of pure indigotin (1 gram) sulphonated with 20 c.c. of 100 p.c. sulphuric acid, and made up to 500 c.c. with water, 25 c.c. of this liquid (containing 1 c.c. of acid) requires 4 grams of the sodium tartrate to give quantitative results when titrated with a solution of titanium chloride containing 1 c.c. of concentrated hydrochloric acid per 50 c.c. of solution.

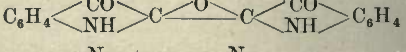
Bloxam (Chem. Soc. Trans. 1905, 87, 975; J. Soc. Chem. Ind. 1906, 25, 735), Orchardson, Wood, and Bloxam (*ibid.* 1907, 26, 4), and Gaunt, Thomas, and Bloxam (*ibid.* 1907, 26, 1174), have critically investigated the subject of indigo analysis. Among the methods for preparation of pure indigotin, that involving the crystallisation of crude material from nitrobenzene was discarded as untrustworthy, but the elaborate process of the B. A. S. F. Co. (Brochure, 1900) was found to give a pure substance. On the other hand, sublimation under reduced pressure in Jena flasks immersed in fusible metal at 370°–390°, gave, with synthetical indigo of 92 p.c. (approx.), a beautifully crystalline substance, which, after washing with boiling acetic acid, followed by boiling alcohol, was usually chemically pure. The permanganate factor resulting from experiments with these specially purified materials was 1 c.c. of permanganate solution 1/1000=0·00222 gram indigotin solution 1/5000, and is in agreement with that previously adopted by the B. A. S. F. Co., but differs considerably from that employed by Rawson (1 c.c. of *N*/50 permanganate=0·0015 indigotin) (*l.c.*). Wangerin and Vorlander (Zeitsch. Farben und Textilchemie, 1902, 1, 281) have stated that indigotin suffers loss of strength by oxidation, even when it is sulphonated by 94 p.c. sulphuric acid at 95°–100° for half an hour, whereas acid of 8 p.c. fuming acid gives a deterioration of from 2 to 14·2 p.c., according to the time of heating. With the indigotin, however, purified as above, Bloxam showed that heating with 20 p.c. fuming acid for $\frac{3}{4}$ of an hour at 97° gave no loss, whereas with 30 p.c. acid for 20 minutes at 97° a deterioration of only 1 p.c. could be observed. In both these cases indigotin tetrasulphonic acid was produced.

The tetrasulphonate method. As a result of these experiments a method for the analysis of indigo based on sulphonation with fuming acid was devised. 1 gram of the indigo, and 2–3 grams of purified sand (powdered glass contains iron, and should not be employed), is treated with 5 c.c. of 25 p.c. fuming sulphuric acid for half an hour in the water oven, and the solution is made up to 500 c.c. with water. 100 c.c. of this solution is treated with 100 c.c. of potassium acetate solution (450 grams per litre) which causes the precipitation of indigotin tetrasulphonate. The mixture is now warmed, and on cooling finally in ice-water, the salt completely separates in a crystalline condition. This is collected by means of the pump on a Gooch crucible, and washed free from the brown supernatant liquid with a solution containing 90 grams of potassium acetate and 5 c.c. of acetic acid in 600 c.c. of water. The product is dissolved in 200 c.c. of water, and 20 c.c. of this solution, diluted with 80 c.c. of water, is treated with 0·5 c.c. of sulphuric acid, and titrated with permanganate (1/1000). In order to verify the accuracy of this method, Orchardson, Wood, and Bloxam studied the behaviour of indigo brown and indigo gluten, the main impurities of indigo, when submitted to the analytical process, as this subject had not been investigated by previous workers. Indigo brown, when sulphonated with 96 p.c. acid gives, when dissolved in water, a dark-brown liquid, which is attacked by permanganate, though not perhaps so readily as the indigotin sulphonic acids, whereas indigo gluten gives similarly a light yellow solution, which is very rapidly oxidised by the reagent. On the other hand, kæmpferol or indigo yellow, treated in the same manner, gave a product which most readily absorbs permanganate, and, indeed, Rawson (J. Soc. Chem. Ind. 1899, 251) had already pointed out its deleterious effect in indigo analyses. Finally, these authors prepared and submitted to analysis by Bloxam's process mixtures containing known quantities of indigotin and one or other of all of these impurities, with the result that the colouring matter was thus estimated with considerable exactness. Bloxam (Chem. Soc. Trans. 1910, 97, 1473), by an adaptation of the pyridine method for the estimation of indirubin (*l.c.*), in which the impurities are eliminated by a process of extraction, has analysed natural indigos, and obtained the same figures as those given by the tetrasulphonate method. Again, by Knecht's titanium chloride method, and employing the modifications above described, this process can also be effectively worked. It is only reasonable to suppose that an analysis based on the selective precipitation of the sulphonated colouring matter is more likely to be efficient, than that which presumes the deposition of varied impurities of a diverse chemical character by one specific reagent, and the somewhat lower results given by the tetrasulphonate method, as distinguished from those yielded by the processes previously in use, are in reality due to the almost complete elimination of these impurities from the indigotin sulphonic acid during the analysis. Rawson (*l.c.*) is, however, of opinion that the effect of these impurities on the analytical results has been much overrated; but, on the other hand, no experimental evidence is given in support of this view (Manual of Dyeing, *l.c.* 818).

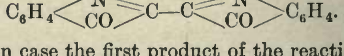
The action of potassium permanganate on solutions of the indigotin sulphonic acids is of interest, because the amount of the reagent necessary for the decolorisation of the liquid varies to some extent with the concentration (Rawson, A Dictionary of Dyes, Mordants, &c., by Rawson, Gardner, and Laycock, 1901, 187). At the concentrations employed by the B. A. S. F. Co., and adopted by Bloxam (*l.c.*), 1 gram of indigotin as sulphonic acid requires 0·45 gram of permanganate for decolorisation, whereas the equation

$$5C_{16}H_{10}O_2N_2+4KMnO_4+6H_2SO_4$$
$$=10C_8H_5O_2N+2K_2SO_4+4MnSO_4+6H_2O$$

implies that 0·4824 gram of the reagent is necessary. Again, for the oxidation under similar conditions of indirubin sulphonic acid considerably less permanganate is required, although the oxidation in this case is of a slower character. Bloxam and Perkin (J. Chem. Soc. 1910, 97, 1462) consider, therefore, that the oxidation is of a complex nature, and consists either (*a*) of two distinct stages in the formation of isatin sulphonic acid, or (*b*) of two distinct reactions involving the production of two separate substances. According to the first suggestion the isatin formation from indigotin would be preceded by that of an intermediate compound (I.), whereas by the latter, in addition to isatin, a dehydroindigotin sulphonic acid (II.) is produced.

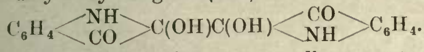
I. 

$$C_6H_4{<}\genfrac{}{}{0pt}{}{CO}{NH}{>}C\overset{O}{—}C{<}\genfrac{}{}{0pt}{}{CO}{NH}{>}C_6H_4$$

II. 

$$C_6H_4{<}\genfrac{}{}{0pt}{}{N}{CO}{>}C—C{<}\genfrac{}{}{0pt}{}{N}{CO}{>}C_6H_4.$$

In case the first product of the reaction consists entirely of dehydroindigotin sulphonic acid; this must, prior to further oxidation to isatin, take up two molecules of water with formation of dihydroxy-indigotin (III.).



$$C_6H_4<^{NH}_{CO}>C(OH)C(OH)<^{CO}_{NH}>C_6H_4.$$

In regard to the very small amount of permanganate required for the decolorisation of the indirubin sulphonic acid a similar explanation can be adopted.

THE ESTIMATION OF INDIGOS RICH IN INDIRUBIN.

It is well known that indirubin is more resistant to oxidation and reduction than indigotin, properties which also apply to the sulphonic acids of these colouring matters. When dealing, therefore, with mixtures of these substances and employing either potassium permanganate, titanium chloride, or sodium hydrosulphite, the indigotin is to some extent preferentially attacked, so that towards the end of the operation the colouring matter consists entirely of indirubin sulphonic acid. In the case of the former reagent, however, Koppeschaar (Zeitsch. anal. Chem. 1899, 38, 1) finds that it is not possible to obtain trustworthy analytical figures with indigos in which some quantity of indirubin is present, although Rawson (*l.c.*) considers that the indirubin may be approximately estimated in this manner. Bloxam and Perkin (Chem. Soc. Trans. 1910, 97, 1462), however, support the view of Koppeschaar. The latter authors, who also experimented with titanous chloride, show that this reagent behaves in an identical manner towards both indigotin and indirubin sulphonic acids, but although the former is somewhat preferentially attacked, it is not possible in this way to differentiate as to the amount of each of the sulphonated colouring matters which may be present in a mixture of the two. On the other hand, according to Knecht, Rawson, and Löwenthal (A Manual of Dyeing, 821) indirubin present in mixtures of the two colouring matters may be approximately estimated by the hydrosulphite method.

For analysis of indigos rich in indirubin, processes of extraction based on the greater solubility of the latter, have been usually employed.

Extraction with ether (Rawson, *l.c.*). From 0·1 to 0·25 gram of the sample is boiled with about 150 c.c. of ether for half an hour. When cold the solution is made up to 200 c.c. with ether, mixed with 10 c.c. of water and well shaken. The suspended particles of indigotin settle immediately, and a clear solution of indirubin is obtained. A measured quantity of the solution is withdrawn, and compared in a colorimeter with a standard solution of indirubin.

Extraction with acetic acid (Koppeschaar, *l.c.*). The indigo is extracted with glacial acetic acid, and the solution, which contains a mixture of indirubin and indigo brown, is treated with caustic soda. The indirubin, which is thus precipitated, is collected, redissolved in acetic acid, and estimated by comparison with a standard solution of the pure colouring matter.

Extraction with acetone (Gardner and Denton, J. Soc. Dyers. 1901, 170). 0·2 gram of the indigo is digested for half an hour with 100 c.c. of boiling acetone. After cooling the solution is made up to 100 c.c. with acetone, and then to 200 c.c. with 10 p.c. salt solution, and well shaken. The precipitate of indigotin, indigo brown, and other impurities, is removed by filtration, and the indirubin solution estimated colorimetrically with a standard solution of indirubin prepared with acetone and salt solution in a similar way.

Extraction with pyridine. Bloxam and Perkin (Chem. Soc. Trans. 1900, 97, 1460) find, as the result of experiments on mixtures of indigotin and indirubin, that neither commercial ether nor acetone are reliable solvents for the complete extraction of indirubin, and that their action, especially in the former case, is chiefly due to the presence of alcohol. Whereas acetic acid is efficient in this respect, and Koppeschaar's process gives approximately good results, pyridine is a much better solvent, and a method for the complete analysis of indigos containing indirubin based on the application of this liquid is described by these authors.

The indigo (0·25–1 gram) evenly incorporated with purified sand (20–30 grams) is introduced into a thin-walled glass tube, termed the 'container,' closed at one end by means of cotton cloth, on which has been placed a layer of asbestos and sand or of sand alone. Sufficient sand is then added to form a layer on the surface of the indigo mixture, which is then covered with asbestos, and the container is now placed in a Soxhlet tube and extracted with boiling pyridine. The extract is distilled down to a small bulk, the residue treated with boiling water and again distilled, and this operation is repeated until the last traces of pyridine have disappeared. The precipitate, which consists of indirubin together with a little indigotin and indigo brown, is collected, freed from the latter by means of dilute alkali, and the residue is sulphonated with 5 c.c. of sulphuric acid at 100°. The product is dissolved in water, filtered, and the amounts of indigotin and indirubin present ascertained by means of the Duboscq tintometer.

The residue in the container is percolated with water, followed with boiling dilute hydrochloric acid to remove indigo gluten, and is now introduced into a beaker and dried. The colouring matter present is sulphonated with 20 c.c. of sulphuric acid in the usual way, the product after dilution is filtered, and the solution of the indigo sulphonic acid is estimated with permanganate, employing the directions given by Bloxam (*l.c.*). Analyses of mixtures of pure indigotin and indirubin, and also of commercial indigos are given in the paper, and it is also pointed out that by this method an approximate estimation of the indigo brown present in the latter can be carried out.

THE ESTIMATION OF INDICAN IN THE LEAVES OF INDIGO PLANTS.

Although some indication of the indigo-yielding capacity of the plant can be obtained by ordinary steeping experiments, this method was found by Rawson (Cultivation and Manufacture of Indigo, *l.c.*) to possess several drawbacks, and numerous experiments were therefore carried out by him on the quantitative formation of indigo from the leaf extract by the simultaneous action of acids and oxidising agents. As regards the latter, ferric chloride, potassium chlorate, and hydrogen peroxide were tried, but persulphuric acid gave much the best results.

Persulphate method. 20 grams of leaves are extracted for 2 minutes with 250 c.c. of boiling water, the solution is strained through muslin, and the residues squeezed and washed with boiling water. The solution is treated with 5 c.c. of 20 p.c. hydrochloric acid, and 40 c.c. of a 5 p.c. solution of ammonium persulphate. The persulphate is not added all at once; at first 2 c.c. are added, after half an hour 2 c.c. more, and again 2 c.c. after another half an hour. After 2 hours the remainder of the ammonium persulphate is added, and when the mixture has stood for a further period of an hour, the indigo is collected and estimated by permanganate in the usual manner. Bergtheil and Briggs (J. Soc. Chem. Ind. 1906, 734) point out, however, that this process of Rawson's requires modification, as the addition of the reagents at such a high temperature involves a loss of indigotin. The main features of a modification of the process devised by these latter authors are the addition of acid to the cooled extract, and a determination of the course of the reaction, after addition of small amounts of persulphate, by filtration of a portion of the mixture and the addition to the filtrate of a trace of the oxidising agent.

Orchardson, Wood, and Bloxam (*ibid.* 1907, 40; *cp.* also Bloxam and Leake, Research Work on Indigo, Dalsingh, Serai, 1905), who employ sulphuric acid and persulphate, arrived independently at the same conclusion. To 200 c.c. of the leaf extracts these authors add 100 c.c. of a mixture of equal parts of 2 p.c. ammonium persulphate, and 4 p.c. sulphuric acid, and the mixture is kept at 60° for 1 hour. A comparison of their methods with that of Bergtheil and Briggs indicated an identical result in each case, and an increase of 20–25 p.c. of pure colouring matter in comparison with that yielded by Rawson's original process.

The isatin method. Beyerinck (Proc. K. Akad. Wetensch. 1899, 120), in discussing indican, suggested the possibility that by warming its solution with isatin a quantitative yield of indirubin might be produced. Orchardson, Wood, and Bloxam (*l.c.*) have employed this reaction for the estimation of the leaf, and have devised the following method for this purpose.

250 c.c. of extract, equivalent to 5 grams of the leaf, is treated with 0·1 gram of isatin, and the mixture boiled for 5 minutes to expel air, carbon dioxide being passed through the flask. 20 c.c. of hydrochloric acid is then added by means of a tap funnel, and the whole kept boiling for 30 minutes. The precipitate is collected on a tared filter, washed with hot 1 p.c. soda to remove brown compounds, then with 4 p.c. acetic acid and dried. An aliquot portion of the crystalline product is sulphonated, and analysed by the titanous chloride method, adopting the modifications employed by Bloxam (*l.c.*). The indirubin thus obtained is usually almost pure (98·5 p.c.), so that for an approximate estimation, the latter part of the process is unnecessary. Gaunt, Thomas, and Bloxam (*ibid.* 1907, 26, 56) have examined the process in greater detail, and point out that by its employment pure indican gives quantitative figures (*cp.* also Perkin and Bloxam, Chem. Soc. Trans. 1907, 91, 90). On the other hand, this method gives considerably higher figures, both with pure indican (15 p.c.) and the leaf extract (25 p.c.), than those which are obtained by the persulphate process (Orchardson, Wood and Bloxam; and Gaunt, Thomas, and Bloxam, *l.c.*). The unsatisfactory figures in the latter cases arise from a further oxidation of the indigo by the persulphate. That this isatin method does not appear to be affected by other plant constituents was shown by the successful estimation of indican, purposely added to an extract of the leaves of the *Tephrosia purpurea* (Pers.), a plant in which this glucoside is absent.

Efficiency of the Process.

The actual yield of indigotin from the plant during the manufacture is not discussed by Rawson (*l.c.*), but this author considers that if the suggestions enumerated in his report are adopted, there is little or no room for a remunerative alteration of the process. Bergtheil, on the other hand, considers that under the conditions he describes (1906, 12) the efficiency is represented by an 82 p.c. yield, or that if to this be added the 5 p.c. believed by Rawson to be retained by the extracted plant, 87 p.c. is thus accounted for. The quantity of indigo estimated refers to the precipitate present in the vat after oxidation, and from this must be, therefore, deducted the indigo (10–20 p.c.) lost by the 'running off' of the 'seet' water, so that the actual yield of dry colouring matter will thus represent from 62 to 72 p.c. of the theoretical quantity. Recent experiments, however, indicate that by adding aluminoferric to the oxidation a more perfect settlement of the indigo is to be anticipated (*ibid.* 1909).

Bloxam (Dalsingh Serai Report, and J. Soc. Chem. Ind. 1906, 25, 735), who examined the daily output of indigo (as pressed cake) from the Pembarandah factory, found that the first cuttings of the plant (Moorhun mahai) represented an approximate value of 0·1495 p.c. of indigotin from the plant, whereas the second cuttings gave a value of but 0·1526. Assigning to the plant the low value of 0·3 p.c., a considerable and serious loss is thus apparent. Moreover, the estimation of the results given by the 'isatin' method of leaf estimation, and of the finished cake by the 'tetrasulphonate' process (*l.c.*), both of which have been standardised with extreme care, point to a loss during the manufacture much greater than has hitherto been acknowledged (Report to Government of India, 1908).

Apart from the retention of indoxyl by the residual plant in the steeping vat, and the mechanical carrying over of indigo by the 'seet' water, the deficiency of colouring matter is chiefly to be attributed to the conversion of indoxyl into products other than indigotin. Rawson (*l.c.*) has pointed out that if the fermented liquid is allowed to stand before oxidation a considerably decreased yield of indigo is ultimately observed. Thus, on the large scale, by standing for 6 hours a loss of 16·1 p.c. was apparent. Perkin and Bloxam (*l.c.*) have found, as a result of their experiments with pure indican, that this alteration or 'decay' of indoxyl takes place not only in this manner during the fermentation process, but they consider that the indoxyl from the moment of its production by the hydrolysis of indican until its final conversion into indigotin is continually suffering this alteration. This peculiar reaction, representing an important defect in natural indigo manufacture is according to these authors, considerably inhibited by the presence of acid.

Commercial Natural Indigos.

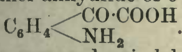
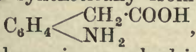
When natural indigo was at its zenith very numerous varieties of this dyestuff were placed on the market, but more recently, owing to its severe competition with the artificial colouring matter, many of these are now rarely met with. From Asia came the indigos of Bengal, Oudh, Madras, Java, Manilla; from Africa those of Egypt and Senegal; and from America those of Guatemala, Caracas, Mexico, Brazil, South Carolina, and the Antilles.

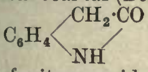
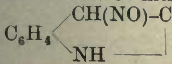
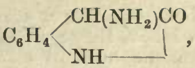
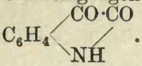
The best varieties are the Bengal, Java, and Guatemala, although in England the Bengal is now mainly employed. Java indigo, formerly largely esteemed for the manufacture of indigo extract, chiefly because of its general purity, at the present time appears to find its market chiefly in the East.

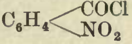
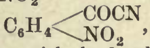
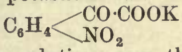
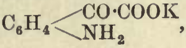
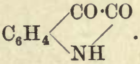
A good quality of natural indigo has a deep violet-blue colour; it acquires a coppery lustre when rubbed with the finger nail; it is light, porous, adhering to the tongue, and can be readily broken and ground. Low qualities, which contain much extractive and mineral matter, are dull and greyish in appearance, heavy, tough, and hard, and do not become bronzy by rubbing with the finger nail.

Synthesis of Indigotin.

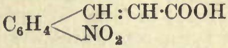
In attempting to reconvert the oxidation product isatin into indigotin by reduction, Baeyer and Knop (1865–66) obtained successively dioxindole $C_8H_7NO_2$, oxindole C_8H_7NO, and, finally, indole C_8H_7N (Annalen, 140, 29). This last product, which is to be regarded as the parent substance from which indigotin is derived, was prepared synthetically in 1869 by Baeyer and Emmerling by heating a mixture of nitro-cinnamic acid, caustic potash, and iron filings (Ber. 2, 680). In 1870 these same chemists succeeded in producing indigotin from isatin by heating the latter with a mixture of phosphorus trichloride and acetyl chloride.

Already in 1869 (Ber. 2, 748) Kekulé suggested, but did not prove, that isatin might be an inner anhydride of *o*-amino-phenyl-glyoxylic acid  $C_6H_4\left<\begin{array}{l}CO\cdot COOH\\ NH_2\end{array}\right.$. In 1878 Baeyer and Suida prepared oxindole synthetically from *o*-aminophenylacetic acid  $C_6H_4\left<\begin{array}{l}CH_2\cdot COOH\\ NH_2\end{array}\right.$, of which they proved it to be an inner anhydride; and in the same year Baeyer produced isatin from oxindole, thus completing the chain of transformations necessary to prepare indigotin, artificially from coal tar (Ber. 11, 582, 584, 1228).

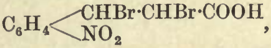
Oxindole  was first changed by the action of nitrous acid into nitroso-oxindole , and this by reducing agents into amino-oxindole , and this finally, by oxidising agents or by nitrous acid, into isatin .

A further synthesis of isatin, and therefore also of indigotin, was effected by Claisen and Shadwell in 1879 (Ber. 12, 350). By the action of silver cyanide on *o*-nitrobenzoyl chloride  $C_6H_4\left<\begin{array}{l}COCl\\ NO_2\end{array}\right.$ they obtained *o*-nitrobenzoyl cyanide  $C_6H_4\left<\begin{array}{l}COCN\\ NO_2\end{array}\right.$, which, by successive treatment with hydrochloric acid and caustic potash, yielded the potassium salt of *o*-nitrophenylglyoxylic acid  $C_6H_4\left<\begin{array}{l}CO\cdot COOK\\ NO_2\end{array}\right.$; this, by reduction in alkaline solution, gave the potassium salt of *o*-aminophenylglyoxylic acid  $C_6H_4\left<\begin{array}{l}CO\cdot COOK\\ NH_2\end{array}\right.$, which on the addition of acid yielded isatin . In this manner the original view of Kekulé concerning the constitution of isatin was verified.

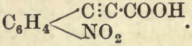
In 1880 (Ber. 13, 2259) Baeyer obtained indigotin in various ways from cinnamic acid, which already, in 1869, had been made to yield indole. By treating *o*-nitro-cinnamic acid


$$C_6H_4\left<\begin{array}{l}CH:CH\cdot COOH\\ NO_2\end{array}\right.$$

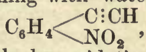
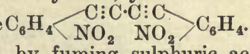
with bromine, there is produced *o*-nitrodibromhydrocinnamic acid

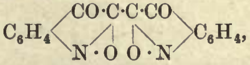

$$C_6H_4\left<\begin{array}{l}CHBr\cdot CHBr\cdot COOH\\ NO_2\end{array}\right.,$$

which, on treatment with caustic alkali, yields *o*-nitro-phenyl-propiolic acid

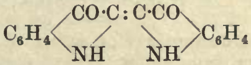

$$C_6H_4\left<\begin{array}{l}C\vdots C\cdot COOH\\ NO_2\end{array}\right..$$

On boiling this substance with caustic alkali, isatin is produced, but if reduced in alkaline solution—*e.g.* with glucose, or xanthates—it yields indigotin. This process was used industrially for some time for the production of *o*-nitro-phenyl-propiolic acid (propiolic acid), its transformation into indigotin being effected on the fabric (calico).

Another method of changing *o*-nitro-phenyl-propiolic acid into indigotin is as follows (Annalen, 143, 325; 147, 78; 154, 137). It is first converted by boiling with water into *o*-nitro-phenyl-acetylene  $C_6H_4\left<\begin{array}{l}C\vdots CH\\ NO_2\end{array}\right.$, the copper compound of which, by oxidation with potassium ferricyanide, yields dinitro-diphenyl-diacetylene  $C_6H_4\left<\begin{array}{l}C\vdots C\cdot C\vdots C\\ NO_2\quad NO_2\end{array}\right>C_6H_4$. This body is changed by fuming sulphuric acid into its isomeride diisatogen

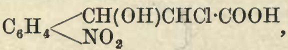


which, by reduction, yields indigotin



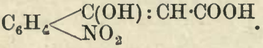
(Ber. 15, 50, 746).

Another of Baeyer's indigotin syntheses (D. R. P. 11857, 1880; Friedl. 127) is to treat *o*-nitro-cinnamic acid in alkaline solution with chlorine, whereby there is produced *o*-nitrophenylchlorlactic acid



$$C_6H_4\begin{matrix}CH(OH)CHCl\cdot COOH\\ NO_2\end{matrix},$$

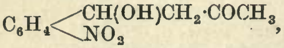
which, by treatment with alkalis, changes into *o*-nitrophenylhydroxyacrylic acid



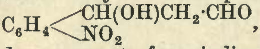
$$C_6H_4\begin{matrix}C(OH):CH\cdot COOH\\ NO_2\end{matrix}.$$

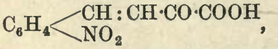
On heating this substance to 110°C. indigotin is produced.

In 1882 (Ber. 15, 2856) Baeyer and Drewsen prepared indigotin from *o*-nitrobenzaldehyde  $C_6H_4\begin{matrix}CHO\\ NO_2\end{matrix}$. If this substance is treated with acetone, acetaldehyde, or pyroracemic acid, products are formed which, under the influence of caustic alkali, readily yield indigotin. The reaction proceeds differently according to the reagent used. With the use of acetone the intermediate product is probably *o*-nitro-β-phenyl-lactic-methyl-ketone



$$C_6H_4\begin{matrix}CH(OH)CH_2\cdot COCH_3\\ NO_2\end{matrix},$$

which, by the action of the alkali, yields indigotin and acetic acid. With acetaldehyde the intermediate body is *o*-nitro-phenyl-lactic-aldehyde  $C_6H_4\begin{matrix}CH(OH)CH_2\cdot CHO\\ NO_2\end{matrix}$, and this the alkali decomposes to form indigotin and formic acid. With pyroracemic acid the intermediate substance is *o*-nitrocinnamylformic acid



$$C_6H_4\begin{matrix}CH:CH\cdot CO\cdot COOH\\ NO_2\end{matrix},$$

which, under the influence of alkali, produces indigotin and oxalic acid.

Meister, Lucius, and Brüning (D. R. P. 20255, 1882; Frdl. 142) patented a method similar to the first of the foregoing processes. Benzaldehyde and acetone are condensed according to Claisen's method to form benzylidene-acetone (cinnamylmethyl-ketone)

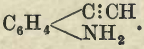
$$C_6H_5\cdot CH:CH\cdot COCH_3;$$

this is nitrated, and of the para- and ortho-nitro- derivatives thus obtained the latter is treated with alkali, and thereby yields indigotin. The yield is small, and the process was soon abandoned. The same firm also patented the manufacture of *m-methyl-indigotin* by the following method, nitrating *m*-methylbenzaldehyde and treating the *o*-nitro- derivative produced, with alkali according to Baeyer and Drewsen's method given above. The methyl-indigotin obtained is very similar in appearance to indigotin, but is remarkable for its solubility in alcohol.

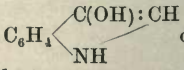
In 1882 (D. R. P. 21592, 1882; Frdl. 138; Ber. 17, 963) Baeyer and Bloem prepared indigotin from *o*-amino acetophenone

$$C_6H_4\begin{matrix}CO\cdot CH_3\\ NH_2\end{matrix},$$

and from *o*-amino phenylacetylene



$$C_6H_4\begin{matrix}C:CH\\ NH_2\end{matrix}.$$

The acetyl derivatives of either of these substances are dissolved in carbon disulphide and treated with bromine in the cold. On dissolving the bromine compound thus produced, in concentrated sulphuric acid, hydrobromic acid is evolved, and a colourless body is precipitated which, by the action of alkalis, decomposes to form indigotin. To ensure success the bromine must enter the methyl group of the acetyl-*o*-aminoacetophenone, and this takes place if the bromine acts in presence of conc. H_2SO_4 or in the dry condition. If the bromine enters only the benzene group (and this occurs when operating in aqueous or glacial acetic acid solutions), no indigotin is obtained; if the bromine enters both the methyl and the benzene groups—*e.g.* by working with chloroform solution—then brom-indigotin is ultimately obtained. During the formation of the indigotin in the subsequent process, indoxyl  $C_6H_4\begin{matrix}C(OH):CH\\ NH\end{matrix}$ occurs as an intermediate product.

Gevekoht obtained indigotin by the prolonged action of an excess of ammonium sulphide on a cold alcoholic solution of *o*-nitro-brom-acetophenone containing the bromine in the methyl group, and finally evaporating the solution (Annalen, 221, 330; D. R. P. 23785, 1883; Frdl. 139). This method is probably essentially the same as that of Baeyer and Bloem, since the first action of the ammonium sulphide is no doubt to produce *o*-amino-brom-acetophenone.

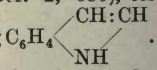
P. Meyer (Ber. 16, 2261; D. R. PP. 25136 and 27979, 1883; Frdl. 148, 149) obtained indigotin or substituted-indigotins by first preparing isatin or substituted-isatins, and then reducing their chlorides by means of zinc or hydrochloric acid in glacial acetic acid in the manner previously known. If 1 molecule dichloracetic acid is heated with 4 molecules aniline there is produced the intermediate substance phenyl-imesatin, which, by boiling with strong acids or bases, yields isatin, thus:

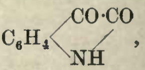
$$\underset{\text{Phenylimesatin.}}{C_8H_5NO\cdot N(C_6H_5)}+H_2O=\underset{\text{Isatin.}}{C_8H_5NO_2}+C_6H_5\cdot NH_2.$$

If in place of aniline in this reaction a *p*-monoamine is employed, *e.g.* *p*-toluidine, the intermediate product obtained is *p*-toluyl-*p*-methylimestan or *p*-methylisatin-*p*-toluylimid $C_8H_4(CH_3)NO\cdot N(C_7H_7)$, and this yields by the action of acids or alkalis methylisatin

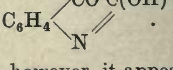
$$C_8H_4(CH_3)NO_2$$

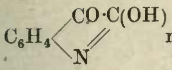
and toluidine.

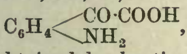
In consequence of Baeyer's synthesis of *indole* from *o*-nitro-cinnamic acid (Ber. 2, 680), its constitution is regarded as being  $C_6H_4\begin{matrix}CH:CH\\ NH\end{matrix}$. Claisen and Shadwell's synthesis of *isatin*, already referred to, indicates its constitution as

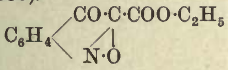


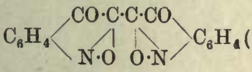
$$C_6H_4\begin{matrix}CO\cdot CO\\ NH\end{matrix},$$

but numerous observations of Baeyer show that it contains a hydroxyl group, and that its formula is  $C_6H_4\begin{matrix}CO\cdot C(OH)\\ N\end{matrix}$. In its substitution products, however, it appears to exist in the above pseudo form.

Isatin  $C_6H_4{<}\begin{array}{l}CO\cdot C(OH)\\ \quad\diagup\!\!\diagup\\ N\end{array}$ may be obtained by oxidation of indigotin with chromic acid or nitric acid (J. pr. Chem. [i.] 24, 11; 25, 434); by the oxidation of amino-oxindole or of carbostyril (Ber. 11, 1228; 14, 1921); by boiling *o*-nitrophenylpropiolic acid with caustic alkali (Ber. 13, 2259); and according to other methods already given. Its constitution is that of an inner anhydride of *o*-amino-phenylglyoxylic acid (Ber. 12, 350). It forms orange-red prisms; m.p. 200°C. With thiophen it forms a blue colouring matter called indophenin ($C_{12}H_7NOS$) (Ber. 18, 2637). By the action of dilute nitric acid it yields nitro-salicylic acid. Heated with caustic alkali it gives aniline. Reduced with ammonium sulphide, isatid ($C_{16}H_{12}N_2O_4$) is formed (J. pr. Chem. [i.] 24, 11; 25, 434). It combines with hydroxylamine to form nitroso-oxindol (Ber. 16, 518, 1714; Annalen, 140, 29).

Isatinic acid  $C_6H_4{<}\begin{array}{l}CO\cdot COOH\\ NH_2\end{array}$, in the form of its salts, is obtained by heating isatin with strong caustic alkali or by reduction of *o*-nitro-phenyl-glyoxylic acid. Only its salts are stable, the free acid decomposing into isatin and water, by merely boiling its aqueous solution. Its constitution is that of *o*-amino-phenylglyoxylic acid (Ber. 12, 350).

Isatogenic acid ether  $C_6H_4{<}\begin{array}{l}CO\cdot C\cdot COO\cdot C_2H_5\\ \quad\diagup\,|\\ N\cdot O\end{array}$ (Ber. 14, 1741; 15, 50, 746) is produced by the action of concentrated sulphuric acid on *o*-nitro-phenylpropiolic-acid-ether, with which it is indeed isomeric. It forms yellow needles; m.p. 115°C.

Diisatogen  $C_6H_4{<}\begin{array}{l}CO\cdot C\cdot C\cdot CO\\ \quad\diagup| \quad |\diagdown\\ N\cdot O\ \ O\cdot N\end{array}{>}C_6H_4$ (Ber. 15, 50, 746) is obtained by the action of concentrated sulphuric acid on dinitro-diphenyldiacetylene. It forms red needles, soluble only in chloroform, nitrobenzene, and concentrated sulphuric acid.

A. G. P.

INDIGO, ARTIFICIAL, AND INDIGOID DYESTUFFS. The elucidation of the constitution of indigo, the result of the brilliant and indefatigable researches of A. von Baeyer (*v. supra*), has led to consequences of extraordinary importance. The methods discovered for the synthetical production of indigo offered at first little or no prospect of the artificial production of this most important dyestuff at prices which could compete with the natural product. But the patient and unceasing work carried on for that purpose in the laboratories of the Badische Anilin- & Soda-Fabrik in Ludwigshafen gradually surmounted the existing difficulties. Artificial indigo appeared in the market in the year 1897, and was soon acknowledged to be cheaper, purer, and more easy of application than the natural product. New synthetical manufacturing processes which have since then been introduced, combined with a strong competition between the various manufacturers, led to a steady reduction of prices, so that at present (1911) the synthetical dyestuff may be said to have driven out the natural one everywhere, even in countries in which the indigo plants are grown, such as India, the Dutch colonies, China, Japan, and South America. The history of artificial alizarin has been repeated in all its details in the progress of artificial indigo. But the consequences of this new triumph of synthetical chemistry have gone further, in that they have revolutionized the old-established European industries engaged in the production as well as the application of artificial dyestuffs.

The old, but difficult and uncertain process of vat-dyeing, necessary for the application of indigo, has been carefully studied by the factories which had taken up the production of the synthetical product. Sodium hydrosulphite, long known to be the best means for reducing indigo in the vat, but unstable and difficult to prepare, has been brought into new forms in which it is quite stable and easily applied. Thus vat-dyeing has become an operation almost as easy and simple as any other process of dyeing, and the consumers of artificial colouring matters became anxious to be furnished with products similar to indigo in its mode of application and its fastness, but differing in shade. This wish has been satisfied almost simultaneously with its being felt. A large and constantly increasing number of new vat-dyes of every conceivable shade has been offered to the dyer and calico-printer, who is able to use them jointly or in mixtures with indigo, and thus to produce goods, the shades of which are quite as durable as the fibre itself. Some of the new vat-dyestuffs not only equal, but actually exceed indigo in fastness to light, air, and all the other influences which attack and destroy the colour of dyed fabrics. The introduction of the new synthetical vat-dyestuffs has inaugurated a new epoch of fast dyeing, the full importance of which will only be recognised in time to come.

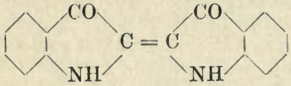
The synthetical manufacture of new colouring matters similar to indigo in their properties was at first the natural consequence of the numerous new syntheses of indigo itself gradually discovered by various chemists, and many of which proved applicable to the production of compounds similar to indigo in their constitution, but differing from it in certain details of composition, and consequently also in their shades. Many of these substances could be made on a large scale, and offered to the consumer at moderate prices. They are now known under the name of 'Indigoids,' and the more important of them will be mentioned further on.

The investigation of indigo and the indigoid dyestuffs led, however, to another result of no small importance. The connection existing between the constitution and the properties of indigo as a dyestuff, so long a mystery, was at last recognised, and the atomic configuration was disclosed which causes a dyestuff to be applicable to vat-dyeing. The natural consequence of this discovery was the possibility of producing, by synthetical methods, a vast number of new vat-dyes, which in their constitution have no longer any similarity to indigo, and the majority of which has been derived from anthraquinone, the mother-substance of alizarin, which has thus assumed a new importance.

The description of these dyestuffs supplementing indigo in its applications, and now already exceeding the indigoids in number is dealt with elsewhere (*see* VAT-DYES, MODERN; INDANTHRENE).

The number of vat-dyes now already in practical use or in the stage of being introduced may be estimated at from 80 to 90, and is constantly increasing. Their discovery is due to the inventive genius of many chemists, amongst whom René Bohn may be considered as the pioneer.

A. **Artificial indigo.** The constitution of indigo is expressed by the formula:



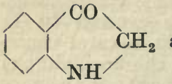
Of the numerous methods which lead to the synthetical production of such a compound very few are applicable to its manufacture, and only the latter will be here mentioned.

The first attempt at a technical synthesis of indigo was made in 1880 by A. von Baeyer in his German patent 11857, which was sold to the Badische Anilin- & Soda-Fabrik and the Höchster Farbwerke jointly. In this *ortho*nitrocinnamic acid is used as a raw material, and transformed into indigo by three different methods. Of these only the one which passes through *ortho*nitrophenylpropiolic acid as an intermediate product found for a short time a limited and almost experimental application as a means of producing indigo on the fibre in calico-printing.

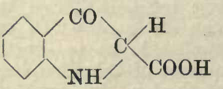
Another method (1882), which consists in adding caustic soda to a solution of *o*-nitrobenzaldehyde in acetone, when the methyl-*o*-nitrocinnamylketone formed as an intermediate product is immediately condensed into indigo, was also, in spite of its simplicity, unable to compete with the natural product.

In 1890 K. Heumann observed that phenylglycine and its *ortho*carboxylic acid are transformed into indoxyl and indoxylcarboxylic acid by being melted with caustic potash; the orange-coloured melts obtained yield indigo on being oxydised with air in aqueous solution. The patents obtained for these reactions (D. R. P. 54626 and numerous additions; also D. R. P. 56273 and additions) passed into the hands of the Badische Anilin- & Soda-Fabrik, but were not considered very promising by the majority of chemists. Yet they were destined to assume fundamental importance in the subsequent development of the indigo industry. It is true that a good many other inventions were necessary to raise them to that position.

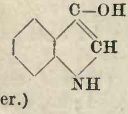
Indoxyl and indoxylcarboxylic acid have the constitution expressed by the formulæ:—



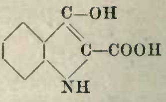
and



These formulæ represent the so-called 'pseudo'-forms, which are the first products of the reaction. Isolated indoxyl and indoxylcarbonic acid are better represented by the tautomesic formulæ:



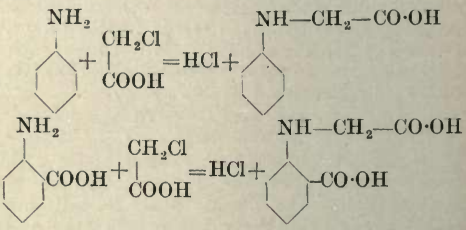
and



(Baeyer.)

On being treated with atmospheric oxygen in alkaline solution the one loses H_2 in the shape of water, the other H_2CO_2 in the shape of carbonic acid (H_2CO_3), and the so-called 'indigo bridge' $>C=C<$ is formed by two such indoxyl complexes being united by double valencies.

Phenylglycine and its *ortho*carboxylic acid are prepared by the action of monochloracetic acid[1] upon aniline and anthranilic acid:—



It was observed, that phenylglycine-*o*-carboxylic acid gave better yields of indigo than phenyl-glycine itself, which was, on the other hand, cheaper and more easily accessible. Later on it was found that both these glycines are capable of being transformed into indigo with very good yields if *every trace* of water is excluded from the alkaline melt. The glycine itself is in this respect more susceptible than its carboxyl derivative. Not only the water invariably retained by all the caustic alkalis hinders the reaction, but also the water formed in the reaction itself. One of the means of overcoming this difficulty consists in the addition of finely ground lime or baryta to the melt.

In taking up the manufacture of artificial indigo by Heumann's method in the beginning of the nineties the Badische Anilin- & Soda-Fabrik decided to use phenylglycine-*o*-carboxylic acid as a raw material. This decision was prompted not only by the better yields which were obtained from this product, but even more so by considerations of quite a different nature.

If it had been necessary to produce the anthranilic acid required for the manufacture of indigo by the oxidation of *o*-nitrotoluene and subsequent reduction of the *o*-nitrobenzoic acid thus obtained, all the toluene produced by the distillation of coal-tar would probably not have been sufficient for the purpose. There is, however, another way of producing anthranilic acid which consists in treating phthalimide with alkaline hypochlorites (Hoogewerff's and Van Dorp's process; D. R. P. 55988, Badische Anilin- & Soda-Fabrik, 1890).

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[1] Instead of this acid, prepared in the old manner from acetic acid and chlorine, ethyl monochloracetate may be used, which can be obtained from acetylene by a simple process (D. R. PP. 154657, 171900, 216940, 209268, 210502, and 216716, Imbert and Consortium für electrochemische Industrie, Nürnberg). See also Chemikerzeitung, 1911, p. 1053.

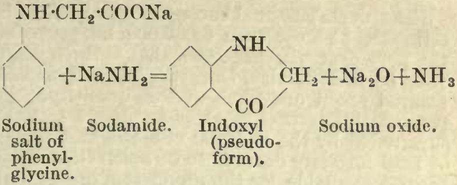
Phthalimide is easily obtained by treating phthalic anhydride with ammonia. Phthalic acid, on the other hand, is best prepared by the oxidation of naphthalene.

Thus it became possible, by using phenylglycine-*o*-carboxylic acid as a starting-point for the synthesis of indigo on a large scale, to base this manufacture on the use of naphthalene as its first raw material, a hydrocarbon which is contained in coal-tar in much larger quantities than any other of its constituents.

Even when these conclusions had been arrived at a great deal remained still to be done. It is now known that the Badische Anilin- & Soda-Fabrik had to invest about 1,000,000*l.* in experiments and new plant before artificial indigo could enter the world's market as a rival to the natural product, and that the ultimate success obtained is mainly due to the courage, inventive genius and perseverance of Rudolf Knietsch, who superintended the whole development of this new industry. But it must also be said that the latter found its advent well prepared by the development which chemical industry as a whole had taken towards the end of the nineteenth century. One of the principal advantages produced by that development was the possibility of obtaining chlorine (which is required both for the chloracetic and the anthranilic acid used in the indigo process) and caustic alkalis at extremely low prices owing to the introduction of the electrolytic decomposition of alkaline chlorides.

The oxidation of naphthalene into phthalic acid as practised in former times was cumbrous and difficult, and gave very poor yields. A new method was discovered for the purpose which consists in the oxidation of naphthalene polysulphonic acids by means of very strong pyrosulphuric acid. To obtain the latter a new process had to be worked out, now known to the world as the catalytic or contact process (*see* SULPHURIC ACID). A certain quantity of mercuric sulphate must be added in the oxidation of the naphthalene sulphonic acid; its action is purely catalytic and indefinite. The sulphur dioxide formed by the reduction of the pyrosulphuric acid returns continuously into the manufacture of the latter. The oxidation of the naphthalene thus practically takes place by means of atmospheric oxygen, and phthalic anhydride is exceedingly cheap if manufactured on a large scale by this process.

The employment of naphthalene as a raw material rendered it possible for artificial indigo to compete commercially with the natural product. But it was destined to meet itself with a very serious competition which arose from a discovery made by J. Pfleger of the Deutsche Gold- & Silber-Scheide-Anstalt in Frankfurt o/M., who observed that the destructive influence of water in the alkali melt of phenylglycine could be completely eliminated by using, not sodium hydroxide, but sodamide for effecting the transformation of the glycine into indoxyl. Sodium oxide and gaseous ammonia are instantly formed by the water produced in the condensation of the glycine according to the following reaction :—



The low melting-point of sodamide, which may be diluted with potassium or sodium cyanides (which also have a low melting-point) makes it possible to carry out the process at the low temperature of 180°–230° C. which favours the production of almost theoretical yields. Of course the process is also applicable to the transformation of phenylglycine-*o*-carboxylic acid into indigo.

It is true, that sodamide can only be prepared by the action of ammonia upon metallic sodium; its price is therefore a high one; on the other hand, the advantages to be obtained by its use are very great and make it possible for this process to compete with the one adopted by the Badische Anilin- & Soda-Fabrik. It was therefore acquired by the Höchster Farbwerke, who are now producing a considerable share of the world's consumption of indigo.

The enormous increase of the world's production of benzene, caused by the general introduction of by-product coke-ovens, and the very low prices of aniline caused by this over-production, has also favoured the success of Pfleger's invention.

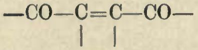
Other synthetical methods have been devised which lead from aniline to indigo, such as Sandmeyer's and Blank's. But they cannot compete with the methods described, and have therefore never been carried out on more than an experimental scale. For details about these processes, some of which are exceedingly interesting from a theoretical point of view, the existing works on the chemistry of colouring-matters and more especially the patent literature should be consulted. Some of these processes may possibly assume considerable importance as a means of producing indigoid dyestuffs.

The complete insolubility of indigo in water and aqueous fluids makes it imperative that the dyestuff should be in a state of extremely fine subdivision, and thoroughly moistened before being introduced into the vat. For this reason the dyers used to grind the natural product with a certain proportion of water in the well-known indigo-mills. The unnecessary trouble caused by this preliminary treatment is spared by the form which has been given to the artificial dyestuff, which is generally sold in the shape of a paste containing 20 p.c. of pure indigotin. For export, where the reduction of carriage, and in many countries also the import duties, have to be considered, stronger pastes may be prepared or even the shape of a dry powder is chosen. Much trouble has been taken to reduce the indigo to the greatest possible fineness. All the modern means of powdering and grinding have been utilized, and also the method of precipitating indigo from its solution in sulphuric acid (in which it is contained as a sulphate) by the addition of water has been resorted to.

The world's annual consumption of indigo is estimated at more than 5,000,000 kilograms of the pure dyestuff. In 1900, that is three years after its introduction, the artificial product had secured about one-tenth of this quantity. At present the natural product is almost entirely superseded by the artificial one, and vast tracts of land formerly devoted to its cultivation have become available for the production of rice and other cereals.

The valuable properties of indigo as a dyestuff are a function of the peculiar atomic configuration which connects the two phenylene radicles. By the reduction in the vat 2 atoms of hydrogen are taken up by this complex and indigo white is formed, the exact constitution of which is doubtful. But it is now generally acknowledged, that in leuco-indigo hydroxyl groups have replaced the ketonic oxygens of indigo. These hydroxyl groups possess auxochromic characters, and are responsible for the absorption of the indigo white by the fibre. It follows that every other strongly coloured aromatic substance which contains at least two reducible carbonyl groups must be endowed with the properties of a vat-dye. This conclusion has been strictly confirmed by modern investigations and the whole modern development in the production of vat dyes has been built up on it.

B. **Indigoids.**—The congeners of indigo may be divided into two different classes. One of them contains the true derivatives of indigo, in which one or more of the 8 hydrogen atoms of the two phenylene groups are replaced by other substituents; the other embraces substances which are strictly analogous to indigo in their constitution but different from it in the construction of the complex connecting the two phenylene groups, which in this case as well as in that of indigo may have their hydrogen atoms replaced by other substituents. An enormous variety of new dyestuffs may thus be synthesised, all of which contain the characteristic chromophoric group of indigo:



$$-CO-\underset{|}{C}=\underset{|}{C}-CO-$$

(*a*) *Substitution products of indigo.*—These may be prepared by treating indigo with suitable reagents or by using suitably substituted ingredients in any of the synthetical methods for the production of indigo.

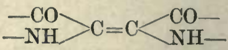
One group of these substitution products has been known for almost a century, and used formerly to be manufactured from natural indigo, viz. the sulphonic acids derived from it, commonly known under the name of *Indigo Carmine.* As these cannot be used as vat-dyes, they need only be mentioned here. They are now invariably prepared from artificial indigo and still used to a moderate extent in wool-dyeing, although they have been largely superseded by other soluble blues. Though derived from one of the fastest dyestuffs known, the indigosulphonic acids are, strangely enough, of an extremely fugitive nature.

The halogen derivatives of indigo are very numerous. As many as six atoms of chlorine or bromine may be introduced into the molecule of indigo. The properties of the products thus obtained, their shade and fastness, vary strongly not only with the number of halogen atoms introduced, but also with their relative position in the molecule. Of the mono- and di-substituted indigos those which contain their halogen atoms in the *p*-position to the imino groups are very similar to indigo itself; those, on the other hand, in which the *p*-positions to the keto groups are taken up are no longer blue but reddish-violet in shade. The dibromo-indigo corresponding to this condition has been proved by Friedländer to be identical with the *purple of the ancients* (*q.v.*). In spite of the fame which this dyestuff once possessed modern industry has not thought it sufficiently valuable to be introduced into commerce.

If more than two atoms of halogen be introduced into the molecule of indigo the dyestuffs obtained become more and more brilliant and greenish in shade. The first of these valuable dyestuffs introduced was tetrabromo-indigo; it was prepared by the Gesellschaft für Chemische Industrie in Basle and brought out as '*Ciba*'*-blue*—'Ciba' being the distinctive name adopted for all the vat-dyes of this factory. The corresponding tetrachlorinated derivative is '*Brillant indigo* 2B' of the Badische Anilin- & Soda-Fabrik. Penta- and hexabromo-indigo are still more greenish, and are now being manufactured by various firms.

It is, of course, also possible to substitute some of the hydrogen of the indigo molecule by organic radicles. Thus we come to the homologues of indigo, several of which have been prepared. They are all very similar to indigo and offer no special interest. This is also the case with naphtylindigo, the shade of which is a dull green. Its dibromo derivative is much clearer in shade; it has been brought out as '*Ciba-Green G*' by the Basle firm already mentioned.

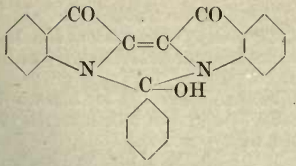
(*b*) *Indigoids, in which the central complex differs from that of indigo.*—In order to understand the nature of these compounds we must reconsider the constitution of indigo. It consists of two phenylene groups, linked together by the complex



$$\begin{matrix}-CO\\-NH\end{matrix}\!\!>C=C<\!\!\begin{matrix}CO-\\NH-\end{matrix}$$

Now in this complex the group $-CO-\underset{|}{C}=\underset{|}{C}-CO-$ is the indigo chromophore which connects all these dyes into one family and it cannot be touched or altered without destroying the whole character of the compound and its nature as a vat-dye. It follows, that the only changes possible in the central complex of the indigo molecule must be confined to the two imino groups, which may either be altered by their hydrogen being substituted, or by their being shifted into other positions, or by being entirely replaced by other atoms or atomic complexes. All these changes have been accomplished.

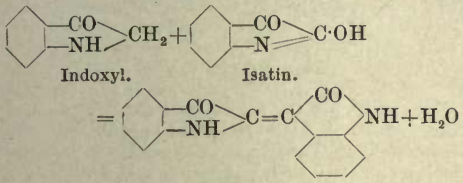
As an interesting example of the first of these alterations two dyestuffs may be mentioned: *Ciba-Yellow G* and *Ciba-Yellow GG.* They are prepared from indigo and tetrabromo-indigo by the substitution of two benzoyl groups for hydrogen in the imino groups. The constitution of Ciba-Yellow G is thus expressed by the formula:—



Benzoyl chloride does not act upon indigo under ordinary circumstances, but if a trace of metallic copper be added, its catalytic action causes the substitution of the hydrogen by the benzoyl group. This interesting manufacturing process has been invented by G. Engi.

If the imino groups are to be shifted or to be exchanged for other complexes, this cannot be done by starting from ready-formed indigo. The new dyestuff has to be built up synthetically. According to the synthetical methods adopted we can obtain indigoids of either symmetrical or asymmetrical constitution.

One of the first instances of such a synthesis was the process by which A. von Baeyer prepared Indirubin, the red dyestuff always contained in natural indigo and first observed by Berzelius. This substance is formed if alkaline solutions of indoxyl and isatin are mixed in the cold—

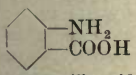


Indoxyl. Isatin.

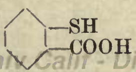
Indirubin.

Indirubin is an assymetrical indigoid in which both the chromophoric complex and the two imino groups are still preserved, but they have changed their relative position in the molecule. Indirubin is of no value as a dyestuff, but its tetrabromo derivative, prepared by G. Engi, is a useful violet and sold under the name *Ciba-Heliotrope.*

If the imino groups are to be exchanged for other divalent complexes, oxygen suggests itself as a suitable substituent. 'Oxygen indigo' has been prepared by Friedländer, but it proved to be a very poor dyestuff. But the same chemist observed in 1905, that sulphur, introduced into the position of the imino groups in indigo, has an excellent effect. A dyestuff of a deep bluish red shade and extraordinary intensity and fastness is formed, which is now known as *Thioindigo red* and manufactured by several firms. It was the first really applicable red indigoid and the process by which Friedländer first prepared it was protected by the German patent 194237 by Kalle & Co. who bought Friedländer's invention. This process is in all its stages strictly analogous to the synthesis of indigo from phenylglycine-*o*-carboxylic acid, but the nitrogen occurring in the latter is everywhere replaced by sulphur. Thus in the first stage anthranilic acid is replaced by thiosalicylic acid—

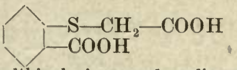


Anthranilic acid.



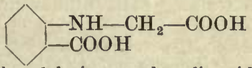
Thiosalicylic acid.

The latter is treated with monochloracetic acid, and thus transformed into



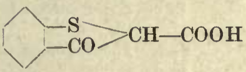
Phenylthioglycine-*o*-carboxylic acid.

which is, of course, quite analogous to

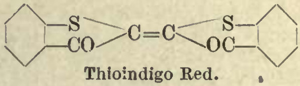


Phenylglycine-*o*-carboxylic acid.

By melting with caustic soda thioindoxylcarboxylic acid—



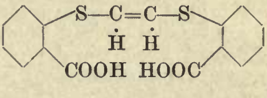
is formed, which, on being oxidised, yields



Thioindigo Red.

This process may be simplified by an invention described in the German patent 187586 of the Gesellschaft für Chemische Industrie in Basle, according to which the phenylthioglycine-*o*-carboxylic acid is simply boiled with nitrobenzene. Condensation and oxydation take place simultaneously and the red dyestuff is deposited in glistening crystals.

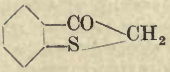
Another extremely simple method for the production of this dyestuff has been invented by E. Münch, and patented by the Badische Anilin- & Soda-Fabrik (French Pat. 385044; German Pat. application B. 47813). It consists in treating the salts of thiosalicylic acid with dichloroethylene. This compound, as a rule so reluctant to part with the chlorine it contains, in this case acts most readily, connecting two molecules of the acid, thus forming the whole chain of atoms required—



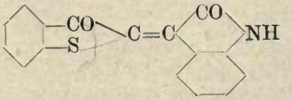
By treating this product with chlorosulphonic acid two molecules of water are eliminated, and the central complex of thioindigo red is formed. It suffices to add water which precipitates the dyestuff in a very pure condition.

Thioindigo red is extremely fast, but unfortunately its shade is not favourable to a very large consumption. An indigoid of a brilliant scarlet shade was required, and this was found in the asymmetrical representative of this group.

Thioindigo Scarlet.—This compound is analogous to indirubin in the same way in which thioindigo red is analogous to indigo, and it is also prepared by the method suggested by this analogy; thioindoxyl—



(or, as it is often called, oxythionaphthene) is treated in an alkaline solution with isatin (see equation for the formation of indirubin). It has consequently the constitution



and is not only asymmetrical, but also a mixed indigoid, containing both sulphur and the imino group.

Both thioindigo red and scarlet yield many new dyestuffs by the substitution of halogens and other substituents for hydrogen in their phenylene groups. They dye various shades of scarlets, bluish reds, and reddish violets, and several of them have come into use as serviceable vat-dyes. O. N. W.

INDIGO COPPER. *Cupric sulphide v.* COPPER.

INDIRUBIN *v.* INDIGO, NATURAL; INDIGO, ARTIFICIAL; INDOXYL COMPOUNDS.

INDIUM. Symbol In. At.wt. 113·97 (Winkler, Bunsen, Thiel, Mathers). Indium belongs to the aluminium group of the elements and was discovered in Freiberg zinc blende by Reich and Richter in 1863 by means of spectrum analysis. It also occurs in small quantities in other zinc blendes, in siderite, and in various manganese ores (Hartley and Ramage, Chem. Soc. Trans. 1897, 533). The metal can be obtained from the oxide by ignition in a current of hydrogen or by fusion with sodium (Winkler, J. pr. Chem. 1867, 102, 273). It can also be obtained pure electrolytically from the chloride, nitrate, or sulphate (Dennis and Geer, Ber. 1904, 37, 961; Thiel, *ibid.* 175; Mathers, J. Amer. Chem. Soc. 1908, 30, 209).

Indium is a white, readily malleable metal, softer than lead, and is not attacked by air at ordinary temperature. It can be obtained as regular octahedral crystals (Sachs, Zeitsch. Kryst. Min. 1903, 38, 495; Thiel, *l.c.*), having sp.gr. 7·12 at 13°/4°, and m.p. 155°. It dissolves slowly in hydrochloric or sulphuric acids but readily in nitric acid, and when heated in the blowpipe gives a blue colour and an incrustation of the oxide. Indium forms a series of isomorphous mixtures with lead (Kurnakoff and Pushin, J. Russ. Phys. Chem. Soc. 1906, 38, 1146; Kurnakoff and Schemtschuschny, Zeitsch. anorg. Chem. 1909, 64, 149). It also combines with selenium and tellurium, forming black masses with a metallic lustre (Renz, Ber. 1904, 37, 2110). In its compounds, indium appears as mono-, di-, and tri-valent, but only the latter are stable in aqueous solution.

Indium oxide In_2O_3 is a pale yellow powder which, according to Renz (Ber. 1903, 36, 1847), is converted into two other amorphous modifications when strongly heated (Meyer, Zeitsch. anorg. Chem. 1905, 47, 281). At 1000° the oxide commences to volatilise and is partially converted into chlorine-green shining crystals (Renz, *l.c.* 2751; Thiel, *l.c.* and Ber. 1906, 48, 201). The lower oxide, InO, possibly also exists.

Indium hydroxide $In(OH)_3$ resembles aluminium hydroxide, is converted into the oxide by heating, dissolves in potash but not in ammonia and readily forms colloidal solutions in the absence of electrolytes.

Indium hydroxide behaves towards bases as a weak acid: when carefully dried at 100°, the *meta* acid $In{\cdot}O{\cdot}OH$ is obtained, and the corresponding magnesium indate $(InO)_2O_2Mg,3H_2O$ is formed by boiling a solution of indium chloride with magnesium chloride (Renz, Ber. 1901, 34, 2763 and *l.c.*).

Halogen salts. Indium forms three *chlorides*, InCl, $InCl_2$, $InCl_3$; the last forms a crystalline compound with pyridine,

$$InCl_3{\cdot}3C_5H_5N,$$

m.p. 253° (Dennis and Geer, *l.c.*; Rengade, Compt. rend. 1901, 132, 472). Three corresponding *bromides* (Thiel, Ber. 1904, 37, 175), a *triiodide*, the *trifluorides*, $InF_3,3H_2O$ and $InF_3,9H_2O$ (Thiel, *l.c.*; Chabrié and Bouchonnet, Compt. rend. 1905, 140, 90), an *oxychloride* InOCl, an *iodate*, and a *perchlorate* (Schleuderberg, J. Amer. Chem. Soc. 1908, 30, 211) are known.

Indium sulphide In_2S_3 is a scarlet powder with metallic lustre which, when heated in hydrogen, forms the lower sulphide In_2S, which is a volatile brown powder. Both sulphides can be obtained in a crystalline form (Thiel, *l.c.*).

Basic indium sulphite $In_2(SO_3)_3In_2O_3,8H_2O$ is a crystalline powder which is obtained when an indium salt is boiled with acid sodium sulphite.

Indium also forms *sulphates*, *nitrates*, the *molybdate* $In_2(MoO_4)_3,2H_2O$, the *platino-cyanide* $In_2[Pt(CN)_4]_3$ (Renz, *l.c.*), a *selenate* (Schleuderberg, *l.c.*), *uranate*, *tungstate*, and *silico-tungstates* (Wyrouboff, Bull. Soc. Franç. Min. 1907, 30, 277).

Indium ammonium alum

$$In_2(SO_4)_3(NH_4)_2SO_4,24H_2O$$

(also with $8H_2O$) forms well-defined regular octahedra. Similar alums are formed with the sulphates of rubidium and cæsium, but the analogous salts with potassium and sodium are not pure alums (Chabrié and Rengade, Compt. rend. 1900, 131, 1300; 1901, 132, 472).

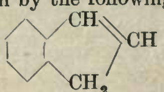
INDOFORM. Trade name for a mixture of salicylic acid, acetyl salicylic acid, moistened with formaldehyde solution, dried, and perfumed with methyl salicylate (*v.* SYNTHETIC DRUGS).

INDOINS (*Safranine azo- colouring matters*). The name Indoin blue R is given to the basic tannin colouring matter which is formed by combining the diazonium salt prepared from safranine and nitrous acid with β-naphthol. The compound is of some technical importance and dyes both unmordanted and tannined cotton fast indigo shades of blue.

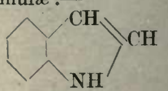
The name indoin was also given by Baeyer (Ber. 1881, 14, 1741) to a blue compound resembling indigo, having the composition $C_{32}H_{20}O_5N_4$, prepared by the action of reducing agents, for example ferrous sulphate, on phenylpropiolic acid dissolved in sulphuric acid. J. F. T.

INDOLES. To this class belong a series of compounds, many members of which are of considerable importance from the bio-chemical standpoint.

They are derived from indole C_8H_7N, a compound which is related to indene in the manner shown by the following formulæ:—



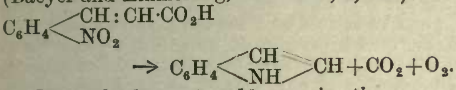
Indene.



Indole.

The indole derivatives which occur in the organism are more or less closely related to tryptophan (*q.v.*), a substance which, according to the latest investigation is an indole-amino-propionic acid.

Indole was first obtained by Baeyer by distilling, with zinc dust, either oxindole  $C_6H_4\left<\begin{matrix}CH_2\\NH\end{matrix}\right>CO$, or the product obtained by reducing indigo with tin and hydrochloric acid. It is also formed when *o*-nitrocinnamic acid is distilled with caustic potash and iron filings (Baeyer and Emmerling, Ber. 1869, 2, 680):



$$C_6H_4\left<\begin{matrix}CH:CH\cdot CO_2H\\NO_2\end{matrix}\right. \rightarrow C_6H_4\left<\begin{matrix}CH\\NH\end{matrix}\right>CH+CO_2+O_2.$$

It can also be produced by passing the vapour of ethyl aniline and other alkyl anilines through a red-hot tube (Baeyer and Caro, Ber. 1877, 10, 692, 1262), but the best method of preparation is by the action of dichlorether

$$CH_2Cl\cdot CHCl\cdot OC_2H_5$$

on aniline. A mixture of 50 grams of aniline with an equal bulk of water is heated, and to the boiling liquid 25 grams of dichlorether are gradually added. The boiling is continued for an hour, after which the water and excess of aniline are distilled off and the residue is heated for about 4 hours at 210°–230°. On distilling the product with steam, indole passes over and may be purified by conversion into the picrate. In this reaction, ethylidene di-aniline is first formed which, on heating to a higher temperature, breaks down into indole and aniline, thus:

$$C_6H_5N:CH\cdot CH_2\cdot NHC_6H_5 \rightarrow C_8H_7N+C_6H_5NH_2.$$

Indole forms colourless, lustrous laminæ, melts at 52° and boils with partial decomposition at 253°–254°. It is readily volatile in steam and is easily soluble in boiling water and in alcohol, ether, and benzene. When nitrous acid is added to an aqueous solution of indole, containing nitric acid, nitrosoindole nitrate is precipitated in the form of small red needles. An aqueous solution, or the vapour of indole, colours a pine chip moistened with hydrochloric acid and alcohol cherry red, the colour afterwards changing to reddish brown. Indole suspended in water and oxidised with ozone yields traces of indigo (Nencki, Ber. 1875, 8, 727). Indole is a weak base and forms, with concentrated hydrochloric acid, a sparingly soluble salt which is dissociated by boiling with water; the picrate is precipitated as dark red needles when a solution of indole in light petroleum is treated with picric acid.

Acetyl indole $C_8H_6N(C_2H_3O)$, which is formed by the action of acetic anhydride, melts at 182°–183°. Indole accompanies scatole as a product of the putrefaction of albumen.

Derivatives of indole.—The homologues of indole are most readily obtained by heating the phenyl hydrazones of ketones of the formula

$$R'\cdot CO\cdot CH_3 \text{ or } R'\cdot CO\cdot CH_2R',$$

or the phenyl hydrazones of the aldehydes of the formula $R'\cdot CH_2\cdot CHO$, with zinc chloride at 180°. The zinc chloride abstracts the elements of ammonia thus:

$C_6H_5NH\cdot N:C(CH_3)_2$

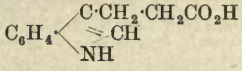
Acetone phenylhydrazone.

$$\rightarrow C_6H_4\left<\begin{matrix}CH\\NH\end{matrix}\right>C\cdot CH_3 + NH_3$$

β-Methylindole.

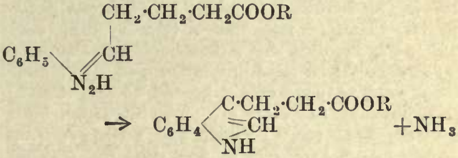
but the reaction is difficult to express by means of structural formulæ. Indole itself cannot be prepared by this reaction.

Indole-3-propionic acid (scatole acetic acid)



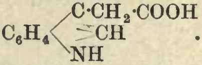
$$C_6H_4\left<\begin{matrix}C\cdot CH_2\cdot CH_2CO_2H\\ \gg CH\\ NH\end{matrix}\right.$$

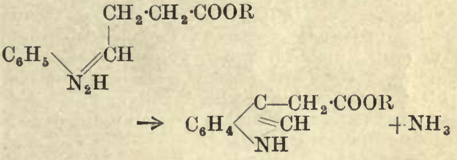
This substance was isolated by Nencki (Monatsh. 1889, 10, 506) from the products of the putrefaction of albumen. It has been synthesised by Ellinger (Ber. 1905, 38, 2884) by the action of alcoholic sulphuric acid on the phenyl hydrazone of γ-aldehydo*iso*butyric ester:



$$C_6H_5\diagdown N_2H \diagup\!\!\diagup CH - CH_2\cdot CH_2\cdot CH_2COOR \rightarrow C_6H_4\left<\begin{matrix}C\cdot CH_2\cdot CH_2\cdot COOR\\ \gg CH\\ NH\end{matrix}\right. +NH_3$$

The acid crystallises from water as prisms which melt at 134°.

Indole-3-acetic acid (scatole carboxylic acid)  $C_6H_4\left<\begin{matrix}C\cdot CH_2\cdot COOH\\ \gg CH\\ NH\end{matrix}\right.$. This substance was isolated by E. and H. Salkowski (Ber. 1880, 13, 2217) from the products of the putrefaction of albumen. It has been prepared by Ellinger (Ber. 1904, 37, 1803) by the action of alcoholic sulphuric acid on the phenyl hydrazone of methyl aldehydopropionate

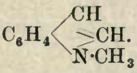


$$C_6H_5\diagdown N_2H \diagup\!\!\diagup CH - CH_2\cdot CH_2\cdot COOR \rightarrow C_6H_4\left<\begin{matrix}C-CH_2\cdot COOR\\ \gg CH\\ NH\end{matrix}\right. +NH_3$$

The acid forms small leaflets from a benzene solution which melt at 165° and at the same time eliminate carbon dioxide, yielding scatole.

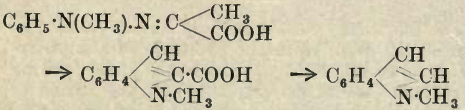
Scatole (3-methylindole)  $C_6H_4\left<\begin{matrix}C\cdot CH_3\\ \gg CH\\ NH\end{matrix}\right.$. This substance occurs as a product of the putrefaction of albumen and is also formed by the fusion of protein substances with potash. It was first discovered in human fæces of which it forms the chief volatile constituent (Brieger, Ber. 1879, 12, 1986); it also occurs in the wood of the *Celtis cinnamomea* (Linol.), Java (Dunstan, Chem. Soc. Proc. 46, 211). It is formed with indole when the product obtained by reducing indigo by means of stannous chloride is distilled with zinc dust (Baeyer, Ber. 1880, 13, 2339), and can be prepared by heating the phenyl hydrazone of propionic aldehyde $CH_3\cdot CH_2CH:N_2H\cdot C_6H_5$, with an equal weight of zinc chloride and distilling the product with steam.

Scatole forms lustrous laminæ, melts at 95° and boils at 265°–266° (corr.) under 755 mm. pressure. It usually has a strong fæcal smell, but when pure is stated to be without odour. It dissolves in concentrated hydrochloric acid, forming a violet solution.



$C_6H_4\left\langle\begin{matrix}CH\\ \geqslant CH\\ N\cdot CH_3\end{matrix}\right.$

1-methyl indole $C_6H_4\langle CH{:}CH\cdot N\cdot CH_3\rangle$. When methyl phenyl hydrazone pyruvic acid is treated with hydrochloric acid it parts with the elements of ammonia yielding 1-methyl indole carboxylic acid



$$C_6H_5\cdot N(CH_3).N:C\left\langle\begin{matrix}CH_3\\ COOH\end{matrix}\right. \rightarrow C_6H_4\left\langle\begin{matrix}CH\\ \geqslant C\cdot COOH\\ N\cdot CH_3\end{matrix}\right. \rightarrow C_6H_4\left\langle\begin{matrix}CH\\ \geqslant CH\\ N\cdot CH_3\end{matrix}\right.$$

On heating this compound to 205° it parts with carbon dioxide, forming 1-methyl indole (E. Fischer and Hess, Ber. 1884, 17, 562). According to Carrasco and Padoa (Gazz. chim. ital. 1907, 37, 11, 49), this substance is also formed when dimethyl-*o*-toluidine is dropped into a tube filled with reduced nickel heated to 300°–330°.

1-methyl indole is a yellow oil which boils at 240°–241° (corr.) under 720 mm. pressure. It has sp.gr. 1·0707 at 0° and does not solidify at −20°. It colours a pine chip moistened with hydrochloric acid reddish violet.

$C_6H_4\left\langle\begin{matrix}CH\\ NH\end{matrix}\right\rangle C.CH_3$

2-Methyl indole $C_6H_4\langle CH=C.CH_3\cdot NH\rangle$. This compound is formed from *o*-nitrophenylacetone by reduction with zinc-dust and ammonia, when the *o*-aminophenylacetone, which is first formed in the reaction, eliminates water and passes into 2-methyl indole (Baeyer and Jackson, Ber. 13, 187). It can also be formed by heating acetone phenyl hydrazone with five times its weight of zinc chloride for half an hour on the water bath and then for a few minutes at 180° (E. Fischer, Annalen, 236, 126). 2-Methyl indole forms needles or laminæ, melts at 59°–60° and boils at 272° (corr.) under 750 mm. pressure. It has a smell resembling that of indole, is sparingly soluble in boiling water, but readily dissolves in alcohol and in ether. It colours a pine chip moistened with hydrochloric acid red. J. F. T.

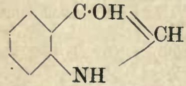
Tryptophan *v.* TRYPTOPHAN.

INDONES *v.* INDENE.

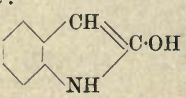
INDOPHENOLS *v.* INDAMINES AND INDOPHENOLS.

INDOPYRIN *v.* SYNTHETIC DRUGS.

INDOXYL COMPOUNDS. When the hydrogen atom attached to one or other of the two carbon atoms present in the five-membered ring of indole is replaced by hydroxyl, two isomeric compounds may be formed which are represented by the two formulæ:

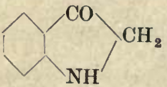


Indoxyl (enol form), stable.

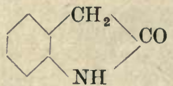


pseudo-Oxindole (enol form), labile.

The presence of the complex CH : C(OH) in these compounds causes them to react in two forms, which may be represented by the further formulæ:



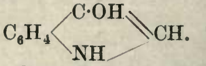
pseudo-Indoxyl (keto form), labile.



Oxindole (keto form), stable.

The two modifications are, in these cases, tautomeric, that is to say, only one form can be isolated (stable form), but this variety can, under certain conditions, yield derivatives of the other modification (labile form).

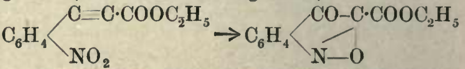
As shown by the above expressions, the enol (or hydroxy) form of indoxyl is the stable variety of this substance, whereas the stable form of oxindole (*q.v.*) is represented by the keto structure.



$C_6H_4\left\langle\begin{matrix}C\cdot OH\\ NH\end{matrix}\right\rangle CH$

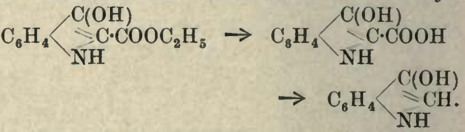
Indoxyl $C_6H_4\langle C\cdot OH{:}CH\cdot NH\rangle$. The isolation of indoxyl was first effected in the following way. It had been noticed from the earliest times that under certain conditions human urine deposited a blue colouring matter, and the first recorded observation of this fact is ascribed by Thudichum (A Treatise on the Pathology of Urine, London, 1877) to Janus Planchus, in the year 1767. Schunck, in 1857, suggested that the chromogen of this blue colouring matter, which had previously been identified as indigo by Heller and Kletzinski, was the same as indican which he had isolated from woad. This was, however, disproved by Baumann (Pflüger's Archiv. 13, 291) who, with Brieger (Zeitsch. physikal Chem. 1879, 111, 258), isolated the chromogen from urine and showed it to be indoxyl sulphuric acid.

Subsequently, Baumann and Tiemann (Ber. 1880, 13, 415) showed that, like phenol sulphuric acid, indoxyl sulphuric acid is decomposed by acids into sulphuric acid and a phenolic substance—indoxyl—and that this compound is quantitatively converted into indigo on oxidation. Subsequently, the synthesis of indoxyl was effected by Baeyer (Ber. 1881, 14, 1741) by the following series of reactions. Ethyl *o*-nitrophenyl propiolate is first converted by shaking with concentrated sulphuric acid into ethyl isatogenate (molecular rearrangement):



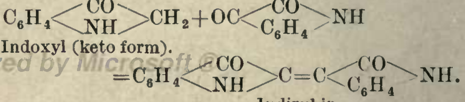
$$C_6H_4\left\langle\begin{matrix}C\equiv C\cdot COOC_2H_5\\ NO_2\end{matrix}\right. \rightarrow C_6H_4\left\langle\begin{matrix}CO-C\cdot COOC_2H_5\\ N-O\end{matrix}\right.$$

This substance on reduction yields ethyl indoxylate, which is then hydrolysed by caustic soda to the sodium salt of indoxylic acid, and the free acid from this, when boiled with water, is transformed into carbon dioxide and indoxyl.



$$C_6H_4\left\langle\begin{matrix}C(OH)\\ \geqslant C\cdot COOC_2H_5\\ NH\end{matrix}\right. \rightarrow C_6H_4\left\langle\begin{matrix}C(OH)\\ \geqslant C\cdot COOH\\ NH\end{matrix}\right. \rightarrow C_6H_4\left\langle\begin{matrix}C(OH)\\ \geqslant CH.\\ NH\end{matrix}\right.$$

Indoxyl when pure forms pale yellow crystals which melt at 85°, but crystallisation cannot be effected in the presence of even slight traces of impurities. It dissolves in water, forming a fluorescent solution and is readily soluble in most organic solvents. It is very unstable and readily oxidises when exposed to the air; the oxidation to indigo takes place rapidly in alkaline solution. It is volatile with steam and when treated with isatin in the presence of potassium carbonate is converted into indirubin, a reaction which may be represented by the following equation:

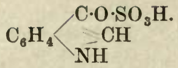


$$C_6H_4\left\langle\begin{matrix}CO\\ NH\end{matrix}\right\rangle CH_2+OC\left\langle\begin{matrix}CO\\ C_6H_4\end{matrix}\right\rangle NH$$

Indoxyl (keto form).

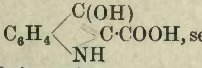
$$=C_6H_4\left\langle\begin{matrix}CO\\ NH\end{matrix}\right\rangle C=C\left\langle\begin{matrix}CO\\ C_6H_4\end{matrix}\right\rangle NH.$$

Indirubin.

Indoxyl sulphuric acid 

$C_6H_4\Big\langle\begin{matrix}C\cdot O\cdot SO_3H.\\ CH\\ NH\end{matrix}$

This substance occurs as the potassium salt (*indicanuria*) in human urine as well as in the urine of certain carnivora. It occurs to a considerable extent in the urine of a dog which has been fed on indole. It can be prepared synthetically from the potassium compound of indoxyl by treatment with potassium pyrosulphate (Baeyer, Ber. 1881, 14, 1744) and also by fusing phenylglycine-*o*-carboxylic acid and treating the melt with potassium pyrosulphate (Baumann and Thesen, Zeitsch. physikal. Chem. 1896, 23, 23). The free acid is unstable, but the potassium salt forms characteristic glistening leaflets from alcohol in which it is sparingly soluble.

Indoxylic acid 

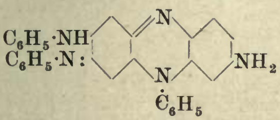
$C_6H_4\Big\langle\begin{matrix}C(OH)\\ C\cdot COOH\\ NH\end{matrix}$

, separates when a solution of its sodium salt is acidified as a white crystalline precipitate which melts at 122°–123° with vigorous evolution of carbon dioxide. J. F. T.

INDULINES. A very numerous class of blue colouring matters belonging or closely related to the safranine group of colours. They are prepared by heating an aminoazo compound with an amine in the presence of the chloride of the latter. As might be expected, such a process allows of an almost infinite series of variations, and a great number of the colours have at various times been made and used.

By far the most important is also the earliest known; the details of its preparation, described below, are practically those of all the others.

250 kilos. of aniline are mixed with 24 kilos. of hydrochloric acid (35 p.c.) and a solution of 14·4 kilos. of sodium nitrite is run in. The mixture is allowed to remain for some time and then heated with steam to 40°–50° in order to complete the transformation of the diazoaminobenzene into aminoazobenzene. The product is then transferred to a cast-iron still capable of holding twice the volume of the melt made in it and provided with an agitator, swan neck, charging hold, thermometer tube and discharge valve. 60 kilos. of aniline salt (aniline hydrochloride) are added and the mixture is heated gradually so that at the end of about 4 hours the temperature of the melt has reached 175°–180° (Schultz, Chemie des Steinkohlentheers, 3rd edit. 1901, ii. 343). The mass is now rendered alkaline with aqueous sodium hydroxide, the excess of aniline distilled off with a current of steam and the residue ground, washed, and dried. A medium shade, as produced by this method, is known as **Induline 3 B spirit soluble**; the formula of its chief constituent is



Red shade indulines (*e.g.* **Fast blue R spirit soluble**) are formed by heating the mixture for a short time only and at a lower temperature (160°–170°). The bluer shades (*e.g.* **Fast blue spirit soluble**; **Induline 6 B spirit soluble**) are obtained by more prolonged heating.

Much of the induline base prepared in this way is sulphonated, but some is dissolved in acetin, lævulic acid, or ethyltartaric acid, forming blue to violet-blue liquors which are used for printing (**Printing blue, Acetin blue, Lævulin blue,** &c.). When spirit-soluble induline is sulphonated it is converted into a sulphonic acid, the sodium salt of which is soluble in water. In this form, various brands of water-soluble indulines are placed on the market under the names of **Induline** (various marks), and **Fast blues, Nigrosine, Coupier's blue.** Another series of blue to blue-grey or black dyes is produced by heating aniline and aniline hydrochloride with nitrobenzene or nitrophenol or both in the presence of iron borings. Typical processes are (*a*) *With nitrobenzene*: 175 parts of aniline, 175 parts of nitrobenzene, 200 parts of hydrochloric acid, and 16 parts of iron borings are heated for 8 hours at 160°–200° until a test portion can be drawn out into a thread. The melt is then run out into an iron tray and ground. (*b*) *With nitrophenol*: 100 parts of aniline hydrochloride, 50 parts of aniline, 50 parts of nitrophenol, and a little iron are heated for 10 hours to 180°. (*c*) *With nitrobenzene and nitrophenol*: 183 parts of aniline hydrochloride, 183 parts of nitrobenzene, 137 parts of aniline, 12 parts of crude nitrophenol, and 3 parts of iron borings are slowly heated for a day, the final temperature being about 215°. Towards the end the melt must be constantly tested and run out immediately it begins to thicken, otherwise it will set in the pan and then must be chipped out when cold. The spirit-soluble nigrosines produced, as described above, are sulphonated as in the case of the indulines, the products being known as **Nigrosine soluble.** J. C. C.

INDURITE *v.* EXPLOSIVES.

INFUSORIAL EARTH *v.* KIESELGUHR.

INGRAIN BROWN, -ORANGE, -RED, *v.* AZO- COLOURING MATTERS.

INGRAIN COLOURS *v.* PRIMULINE AND ITS DERIVATIVES.

INK. A coloured fluid used in writing, printing, &c. (Gr. *engkauston—engkaio,* to burn in; Lat. *encaustum,* the purple-red ink used only in the signature of the emperors; It. *inchiostro*; Fr. *encre*; Dutch, *inkt.*)

It may be a convenient although not rigidly accurate division of the subject to recognise a distinction between ink prepared for writing and that prepared for printing.

Writing ink. Black writing ink, as commonly prepared, is a ferroso-ferric gallate suspended in a solution of gum in water, obtained by adding a decoction of substances containing tannin (usually nut-galls) to a solution of copperas.

Galls contain gallotannic and gallic acids, which, with ferric salts, form a black precipitate; with ferrous salts the precipitate is white, but becomes black when oxidised by exposure to air. A proportion of gum is added for the purpose of suspending the precipitate equally throughout the solution and of preventing its deposit.

Although other materials may be used, it has been found that the best properties of writing ink—viz. fluidity, penetration, and permanence—are obtained by the use of the ingredients above-named. Such inks fall into two main classes.

Tannin-iron inks are manufactured from the above materials without additions and without previous treatment of the materials. The following typical recipes are taken from the sources named :—

No. 1 (Cooley's Cyclopædia).—Aleppo galls, well bruised, 4 oz. ; clean soft water 1 quart ; macerate in a clean corked bottle for 10 days or a fortnight, or even longer, with frequent agitation ; then add 1¼ oz. of gum arabic dissolved in a wineglassful of water and ½ oz. lump sugar; mix well, and afterwards further add of ferrous sulphate (green copperas), crushed small, 1½ oz. ; agitate occasionally for 2 or 3 days, when the ink may be decanted for use, but is better if the whole is left to digest together for 2 or 3 weeks. *Product* : 1 quart of excellent ink, writing pale at first, but soon turning intensely black.

No. 2 (Ure).—12 lbs. of nut-galls, 5 lbs. ferrous sulphate, 5 lbs. Senegal gum, 12 gallons of water. The bruised nut-galls are to be put into a cylindrical copper of a depth equal to the diameter, and boiled during 3 hours with three-fourths of the above quantity of water, taking care to add fresh water to replace what is lost by evaporation. The decoction is to be emptied into a tub, allowed to settle, and, the clear liquid being drawn off, the lees are to be drained. The gum is to be dissolved in a small quantity of hot water, and the mucilage thus formed, being filtered, is added to the clear decoction. The ferrous sulphate must likewise be separately dissolved and well mixed with the above. The colour darkens by degrees in consequence of the peroxidation of the iron on exposing the ink to the action of the air. *Product* : 12 gallons.

No. 3 (Lehner, Ink Manufacture, p. 28).

Ingredients—

Galls	1200	parts by weight.
Ferrous sulphate	800	,, ,,
Gum arabic	800	,, ,,
Water	24,000	,, ,,
Creosote	3	,, ,,

Cover the galls with part of the water and dissolve the green vitriol, gum, and creosote separately in the rest of the water. Pour the solution on to the galls, cover up the vessel, and allow to stand for 3 weeks, stirring every day. The ink will then have reached its full blackness and can be bottled for use.

In other processes the galls are repeatedly extracted with boiling water and the extracts united and then mixed with the other constituents ; or the tannin is extracted from the bruised galls with ether and the dry product dissolved in water for ink-manufacture. The quality of the product seems to be equally good whatever method is used, provided the ratio between the weights of galls and of ferrous sulphate taken is always about 3 : 2. The addition of an antiseptic substance such as carbolic acid is to be recommended, as the ink is thus preserved indefinitely from the attacks of mould.

Gallic acid inks are also made from galls, ferrous sulphate, gum, and water, with the difference that the galls are first allowed to ferment, whereby the quercotannic acid is converted into gallic acid. The following is a typical recipe :—

Gall nuts	50 parts.
Ferrous sulphate	10 ,,
Gum	10 ,,
Water	2000 ,,
Carbolic acid	2 ,,

The crushed galls are soaked in the water and allowed to ferment. The mass may be inoculated with mould from a mouldy piece of bread or leather. After 8 to 10 days, boiling water is poured on to kill the ferment and the liquid drawn off and used to dissolve the other ingredients.

These inks have a fine blue-black colour and are not so susceptible to change as the tannin inks, but they have fallen into disfavour because they must be partially oxidised before use and thus take a considerable time to manufacture, and even then give a very pale impression on paper. Most of the inks now used contain a '*provisional colouring matter*,' the function of which is to render the ink easily visible at the time of writing and until such time (7–10 days) as it shall be completely oxidised to black ferric gallate.

Logwood tannin inks are made by substituting logwood chips or logwood extract for part of the galls in a tannin-ink recipe, *e.g.* :—

Galls	36 parts.
Ferrous sulphate	36 ,,
Logwood extract	9 ,,
Gum	36 ,,
Water	300 ,,
Vinegar	60 ,,

The method of preparation is similar to that already described.

Logwood gallic acid inks are similarly made but with preliminary fermentation of the galls. These inks have a deep blue-black colour and attack steel nibs less than pure tannin inks.

Alizarin inks are those inks which contain a provisional colouring matter other than logwood. They contain a sufficient proportion of acid (sulphuric or acetic) to keep the iron gallate or tannate in solution, and therefore may be prepared with much less gum than those previously described.

Of the colouring matters used the most important is indigo-carmine, which is prepared by dissolving dry indigo in fuming sulphuric acid, and after 24 hours neutralising with potassium carbonate. The free acid in the indigo solution may also be used to dissolve metallic iron, thus dispensing with the use of green vitriol.

The following recipe is stated to produce an excellent ink :—

Galls	40 parts.
Iron solution	15 ,,
Indigo-carmine	5 ,,
Gum	10 ,,
Pyroligneous acid	10 ,,
Water	100 ,,

The galls are powdered and soaked in the water and half the acid for a week. The iron solution is prepared from scrap iron and crude pyroligneous acid left together for a week. These solutions are then mixed and the other ingredients added.

At the present time, many other tannin-containing substances, besides galls, are used in the manufacture of inks. It has been shown that *sumach, valonia,* and *logwood* produce an ink which is indistinguishable from gall-inks (Hinrichsen and Kedesdy, J. Soc. Chem. Ind. 1909, 831), and good inks may be produced from tanner's barks (elm, oak, pine, poplar, willow, &c.), cutch, gum kino, fustic, elder-berries, the unripe fruit of the chestnut, walnut, &c.

In many cases other and cheaper synthetic dyes are substituted for the indigo-carmine, but this is not necessarily detrimental to the quality of the ink.

Mitchell (Analyst, 1908, 33, 81) has analysed a large number of English writing inks and finds that, although the composition of any one manufacturer's ink remains fairly constant over long periods, there are marked differences between the inks of different manufacturers. The total solid matter ranges from 1·89 to 7·94 p.c., the ash from 0·42 to 2·52 p.c., and the iron from 0·18 to 1·09 p.c.

The age of handwriting can be estimated up to the seventh or eighth day, when oxidation is complete, but after that no distinction can be made until the provisional colour begins to fade, usually after about a year.

It is probable that in oxidised ink the iron exists as the tannate

$$(C_{14}H_9O_9)_3Fe{\cdot}Fe(C_{14}H_9O_9)_3,$$

described by Wittstein (J. 1848, 28, 221) and by Schiff (Annalen, 1875, 175, 176). (*See* also Ozorowitz, Chem. Zentr. 1908, 2, 1024.)

Runge prepared a writing fluid, under the name of 'chrome ink,' which was cheap, intensely coloured, non-corrosive to steel pens, and extremely permanent on paper. The manner of preparing chrome ink is as follows: 1 part of potassium chromate (not dichromate) is added to 1000 parts of a saturated solution of logwood made by boiling 22 lbs. of logwood in a sufficient quantity of water to give 14 gallons of decoction. The potassium chromate is introduced gradually when the solution is cold, the mixture being constantly stirred during the addition. Gum is injurious to the mixture. It may be prepared more simply by dissolving 2000 parts of logwood extract in a solution of 10 parts of pure potassium chromate in 100,000 parts of water.

Ink powders are very little used but can easily be made either by cautiously evaporating an ordinary ink to dryness and powdering the residue, or by mixing the carefully dried and powdered ingredients in the proportions used for the fluid ink.

Indelible or safety inks. Compositions passing under these names consist of finely divided carbonaceous substances, such as Indian ink or lampblack, held in suspension in a glutinous or resinous liquor. They are devised so as to resist the action of strong acid or alkaline solutions. An ink having these properties may be made of Indian ink rubbed into ordinary writing ink.

A suspension of lampblack in sodium silicate solution makes an excellent safety ink but has the disadvantage that it must be kept in airtight bottles.

Vanadium ink is prepared very simply by adding a small proportion of ammonium vanadate to a filtered decoction of galls. It is a deep black ink, which flows freely from the pen and cannot be removed without destruction of the paper.

Copying ink. Any ink which retains enough solubility to give an impression from the written sheet on to a sheet of damp paper may be used for copying. Runge's chrome ink described above may be so used. Other logwood inks and ferrous gallate inks being soluble only until oxidised by exposure to the air, require the addition of some substance which forms a glaze, arresting the action of the air. This glaze must be soluble when brought into contact with the damped copying paper; the pigment is then freed so as to produce the impression. Such substances are gum arabic, gum Senegal, dextrin, and glycerol. Where several copies are required, the ink employed should contain more staining matter in proportion.

Hektograph inks are used to give a large number of copies, and must therefore contain a powerful colouring matter. The original is written on ordinary paper with the ink and is laid face-down on a sheet of a composition of glue and glycerol (about 1 : 5) until the ink has been absorbed into the surface of the composition.

By applying sheets of paper with slight pressure, 60 to 100 copies can then be obtained.

A typical ink contains: water-soluble blue 10 parts, glycerol 10 parts, and water 50–100 parts.

Dyes not easily soluble in water or glycerol are first dissolved in alcohol and then mixed with the other ingredients. Thus a red hektograph ink may contain: magenta 20, alcohol 20, acetic acid 5, gum 20, and water 40; or magenta 10, alcohol 10, glycerol 10, and water 50.

Red ink was formerly prepared from Brazil wood or extract of Brazil wood, with the addition of alum or stannous chloride: *e.g.*

(1) Brazil wood, 280 parts; tin-salt, 10 parts; gum, 20 parts; boiled with 3500 parts of water and evaporated down until the proper depth of colour is attained.

(2) Extract of Brazil wood, 15 parts; alum, 3 parts; tin-salt, 2 parts; tartaric acid, 2 parts; water, 120 parts.

Cochineal or carmine inks are prepared by boiling cochineal in water, precipitating the colour with alum and tin salt and dissolving this carmine in the requisite amount of strong ammonia. Another method is to dissolve 2 parts of ammonium carbonate in 200 parts of water and macerate for 3–4 hours with 40 parts of cochineal and 2 parts of alum.

Most of the red inks now used are solutions of magenta or eosin in water, together with a little gum. Glycerol also is added if the ink is to be used for copying.

Blue ink. Prussian blue is the colouring matter commonly employed. The pigment is placed in an earthen vessel, and either strong hydrochloric acid, nitric acid, or sulphuric acid is added to it. After the mixture has remained 2 or 3 days, much water is added, and after settling the supernatant liquor is drawn off from the sediment. This sediment is well washed until all traces of iron and free acid disappear from the water, after which it is dried and mixed with oxalic acid in the proportion of 8 parts of Prussian blue to 1 part of acid. The pigment being now soluble in water, so much of this latter is added as will bring it to the required intensity.

An excellent blue ink can be made by

dissolving 10 parts of indigo-carmine and 5 parts of gum in 50–100 parts of water. Solutions of blue aniline dyes may be used but are easily effaced by bleaching agents and fade on exposure to light.

Inks of other colours can be made from decoctions of dyestuffs mixed with alum (used as a mordant) and gum Senegal or gum arabic; as, *e.g.*, brown ink from catechu or logwood, to which a little potassium dichromate is added; violet and purple inks from logwood with a small admixture of chloride of tin or of alum; yellow ink from gamboge, &c., &c. Aniline colours also offer a selection of tints for this purpose.

Gold and silver inks are prepared from gold and silver, or from cheaper substitutes such as bronze powder and Dutch leaf. The leaf metal mixed with honey is carefully ground down to the finest possible condition; it is then well washed and dried. A medium is furnished by a preparation consisting of 1 part of pure gum arabic and 1 part of soluble potash glass in 4 parts of distilled water. As a rule, 1 part of the powder is sufficient for 3 or 4 parts of the medium.

Imitation silver ink is best made by rubbing up aluminium foil or powder with gum.

Sympathetic, Diplomatic, or Secret inks. These preparations are devised to trace words or figures which are invisible when written but which become visible when subjected to heat or appropriate chemical reagents. Examples:—A weak infusion of galls is colourless on paper, but becomes black when moistened with a solution of copperas; and if a weak solution of copperas be used, the writing will be invisible, till the paper is moistened with a weak solution of galls. Equal parts of copper sulphate and sal ammoniac dissolved in water form a colourless ink, the writing of which turns yellow on the application of heat. Weak solutions of silver nitrate or of auric chloride when exposed to the sunlight become dark brown and purple respectively. Solutions of cobalt chloride or nitrate give tracings which become green or blue when heated and disappear again as the paper cools.

Ink for indiarubber stamps. The following preparation produces ink adapted for this purpose. It does not easily dry upon the pad, and is readily taken up by the paper:—Aniline colour in solid form (blue, red, &c.), 16 parts; boiling distilled water, 80 parts; glycerol, 7 parts. The colour is dissolved in the water, and the other ingredients are added whilst agitating. The '*carbon papers*' used for giving two or more copies of written or typed matter are coated on one side with a mixture of yellow wax and tallow containing a suitable pigment such as lampblack or Prussian blue, or some aniline colour.

Ticket-writer's ink is made of good black ink, with liquid gum added to produce a gloss.

Ink for writing on glass is a solution of gum arabic in strong hydrofluoric acid coloured with some matter which can withstand the acid: cudbear is used for this purpose.

For enamelled cards ordinary printing ink is mixed with a few drops of equal parts of copal varnish and mastic varnish.

Lithographic ink ought to conform to the following requirements. It should be flowing on the pen, not spreading on the stone; capable of forming delicate tracings, and very black to show its delineations. The most essential quality of the ink is to sink well into the stone, so as to reproduce the most delicate outlines of the drawing and to afford a great many impressions. It must therefore be able to resist the acid with which the stone is moistened in the preparation without letting any of its greasy matter escape.

Lithographic ink may be prepared as follows:—Mastic (in tears) 8 oz., shellac 12 oz., Venice turpentine, 1 oz.: melt together; add of wax 1 lb., tallow 6 oz.; when dissolved, add further of hard tallow soap in shavings 6 oz.; and when the whole is perfectly incorporated, add of lampblack 4 oz.; lastly, mix well, cut in moulds, and when cold cut it into square pieces.

Another recipe is as follows:—Fuse together wax, 18 parts; soap, 18 parts; shellac, 14 parts; resin 6 parts; and tallow, 10 parts. Then stir in 2 parts of india-rubber dissolved in 5 parts of oil of turpentine, and 6 parts of lampblack. The whole is heated till the smell of turpentine has nearly disappeared and is then cast into sticks.

Autography is the operation by which a writing or a drawing is transferred from paper to stone. For autographic ink:—White wax 8 oz., white soap 2 oz. to 3 oz.; melt, and add lampblack 1 oz.; mix well, heat strongly, and add shellac 2 oz.; again heat strongly and stir well together. On the mixture cooling pour it out as before. With this ink lines may be drawn of the finest and fullest class, without danger of its spreading; and the copy may be kept for years before being transferred. These inks are rubbed down with a little water in the same way as Indian ink.

Printing ink. Ink prepared for use with type, copper-plates, &c., is composed of a vehicle and pigment. The chief properties required in a good printing ink are:—

(1) A perfectly uniform syrupy consistency.

(2) Must be easily transferred from the ink-rollers to the type, and from the type to the paper.

(3) Must not smudge types, and must be easily washed off them with printer's lye.

(4) The ink must not dry so quickly as to set on types or rollers, but must not dry so slowly on the paper as to hinder folding, &c., of sheets.

(5) When dry, the ink must not set off from the paper on to anything with which it comes in contact.

(6) The printed characters should not show a greasy margin.

(7) The ink should not have a strong smell.

The ink which most nearly fulfils all these requirements is composed of the finest quality of lampblack incorporated with a pure linseed oil varnish. The demand for cheap inks for the printing of newspapers and cheap books has been met by using cheaper qualities of lampblack and substituting for the varnish various compositions of oils and resins with soap, which may or may not contain a proportion of linseed oil.

The linseed oil varnish used for good ink was formerly prepared by heating a quantity of linseed oil in a boiler until the vapour evolved could be ignited. A light was then applied and the whole allowed to burn for about half an hour, until a trial showed that the oil was of the right consistency. The practice of burning the oil gave a dark-coloured product and has now been discontinued.

The present practice is to heat the oil to about 380° to 400°, taking every precaution to avoid its ignition. The boiler is provided with a closely fitting lid or, better, with a cover of wire-gauze, which extinguishes a flame while allowing the vapours to escape.

Provision is made for lifting the boiler from the fire or withdrawing the fire from the boiler, or, in some cases, for running off the oil into a cold vessel. A gutter round the furnace above the fire-door prevents any chance of the oil reaching the fire, even should it boil over the top of the pot. In some modern plant the oil is heated by means of superheated steam. A varnish so prepared is insoluble in water or alcohol, but it mingles readily enough with fresh oil and unites with mucilages into a mass diffusible in water in an emulsive form. The oil loses from one-tenth to one-eighth of its weight by boiling into the thick varnish (Watts).

An average letterpress ink may be made by reheating a varnish produced as above and adding for each gallon of the original oil 4 lbs. resin and 1 lb. brown soap in slices. This is then mixed with the requisite quantity of pigment—rather less than $\frac{1}{4}$ of its weight in the case of lampblack—and the whole thoroughly ground and incorporated in a suitable machine, usually between rollers of polished granite or steel, as in Lehmann's apparatus. The presence of soap in the ink causes it to ' lift ' well, *i.e.* to be completely transferred from the type to the paper. The following recipes represent vehicles of a cheaper class :—

Linseed oil and resin vehicle.—Resin 50, boiled linseed oil 100, resin soap 10, partly boiled oil, 6 parts by weight.

Resin oil vehicle.—Resin oil 50, resin 50, boiled linseed oil 50, resin soap 5, thin boiled linseed oil 6 parts.

Cheap mineral oil vehicle.—Resin is dissolved in about an equal weight of heated mineral oil (petroleum) of sp.gr. 0·880–0·920 (Wass, Fr. Pat. 322298, 1908).

Composition vehicles. 5 kilos. Venice turpentine, 15 kilos. castor oil, and 1 kilo. white wax, mixed at 100° (Knecht). 9 kilos. thick turpentine, 10 kilos. soft soap, and 4 kilos. oleine, mixed hot (Rösl).

The lampblack used is of various qualities according to the price of the ink. The proportion used is just sufficient to give a full black impression, and this is less with the better qualities of lampblack. The ink for rotary machines contains about 28 p.c. of lampblack, that for high-speed newspaper printing about 24 p.c., that for book-printing about 21 p.c., and and that for illustration work about 19 p.c. with 2 p.c. of Prussian blue and 1 p.c. of indigo.

Brackenbusch's inks consist of 25 parts paraffin oil, 45 parts of fine colophony, and 15 parts of lampblack. The amount of colophony is reduced in soft inks for high-speed work.

It has been proposed to use oxides of iron or manganese as black pigments for printing inks, in which case the paper could be bleached and subsequently re-made into white paper. This cannot be done with the lamp-black inks now used (*see e.g.* Fireman, U.S. Pat. 802928, 1905).

It is said that so marvellously thin is the layer of ink on small type that one pound weight even of cheap newspaper ink will cover no less than 7000 square feet of type matter.

Coloured printing inks. These inks are made from the varnishes above described by the addition of dry colours, taking great care that the colours are thoroughly well ground and assimilated with the varnish, since lumps of any kind not only clog the type but alter the tint. Some tints which are exceedingly light will require an admixture of white powder to give the necessary body to the ink.

The following pigments are eligible for incorporation in printing inks :—

White.—Heavy spar (barium sulphate) and zinc white.

Red.—Orange lead, vermilion, burnt sienna, Venetian red, Indian red, lake vermilion, orange mineral, rose pink, and rose lead.

Yellow.—Yellow ochre, gamboge, and lead chromate.

Blue.—Cobalt, Prussian blue, indigo, Antwerp blue, Chinese blue, French ultramarine, and German ultramarine.

Green.—Usually mixtures of yellow and blue, but sometimes chrome green, cobalt green, emerald green, or *terre verte.*

Purple.—A mixture of those used for red and blue.

Deep brown.—Burnt umber with a little scarlet lake.

Pale brown.—Burnt sienna : a rich shade is obtained by using a little scarlet lake.

Lilac.—Cobalt blue with a little carmine added.

Pale lilac.—Carmine with a little cobalt blue.

Amber.—Pale chrome with a little carmine.

Pink.—Carmine or crimson lake.

Shades and tints.—A bright red is best got from pale vermilion with a little carmine added ; dark vermilion when mixed with the varnish produces a dull colour. Orange red and vermilion ground together also produce a very bright tint, and one that is more permanent than an entire vermilion colour. Cheaper substitutes are orange mineral, rose pink, and red lead. Lead chromate makes the brightest colour. For dull yellow, use yellow ochre. Indigo is excessively dark, and requires a good deal of trouble to lighten it. It makes a fine showy colour when brightness is not required. Prussian blue is useful, but it dries very quickly, hence the roller must be frequently cleaned. The objection to Prussian, Antwerp, and Chinese blues, is that they are hard to grind and likely to turn greenish with the varnish when used thin. For green any of the yellows and blues may be mixed. The varnish itself having a yellow tinge will produce a decidedly greenish tint with a small quantity of Antwerp blue. Emerald green is got by mixing pale chrome with a little Chinese blue, and then adding the mixture to the varnish until the tint is satisfactory.

In using painter's colours it is advisable to avoid as much as possible the heavy ones. Some colours require less oil in the varnish than others. For the comparative permanence of colouring matters, *v.* PIGMENTS.

A bronze of changeable hue may be given to inks with the following mixture (Southward):—Gum shellac 1½ lbs. dissolved in one gallon of 0·95 p.c. alcohol or Cologne spirits for 24 hours. Then add 14 oz. aniline red. Let the mixture stand for a few hours longer, when it will be ready for use. When added to good blue, black, or other dark ink, it gives a rich hue to it. The quantity must be carefully apportioned.

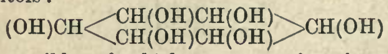
Bronzing, the production of printed matter having the colour and lustre of gold or silver, is carried out by printing with a varnish which remains 'tacky' for a time, and then dusting over the whole surface with bronze powder or aluminium powder or similar substances. The powder adheres only to the varnish and thus produces the desired effect.

Such a varnish may be produced by melting into a good linseed oil varnish sufficient beeswax to give it the consistency of lard or tallow. (*See* Ure's Dict. of Arts, Manufactures, &c.; Cooley's Cyclop. of Practical Receipts; Lehner's Ink Manufacture; Southward's Practical Printing; Noble's Principles and Practice of Colour Printing; L. E. Andés' Oil Colours and Printer's Inks; and Seymour's Modern Printing Inks.)

INKANI FAT. A fat obtained from the seeds of the East African tallow tree, *Stearodendron Stuhlmannii* (Engl.).

INOSIC ACID, INOSINE *v.* CARNINE.

INOSITOL (*Inosite*). A number of natural substances having the composition of cyclic polyalcohols, *e.g.* hexahydroxy*cyclo*hexanes $C_6H_6(OH)_6$, are often classed with the carbohydrates since they have the same formula, taste sweet, occur along with them in nature, and possibly have been formed from them by the junction of the ends of the six carbon chain, although such transformation has never been realised in the laboratory. Typical of the class is inositol. No less than nine stereoisomeric inositols:



$$(OH)CH\begin{array}{l}\diagup CH(OH)CH(OH)\diagdown\\ \diagdown CH(OH)CH(OH)\diagup\end{array}CH(OH)$$

are possible, of which seven are inactive and two optically active and enantiomorphic. Five of these have been described, viz. optically active *d*- and *l*-inositol, and inactive inositol, cocositol and scyllitol. Similar pentahydroxy*cyclo*hexanes are likewise found in plants. These are *d*- and *l*-quercitol.

The formation of furfural on distillation of *meso*inositol with phosphoric anhydride in a copper vessel (Neuberg, Biochem. Zeitsch. 1908, 9, 551) is the only instance in which a complex substance has been obtained common to both the carbohydrates and inositol.

d-**Inositol** (*matezodambose*) is prepared by demethylation (boiling with concentrated hydriodic acid) of the naturally occurring methyl ether, pinitol. It crystallises in anhydrous prisms, m.p. 247°–248°, $[\alpha]_D+65°$ without mutarotation and forms hexacetyl and hexabenzoyl derivatives.

Pinitol (*pinite*) $C_7H_{14}O_6$, also called *matezite* and *sennite* was discovered in the resin of the Californian *Pinus lambertiana* (Dougl.) (Berthelot, Compt. rend. 1856, 41, 392). It occurs in the residues of the manufacture of coniferin, in senna leaves, and in the liana of Madagascar rubber (*mateza roritina*). It crystallises in colourless rhombs, m.p. 186° $[\alpha]_D+65{\cdot}5°$. The structure of pinitol was established by Maquenne (Compt. rend. 1889, 109, 812).

l-**Inositol** was obtained by Tanret (Compt. rend. 1889, 109, 908) by demethylation of quebrachitol. It crystallises in needles; m.p. 247° $[\alpha]_D-65°$.

Quebrachitol (quebrachite) occurs in quebracho bark. It crystallises in prisms; m.p. 186° $[\alpha]_D-80°$.

r-**Inositol**, obtained by mixing the *d*- and *l*-isomerides in equal quantities, is optically inactive, m.p. 253°. Tanret (Compt. rend. 1907, 145, 1196) has obtained both racemic- and meso-inositol from fresh ripe berries of mistletoe.

Meso- or *i*-**Inositol** (*dambose, nucite*) is widely distributed in both plants and animals. It occurs in muscles, in the heart, lungs, and liver, in beef and horse flesh, and in the urine in cases of Bright's disease. In plants, it is found in beans, peas, &c., in the leaves of asparagus, oak, ash, walnut, &c., in all parts of the grape vine and hence in wines and in fungi. The chief source is the leaves of the walnut tree (Tanret and Villiers, Compt. rend. 1877, 84, 393; 1878, 86, 486), but very much larger quantities are afforded by mistletoe. It may also be prepared from cochineal mother liquors. It crystallises in bunches of needles, m.p. 225°, and does not reduce Fehling's solution. Yeast is without action, but certain fungi decompose it. The hexacetate forms monoclinic plates, m.p. 212°. Hugo Müller (Chem. Soc. Trans. 1907, 91, 1780) has described and measured the crystals of the monobromopentacetate, minute crystals, m.p. 240°, the dibromotetracetate broad transparent prisms, m.p. 140°, and scaly crystals, m.p. 235°; also of inositoldibromohydrin, m.p. 210°.

When inositol is evaporated with nitric acid almost to dryness and then again carefully evaporated with ammoniacal calcium chloride, a rose red colouration is obtained which enables 0·0005 gram to be detected with certainty (Scherer, Annalen, 1850, 73, 322). With ammoniacal strontium acetate, a still more delicate violet colouration is obtained.

Bornesitol, the monomethyl ether, occurs in Borneo rubber: it forms rhombic prisms, m.p. 199°–203°.

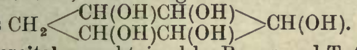
Dambonitol, the dimethyl ether, is found in Gabon rubber: it crystallises in hexagonal prisms, m.p. 195°.

Phytin, which is present in many plant seeds and has been isolated from rice bran, is inositol phosphoric acid (Winterstein, Zeitsch. physiol. Chem. 1908, 58, 118).

Cocositol (cocosite) $C_6H_{12}O_6$, was discovered by Hugo Müller in the leaves of *Cocos nucifera* (Linn.) and *Cocos plumosa* (Hook.) (Chem. Soc. Trans. 1907, 91, 1767). It crystallises from water in large transparent lustrous monoclinic crystals, m.p. about 345°–350°, and is optically inactive. It forms a hexacetate, giving prismatic crystals, m.p. about 300°, also a benzoate and nitrate. It gives the red colouration characteristic of inositol (Scherer's reaction). H. Müller (private communication) regards it as identical with scyllitol: the occurrence of this substance in two such different organisms as the cocoa-nut palm and the dog-fish is most remarkable.

Scyllitol (scyllite) $C_6H_{12}O_6$, discovered by Staedeler and Friedrichs (J. pr. Chem. 1858, (i.) 73, 48) in various organs of the *Plagiostomi* (dog-fish) has been investigated by J. Müller. It is inactive, crystallises in hard lustrous monoclinic prisms, m.p. above 339° and is sparingly soluble in water. It gives Scherer's reaction and forms a hexacetyl derivative.

d-**Quercitol** $C_6H_{12}O_5$ is found in the acorn and in minute quantity in the cork and bark of the oak. Hugo Müller (Chem. Soc. Trans. 1907, 91, 1766) has also obtained it from the leaves of *Chamærops humilis* (Linn.), the only Eurpoean representative of the palm family, which was formerly used like esparto for making paper. The leaves contain 1·35 p.c. of quercitol. They are crushed, extracted with boiling water, and the extract precipitated first with neutral and then with basic lead acetate. The lead in solution is removed and the filtrate evaporated until crystals appear. It crystallises in prisms, m.p. 234° $[\alpha]_D + 20{\cdot}16°$. It is not fermentable and forms acetyl and similar esters, showing that it contains five hydroxyl groups. Potassium permanganate oxidises it to malonic acid and other products, confirming the structural formula as



$$CH_2<\begin{matrix}CH(OH)CH(OH)\\CH(OH)CH(OH)\end{matrix}>CH(OH).$$

l-**Quercitol** was obtained by Power and Tutin (Chem. Soc. Trans. 1904, 85, 624) from the leaves of *Gymnema sylvestre* (R.Br.). It crystallises in prisms from water or needles from alcohol, m.p. 174° $[\alpha]_D - 73{\cdot}9°$, and forms penta-acetyl and pentabenzoyl derivatives. On oxidation with potassium permanganate, malonic acid is formed; with sodium hypobromite, the product is diketotrihydroxyhexahydrobenzene $C_6H_5O_2(OH)_3$. It is not the optical antipode of *d*-quercitol.

Quercitol contains 4 asymmetric groupings and therefore 8 optically active and two unresolvable inactive modifications are possible.

E. F. A.

INSECTICIDES *v.* Plant-sprays.

INSECT WAX *v.* Waxes.

INTENSIFIERS *v.* Photography.

INULA CAMPHOR *v.* Camphors.

INULIN *v.* Carbohydrates.

INVERTASE (*Sucrase*). Invertase is the enzyme which hydrolyses or inverts sucrose to dextrose and lævulose. It is present in all yeasts except *S. octosporus*, *S. capsularis*, and *S. membranæfaciens* (Hans.), and is extremely active. According to O'Sullivan and Thomson (Chem. Soc. Trans. 1890, 57, 834), whose contribution to the subject is still a classic, it can hydrolyse 200,000 times its weight of sucrose, and probably this figure is much understated, as is the case with other enzymes, but little is known of its nature.

O'Sullivan purified invertase by fractional precipitation so long as it remained active, and found that the proportion of carbohydrate increased. He identified this as mannose, as was also done by Koelle (Zeitsch. physiol. Chem. 1900, 29, 429). A very pure preparation was obtained by Osborne (*ibid.* 1899, 28, 399) which gave none of the protein reactions, except precipitation by copper sulphate, lead acetate, and phosphotungstic acid; it gave the biuret, xanthoprotein, and Millon's test faintly, and could not be freed completely from carbohydrate. It also always contained nitrogen and ash. Salkowski (Zeitsch. physiol. Chem. 1909, 61, 124) considers that invertase does not contain carbohydrates and that the yeast gum which accompanies it is an impurity.

According to Mathews and Glenn (Bio-Chem. J. 1911, 9, 29), the most active preparation contains about 2 p.c. of ash and 2·2 p.c. of nitrogen. It consists of a gum and a nitrogenous portion yielding 70–76 p.c. of mannose on hydrolysis. These authors consider invertase to consist of a union of an inactive colloidal gum with an active protein ferment: by the action of acid, the ferment is freed from the carrier and rendered active.

Invertase appears to be effective in all cases where dextrose and lævulose are united, even when a third sugar molecule is attached to these. Thus it hydrolyses raffinose, gentianose, melicitose, and stachyose, splitting off lævulose in each case.

Invertase is of common occurrence in the vegetable kingdom: it is present in buds, flowers, and leaves of the higher plants and in numerous mould fungi. It is not so widespread in the animal body as maltase, being practically limited to the mucous membranes of the alimentary canal.

The laws regulating the velocity of invertase action are dealt with elsewhere (*v.* Fermentation and Hydrolysis).

It is very sensitive to the minutest quantities of alkali, which retards or stops its action, and for this reason its action is accelerated by dilute acids or acid salts, although probably, like diastase, it is most active in truly neutral solution. Quantitative work with invertase must be carried out in hard glass vessels and with solutions which have been stored and measured in such vessels. It is the neglect to avoid alkaline impurity which has occasioned many of the controversial statements in the extensive literature relating to this subject.

The rate of action is much influenced by temperature: 55°–60° being that of maximum activity, beyond which it becomes weakened by heat (*see* also papers by Euler, Zeitsch. physiol. Chem. 1910 and 1911). It is destroyed between 65° and 70°. The power of the enzyme to resist heat is considerably increased by the presence of sucrose: according to O'Sullivan, it will withstand a temperature 25° higher.

An active solution of invertase is readily obtained by extracting dried yeast with water or by shaking up living yeast with chloroform water. A very active permanent preparation may be prepared by setting aside washed pressed yeast with a little water to autolyse at 37° for a few days. The liquid is filtered and alcohol added a few cub. cm. at a time to the filtrate so as to keep the precipitate in a granular form. The liquid is decanted, the precipitate washed first with a little 60 p.c. and then with 80 p.c. alcohol and at once dissolved in a minimum quantity of water. The precipitation process may be repeated and the final product dissolved clear in the smallest quantity of water and bottled with a little toluene. This solution, which is of very high activity, may be kept for years without its activity materially changing (*v.* Fermentation).

E. F. A.

IODALBACID, IODALBIN, IODANISOL, IODEIGONS, *v.* Synthetic drugs.

IODEMBOLITE *v.* Cerargyrite.

IODGLIDIN, IODIN, *v.* Synthetic drugs.

IODINE. Symbol I. At.wt. 126·92. This element was discovered in 1812 by Courtois in the mother liquor of kelp. The discovery was first announced to the French Institute in 1813. The properties of the new element were further investigated by Clement and Desormes, Gay-Lussac, and Davy.

Iodine is a crystalline solid of greyish-black colour and bright metallic lustre resembling plumbago. Its sp.gr. is 4·948. It is obtained by sublimation in brilliant rhomboidal plates, or in elongated octahedrons belonging to the trimetric system. In very thin plates it transmits light of a red colour. It melts at 114·15°, and boils at 184·35° (Ramsay). It volatilises at ordinary temperatures spontaneously in the air, diffusing an odour resembling chlorine. It is sometimes employed in this way in hospitals as a disinfectant. The vapour has an intense rich violet colour, and is one of the heaviest of all known gases, having a sp.gr. of 8·801. A stratum 4 inches thick presents a black mass quite impervious to light. It is very slightly soluble in water, requiring about 7000 parts for solution. It is soluble in chloroform, bromoform, carbon disulphide, light petroleum, and benzene, forming violet solutions; also in ethyl, methyl, and amyl alcohols, and in ether and glycerol, forming brown solutions. It is very soluble in potassium iodide, of which 1 part in 2 parts of water will dissolve 2 parts of iodine. In reactions it resembles chlorine and bromine, but is less energetic, and is displaced by these elements from its compounds with hydrogen and the metals. It has a strong affinity for most of the metals, and in the presence of water, attacks and dissolves gold. The most characteristic reaction of free iodine is the dark blue compound formed with starch; this test is extremely sensitive, and will reveal the presence of one-millionth part in any liquid containing it. Another characteristic reaction is to liberate the iodine from a solution by nitrosulphuric acid, and dissolve it out by carbon disulphide; this affords an accurate and easy method of estimating it by the depth of the crimson colour of the solution; it is also extremely sensitive, and well adapted to estimate small quantities of the element.

Iodine in minute quantities is very largely distributed throughout the animal, vegetable, and mineral kingdoms. As a mineral it occurs in combination with silver, mercury, and lead, in ores from Mexico, Chile, and Spain, with zinc in Silesia, and with lead in South America. It is also found in dolomite from Saxony, in limestone from Montpellier, in shale from Sweden, and in calcium phosphate from France. It exists also in the 'caliche' of Chile in the form of sodium iodate. This is the only mineral source from which it is manufactured, and has been for many years the most important of all the commercial sources.

Many mineral waters contain iodine, notably those of Carlsbad in Bavaria, Hall in Austria, Marienbad in Bohemia, Holberg in Pomerania, Halle in Saxony, Sales in Piedmont, Nix in Savoy, Kreuznach in Galicia, Halse in Java, and Jallien in France. It is also found in the waters of Friedrichshall, Castellamare, Heilbrun, Homburg, Seidchutz, and Vichy; and in this country in those of Leamington, Bonington, Bath, Cheltenham, and Woodhall. It is a valuable remedy in skin diseases. The sea is an abundant source of it. Iodine is always present in sea-water, but in such a very minute proportion that it is difficult of detection except by operating on large quantities. It has been estimated in the Atlantic at 1 part in 280,000,000 (Stanford); all fishes and all animal products from the sea appear to contain iodine, but in very minute quantity. The following table shows a few of the marine products in which it has been estimated:—

Cod-liver oil	0·000322	p.c. iodine.
Cod-liver	0·000817	,,
Codfish	0·000160	,,
Herring, salt	0·000650	,,
Whale oil	0·000100	,,
Seal oil	0·000050	,,
Oysters (Portuguese)	0·000040	,,
Prawns	0·000440	,,
Limpets	0·003200	,,
Cockles	0·002140	,,
Whelks	0·008920	,,
Mussels	0·035720	,,
Sponge (Turkey)	0·200000	,,
Sponge (Honeycomb)	0·054000	,,

Nearly all seaweeds or marine algæ contain it. It is present even in the *Zostera marina* (L.) or grass wrack, natural order *Naiadaceæ*, a flowering plant growing only in the sea; but there are some remarkable exceptions. The gelatinous species of algæ, the *Chondrus crispus* (L.) (or Irish moss), and *Gelidium corneum* (Lam.) of British species, and the *Eucheuma spinosum* [(L.) J.Ag.], or *Agar agar* of foreign species, do not contain iodine. The *Enteromorpha compressa* [(L.) Grev.], or common sea grass, when dry has a strong odour of the sea, but does not contain iodine. The salsola or salt wort, *Salsola Kali* (L.), natural order *Chenopodiaceæ*, growing on the seashore, and from which barilla was made, contains no iodine. Some of the algæ are comparatively rich in iodine, and the ash of these plants, known as kelp, for many years formed the only commercial source of this important element.

Manufacture.—By far the greater bulk of all the iodine produced is now extracted from the mother liquors of the nitrate works in Chile, but the manufacture of iodine from kelp has for long been carried on in Scotland and in France, and within recent years has been started in Norway and in Japan. Courtois, a saltpetre maker in Paris, who discovered iodine, obtained it from the kelp liquors which were used to furnish the salts of potash required in his manufacture, and this was for many years the only commercial source of iodine. The manufacture was unsuccessful commercially in the hands of the discoverer, and he died in poverty. It was afterwards successfully carried out by MM. Cournerie, of Cherbourg, and has continued to be an important manufacture on the Normandy coasts. In this country it was first made on the small scale by Dr. Ure of Glasgow, and the manufacture has since been almost exclusively confined to that city, where it has assumed considerable importance. It was first made there in quantity in 1841, and the imports of kelp into the Clyde in that year amounted to 2,565 tons. In 1845, there were four small works engaged in the manufacture of iodine. Kelp was then used for soap making on account of the sodium carbonate it contained, and the iodine was extracted from the lyes of the soapboilers. In 1846 there were twenty makers of iodine in Glasgow, who then treated the kelp directly, extracting also the potash salts which had a high value in the market. The fall in the price of potash salts owing to the discovery of the Stassfurt mineral, which reduced the price to one-third, the very variable character of the kelp used, and the extreme fluctuations in the price of iodine, ranging from 4*s.* to 34*s.* per lb., soon reduced the number of makers, and now there are only three works in Scotland. The produce of iodine from kelp was so limited that it offered unusual temptations to speculators, who derived most of the benefit from the high prices, the manufacturers suffering the losses during the low prices.

The history of kelp, or *varec* as it is called in France, is extremely interesting. It is a crude rough slag made by burning seaweed in long shallow pits. For many years it was a large and valuable article of commerce, and greatly enriched the proprietors of the West Highland estates where it was principally made. It was then the only source of soda. At the beginning of last century it realised 20*l.* to 22*l.* per ton, and the Hebrides alone yielded 20,000 tons per annum, worth upwards of 400,000*l.*; and as the burners only received 35*s.* to 40*s.* per ton for their share, the profit to the Highland lairds was enormous, and it induced an amount of extravagance which ruined most of them. It was largely used in soap making and in glass making, and within the last hundred years there were glass works at Dumbarton using this material, which were celebrated for the quality of their glass. At a glass works in Drontheim in Norway, it was still used for this purpose up to about forty years ago. The importation of barilla gave the first blow to kelp, and it fell in price, and for the twenty-two years ending 1822, the average price was 10*l.* 10*s.* The duty was then taken off barilla, and the price of kelp again fell to 8*l.* 10*s.*; in 1823, the salt duty was repealed and kelp fell again to 3*l.*, and in 1831 to 2*l.*, at which price there was no further profit on the manufacture. In the meantime soda was being largely made by the Leblanc process, and kelp was superseded altogether as a source of soda. It must have been a most expensive source, as it yielded only about 4 p.c. of alkali and often less than 1 p.c.; and at one time must have cost the soap makers what would have been equal to 100*l.* per ton for soda ash, worth now about 5*l.* 10*s.*

The manufacture of iodine and potash salts then began to assume some importance, but the kelp required was not the same, that which contained the most soda containing the least potash and iodine. Moreover the kelpers had been taught to burn at a high temperature, which improves the yield of sodium carbonate but volatilises much of the potash and some of the iodine. The seaweed employed by the kelpers was of a kind containing little iodine, and not very rich in potash. They used almost exclusively the black wrack, cut in large quantities in the Highland lochs, and consisting of the three fuci, *Fucus vesiculosus* (L.), *Ascophyllum nodosum* (Le Jol.), and *F. serratus* (L.), which are all uncovered at low tide. This is now entirely unutilised: the kelp made from it was known as *cut-weed kelp.* The following is the average analysis from numerous cargoes of the kelp:

Potassium sulphate	23·08
Potassium chloride	1·45
Sodium chloride	19·13
Sodium carbonate	6·48
Insoluble	43·71
Water	6·22
	100·07
Total potash, K_2O	13·40
Iodine, lbs. per ton	4·18 =0·18 p.c.

Drift kelp is the only variety now employed as a source of iodine. It is made from the red wracks, the *Laminaria digitata* [(L.) Lamx.], or tangle, and the *L. stenophylla*, which are always submerged by the tide, and contain about ten times as much iodine as the fuci. These seaweeds are torn up by the storms from the rocks on which they grow, and cast ashore; unlike the black wrack, these plants suffer much from rain, the more valuable salts being completely washed away, and are often after drying quite valueless, the kelper losing all his labour. From the time of its discovery, the iodine was the most important product, but the potash salts were also very remunerative at first. Potassium chloride, or 'muriate,' as it is technically called, was worth 25*l.* per ton. The discovery of the Stassfurt mineral reduced its value to about one-third, and the further discovery of bromine in the same mineral reduced the price of that element from 38*s.* to 1*s.* 3*d.* per lb., the present value. The amount of bromine in kelp is small, only about one-tenth of the iodine, and it has not been extracted from this source for the last forty years. It is remarkable that the algæ should select iodine, as bromine is a much larger constituent of sea-water, which usually contains about 6 parts in 100,000, and according to Dittmar appears to bear the constant relation to the chlorine of 0·34 to 100, whereas iodine exists only as a minute trace, difficult even of detection, although the aggregate amount in the ocean must be enormous.

The algæ differ considerably in the proportion of iodine which they take up from the sea-water, and only two species, the *Laminaria digitata*, and the *L. stenophylla* are worth burning for kelp.

It is remarkable that the giant algæ of the Falkland Islands contain very little iodine, although these are the largest sea-plants in the world. The *Duvillœa utilis* (Bory.), a marine tree with a stem a foot in diameter, and the *Macrocystis pyrifera* (Turn.) which grows to the length of 1500 feet, contain only traces of iodine; in some samples it can scarcely be detected.

The following table shows the average yield of the most important varieties. The kelp plant figures are taken from a large number of analyses, from seaweed gathered all around the shores of Great Britain and Ireland; also Denmark, Norway, and Iceland.

Dry weeds	Per cent.	lbs. per ton.
Drift Kelp:		
Laminaria digitata [(L.) Lamx.], Tangle, stem	0·4535	10·158
„ *stenophylla*	0·4777	10·702
„ *saccharina* (Lamx.), Sugar Wrack	0·2794	6·258
Cut Kelp:		
Fucus serratus (L.), Black Wrack	0·0856	1·807
Ascophyllum nodosum (Le Jol.), Knobbed wrack	0·0572	1·281
Fucus vesiculosus (L.), Bladder Wrack	0·0297	0·665
Various:		
Halidrys siliquosa [(L.) Lyngb.], Sea Oak	0·2131	4·773
Japanese Seaweed, edible	0·3171	7·102
Himanthalia lorea [(L.) Lyngb.], Sea Laces	0·0892	1·998
Rhodymenia palmata [(L.) Grev.], Dulse, edible	0·0712	1·594
Chorda Filum [(L.) Stackh.], Sea Twine	0·1200	2·688
Zostera marina (L.), Grass Wrack	0·0457	1·023
Duvillœa utilis (Borg.), Falkland Islands	0·0075	0·179
Macrocystis pyrifera (Turn.), Falkland Islands	0·0308	0·690

The seaweeds chiefly used in Japan for the extraction of iodine are *Laminaria, sp. Ecklonia cava, E. bicyclis* (Kjellm.), and *Sargassum sp.* The iodine content varies with the age of the algæ and also with the time of year, being greatest during June to September; the following figures give the iodine content of some of the raw seaweeds: *Ecklonia cava*, 0·23 p.c.; *E. bicyclis*, 0·27 p.c.; *Sargassum sp.*, 0·05 p.c.; *Laminaria angustata*, (Kjellm.), 0·18 p.c.; *L. longissima*, 0·17 p.c.; *L. ochotensis*, 0·19 p.c.

It will be seen that even in the drift weeds the quantity of iodine is inconsiderable, but if the plants are properly burnt to a loose ash at a low temperature, they ought to yield a kelp containing 25 to 30 lbs. of iodine to the ton. 12 lbs. per ton is, however, above the average yield from ordinary drift kelp. The kelpers often neglect to protect the seaweed from the action of rain, which washes out the soluble iodides, and moreover it is difficult to prevent them from burning it into a hard slag by working it up, when molten, with iron clauts. Sand and stones are thus mixed up with it, and the great heat employed drives off some of the iodine. The result is a hard slag of great density, and this density forms one of the difficulties in inducing the kelpers to burn the weed to a loose ash, which they imagine, from the lightness, will not give them the weight they expect. As an actual fact, of course, the total weight of the ash so produced is considerably more, from the same quantity of weed used; but old fallacies die hard, especially amongst the poor and ignorant people who do this work. There is the further disadvantage that the sulphates are reduced to sulphides or oxysulphides, and a considerable extra expenditure of oil of vitriol to decompose these is entailed; sulphur is thus obtained as one of the by-products of the lixiviation of kelp, in which it ought not to exist at all. The presence of silica as sand greatly assists the volatilisation of the iodine.

The table at top of next column shows the analyses of very good samples of Irish and Scotch kelp, and also of the latter burnt into loose ash, and the comparison of these indicates clearly the effect of the heat of burning.

—	Kelp		Ash
	Irish	Scotch	Scotch
Potassium sulphate	11·14	13·95	12·71
„ chloride	27·17	17·79	18·09
Sodium „	9·00	14·00	6·80
„ carbonate	5·82	3·92	3·43
„ sulphide	Heavy trace	Heavy trace	Slight trace
„ thiosulphate	1·22	0·75	0·17
„ iodide	0·82	0·76	1·48
„ thiocyanate	Heavy trace	Heavy trace	Slight trace
Soluble organic matter	Nil	Nil	0·42
Insoluble	41·41	44·80	49·75
Water	3·10	4·05	7·00
	99·68	100·02	99·85
Total potash, K_2O	23·17	18·77	18·32
Iodine, lbs. per ton	15½	14½	28
Carbon in insoluble part	Nil	Nil	9·00

A different method of manufacture was introduced by Stanford in 1863, when works were erected in the outer Hebrides for the carbonisation of the stems of tangle (*L. digitata*) in closed retorts, thus converting the tangle into charcoal and collecting the products of destructive distillation, consisting principally of tar and ammoniacal liquor, in suitable condensers. A very porous charcoal is thus produced which contains all the iodine present in the seaweed employed; when lixiviated it gives very white salts containing no sulphides. The residual charcoal, after lixiviation, does not resemble that from wood, which is principally carbon with a small percentage of ash, but in its composition and general character approaches animal charcoal obtained from bone. The following table shows the comparison:—

—	Seaweed	Bone
Carbon	52·54	11·77
Calcium phosphate	10·92	77·70
„ carbonate	15·56	1·43
„ sulphate	—	0·35
Magnesium carbonate	11·34	—
Alkaline salts	5·70	1·09
Silica, &c.	3·94	0·66
	100·00	100·00

The presence of magnesium carbonate is a peculiar characteristic of this charcoal, as all seaweeds are rich in magnesium salts. Seaweed charcoal, as might be expected from its composition, is an excellent decoloriser and deodoriser. As compared with animal charcoal it is much lighter and more bulky, and therefore has not replaced it as a decoloriser, although from its high percentage of carbon it would well stand the constant re-burning required in sugar works, and be improved by this treatment.

This process by carbonisation was in use in the islands of Tyree and North and South Uist for a number of years, with great benefit to the crofters and cottars of these islands. It required, however, the erection of separate carbonising works in each island, and, as the winter tangle only was used, it was difficult to secure sufficient supplies except from a large area. Moreover, it was found in practice very troublesome to completely extract the soluble iodides from the charcoal, and ultimately the process was abandoned in favour of the older and simpler method of kelp burning. A wet process of extracting iodine from seaweeds has also been tried. It had been noticed by Stanford that the whole of the alkaline salts present in the seaweed, and a considerable quantity of extractive matter containing dextrin and mannite, could be extracted from the fronds of the *Laminaria* or red seaweeds by simple maceration in cold water. The residue, which is the plant apparently unaltered, consists of a nitrogenous substance resembling albumen, to which the name of 'algin' has been given, and the algic cellulose or algulose, which represents the cellular fabric of the plant. The algin or alginic acid is removed by digesting it with solution of sodium carbonate, which dissolves it as sodium alginate, leaving the algulose. The solution can be effected in the cold, but it is necessary to employ heat, otherwise it is impossible to filter off the algulose. A Taylor filter is the only one that can be employed, the filtration being extremely difficult on account of the great viscosity of the algin or sodium alginate and the extreme fineness of the cellular algulose. The process adopted is to boil the seaweed with sodium carbonate, and filter; the algulose is separated by filtration, and the filtrate is mixed with hydrochloric acid, and the alginic acid is then easily filtered off; the solution is neutralised with caustic soda, evaporated to dryness, and carbonised, the residue forming the 'kelp substitute.' The alginic acid, which has a slight amber colour, is washed, bleached, and redissolved in sodium carbonate; the resulting liquor, evaporated in a vacuum pan, forms the commercial alginate of soda or 'soluble algin.' By evaporation on glass plates or porcelain slabs, the algin is obtained in the form of a transparent flexible sheet, which, however, tends to crack as it approaches dryness, and by immersing this in a very dilute solution of hydrochloric acid it is converted into alginic acid or 'insoluble algin,' which, without altering its appearance, renders the sheet perfectly insoluble in water. The soluble algin is a definite salt of sodium, having the composition, when pure, $C_{76}H_{75}O_{22}N_2Na_5$.

Commercial algin or sodium alginate resembles gum arabic, and in the sheet form can scarcely be distinguished from gelatin from which it differs by the solution not gelatinising, and by giving no reaction with tannin. It is distinguished from albumen by not coagulating on heating; from starch by giving no colour with iodine; from dextrin and gum arabic by its insolubility in dilute acids. All mineral acids, and citric, tartaric, lactic, oxalic, and picric amongst the organic acids, precipitate alginic acid in a gelatinous form.

It precipitates all the alkaline earths as alginates, with the exception of magnesium, the alginate of which is soluble. It precipitates nearly all the heavy metals as alginates, but gives no precipitate with mercuric chloride, nor with potassium silicate. The following analyses show the usual composition of the commercial algin :—

——	No. 1		No. 2		Average	
Water	17·13		19·30		18·22	
Organic matter . . .	59·97		58·13		59·05	
Sodium carbonate . .	18·32	per cent. ash 22·90	17·78	per cent. ash 22·57	18·05	per cent. ash 22·73
Neutral salts . . .	2·98		2·77		2·87	
Insoluble ash . . .	1·60		2·02		1·81	
	100·00		100·00		100·00	
Soda, Na_2O	10·71		10·40		10·55	

This substance, known as soluble algin, is sodium alginate, but potassium, ammonium, lithium, or magnesium alginate are all soluble algins, and scarcely distinguishable in appearance. These all present the form of thin flexible sheets, resembling gelatin, and having the same colour, but none are gelatinous. The solution of algin resembles that of gum arabic, which in many of its applications it may be expected to replace; it is quite soluble in cold water, but the solution takes about 12 hours to complete. It is so extremely viscous that a 2 p.c. solution is as thick as a 50 p.c. solution of gum arabic, and a 5 p.c. solution is poured with difficulty out of a wide-mouthed bottle. Nearly all the mineral acids precipitate alginic acid ($C_{76}H_{80}O_{22}N_2$) from the solution as a very gelatinous precipitate; a 2 p.c. solution becomes semi-solid when thus treated. In this respect, it resembles a strong solution of egg albumen, and it can be employed for thickening colours in printing, or as a mordant in the same manner. Alginic acid is insoluble in water, so that in dressing fabrics the soluble algin forms a flexible varnish, which can be converted into a lustrous hard glaze by passing it through a weak mineral acid. This process, which would destroy the ordinary starch and gum dressings, renders it also permanent and insoluble in water, the fabric becoming waterproof. As the alginates of calcium, aluminium, iron, &c., are all insoluble, the same effect is obtained by the use of solutions of these metals for the final wash. Alginic acid when dry resembles albumen, but it can be obtained also in thin transparent sheets, and readily coloured like gelatin, from which, however, it differs in being insoluble in hot water. It can also be obtained in blocks. Calcium alginate ($C_{76}H_{74}Ca_3N_2O_{22}$) resembles it, but is whiter, like bone.

Aluminium alginate is very soluble in ammonia, and the aluminium ammonio-alginate is insoluble when dry, so that it makes a cheap waterproof varnish. It forms a good mordant or dung substitute in dyeing. Copper alginate is soluble in ammonia, forming a beautiful blue copper ammonio-alginate, which is also insoluble when dry, and makes a varnish useful for waterproofing fabrics which are liable to decomposition or to attacks of insects.

Ferric alginate is also soluble in ammonia, forming a bright red ferro-ammonio-alginate; insoluble when dry, and proposed as a styptic, and for administering iron internally. These metals are most completely precipitated from solution by sodium alginate.

Nickel, cobalt, zinc, cadmium, manganese, chromium, uranium, silver, platinum, tin, arsenic, and antimony all form soluble ammonio-alginates some of which are beautiful salts. Sodium alginate, mixed with a dichromate, is sensitive to light in the same way as gelatin, the mixture becoming insoluble in water after exposure to light.

Alginic acid is a moderately strong acid, liberating carbon dioxide in the cold from the alkaline carbonates and from magnesium carbonate; in the latter case, the two insoluble substances in the presence of water form soluble magnesium alginate. The use of algin requires a thorough knowledge of its properties, on account of the numerous metallic salts which precipitate it, and with which it is therefore incompatible; these reactions limit to a great extent the application of the substance in solution as a substitute for gum and other bodies used for thickening purposes.

Algulose or algic cellulose contains no fibre, but consists of fine cellular tissue, which makes a transparent and very tough paper. It dries to a hard mass resembling ebony, but denser.

The kelp substitute in this wet process was obtained by evaporating and carbonising the acid liquor from which the alginic acid has been precipitated, after neutralising it with caustic soda. It should contain all the iodine and potash salts of the weed but no sulphides, and should yield about 30 lbs. of iodine to the ton. At the same time, in spite of the advantages which apparently would attend the adoption of this process, the manufacturing costs are so high and the demand for the products, other than iodine and potash salts, is so limited, that the process has not met with success on the commercial scale.

Lixiviation of kelp.—Little improvement has taken place in this process; the same simple method which has been in use for many years is still adopted in the Scotch works.

The kelp reaches the factory in large masses; these are first broken up into pieces about the size of road metal. The lixiviation is effected in rectangular iron vats with false bottoms; the vats are coupled together and heated by steam, and treated exhaustively. The whole arrangement is similar in every respect to that adopted in the lixiviation of black ash in the Leblanc process of soda manufacture. The solution is run off at about 40° to 45°Tw. This is evaporated in open hemispherical cast-iron boiling pans, about 9 feet in diameter, and the salts which deposit are fished out. In some works this boiling down is effected in cylindrical wrought-iron closed pans, heated by a coil of steam pipes round the inside of the pan, and provided with mechanical stirrers to keep the deposited salts in suspension. When the liquor is concentrated to 62°Tw., the whole is run out into a settler to allow the salts to deposit, and the supernatant liquor is run off hot into the crystallisers. In both cases the salt fished out or deposited is a crude potassium sulphate, which adheres a good deal to the pan and contains 50 to 60 p.c. of potassium sulphate, mixed with sodium sulphate and chloride. The liquid is run into cylindrical iron coolers, and a crop of potassium chloride crystallises out in two or three days. The mother liquor is again boiled down, and the salt deposited is fished out; this salt is known as 'kelp salt,' and consists of sodium chloride, containing sodium carbonate equal to 8 to 10 p.c. of alkali (Na_2O). The hot liquor is again run into the cooler, and another crop of potassium chloride is obtained. This process is repeated several times, kelp salt being fished out in the boiling pan, and potassium chloride crystallised out in the cooler. These successive crops of 'muriate,' as it is technically called, range in strength from 80 to 95 p.c. of potassium chloride.

The mother liquor is now rich in iodine, and is treated for its extraction. The several salts all contain iodine, and require careful washing to obtain it. These salts are known as 'Kelp salt,' which was formerly used for reducing the strength of soda ash, but is now unsaleable, 'Sulphate,' which is sold at a low price for manurial purposes, and 'Muriate,' which is largely used for the manufacture of saltpetre, potassium carbonate, chlorate, and dichromate, and the prussiates. The residual kelp waste formerly realised about 5*s.* per ton, and was employed in the common bottle glass manufacture; it consists principally of the carbonates of lime and magnesia, and some phosphates. It is all used as a manure in France, but in this country the farmers have always rejected it.

The following is the analysis of an average sample:

Salts of sodium and potassium .	1·50
Carbon	3·09
Calcium sulphate . . .	3·06
,, sulphide . . .	1·70
,, carbonate . . .	20·50
*Calcium and magnesium phosphates	6·72
Magnesium carbonate . .	6·89
Magnesia	2·22
Silicic acid and sand . . .	20·82
Water	33·50
Total	100·00
*Containing phosphoric acid . .	2·70

The mother liquor, containing the iodides and bromides, also contains considerable quantities of sulphides, sulphites, and thiosulphates of sodium and potassium; it is mixed with about one-seventh of its volume of sulphuric acid, free from arsenic, about 145°Tw. (sp.gr. 1·725), and allowed to settle for 24 hours. This is effected in a closed lead-lined wooden vessel, provided with means to collect any sulphuretted hydrogen which may be given off. The sulphur compounds are decomposed, and a considerable deposit of sulphur takes place. This is known as 'Sulphur waste'; when dry it contains about 70 p.c. of sulphur, and is used in vitriol making. It also obstinately retains iodine, and long steaming is required to extract it. The liquor is strained off from the sulphur and run into the iodine still. This was formerly made of lead, but it now assumes the form of a deep hemispherical iron pot, heated by an open fire, and covered with a strong leaden lid, to which are luted two earthenware arms; these are connected with two series of stoneware udells, about ten in each set. These udells have stone stoppers beneath to allow any water containing chlorine, bromine, and iodine to drain off. The apparatus is shown in Fig. 1. Manganese dioxide is added at intervals to the contents of the still, and the iodine is carried over with the steam. The reaction is as follows:

$$2NaI+3H_2SO_4+MnO_2 \\ =I_2+2NaHSO_4+MnSO_4+2H_2O.$$

Repeated distillations go on, without changing the udells, until these are full of iodine, the bulk of which, and the best, is found in the udells forming the centre of the series. The deposition of the iodine in successive layers squeezes much of the moisture out, and it is obtained in a firm, well crystallised form. The iodine on removal from the udells still contains moisture, and requires further treatment before the state of purity now demanded by consumers is attained. This old-fashioned process is the only one adopted in this country; many others have been proposed and tried, but have not been commercially successful. Commercial iodine is always sent out in 1 cwt. kegs; the consumption is usually reckoned in kegs, which means 1 cwt. It improves by keeping, becoming perfectly dry; and as it can be stored in a small compass, and often represents considerable value, it has been a favourite commodity for small speculative buyers. Bromine does not pay for the collection, but if it were required the arms would be changed and a simple worm-condensing arrangement of lead or earthenware, or a series of stoneware Woulff bottles attached: a further quantity of manganese dioxide would be added to the still, and the bromine distilled over. The liquor remaining in the still, and known as 'waste still liquor,' is a dense acid liquid of sp.gr. 1·235 to 1·500, containing sulphates of iron, manganese, potassium, and sodium; it is very troublesome to deal with and is run away as useless.

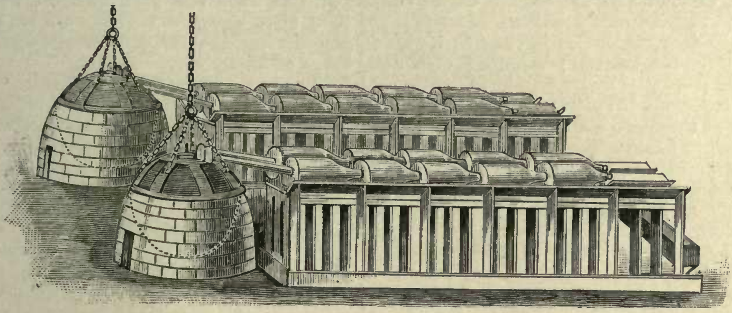


Fig. 1.

The following is the analysis of an ordinary average sample. One gallon contained 3·327 lbs. of dry salts:—

—	Liquor per cent.	Dry salts per cent.
Potassium sulphate .	5·13	15·42
Sodium sulphate .	9·10	27·36
Sodium chloride .	6·80	20·43
Manganous sulphate .	3·75	11·27
Ferric sulphate . .	3·00	9·02
Calcium sulphate .	0·19	0·57
Magnesium sulphate .	0·04	0·12
Sulphuric acid, free .	5·26	15·81
	33·27	100·00

The iodine used for medicine is resublimed in small earthen or porcelain covered pans, and is then known as 'resublimed iodine'; it is obtained in large brilliant plates, and is anhydrous. The pans employed must be shallow, as the vapour is very dense.

When iodine is badly made it may contain white needles, which consist of iodine cyanide; it is now a rare impurity, but a very poisonous one.

In France a different method is adopted. After the precipitation of the sulphur in the mother liquor by addition of hydrochloric acid in slight excess, and boiling for some time, the clear liquor is drawn off and diluted with water to 40°Tw. Chlorine is then passed into the solution, until saturated, and the iodine is precipitated in a pulverulent form. Sometimes, instead of passing in chlorine, the calculated quantity of potassium chlorate is added to the solution; by interaction with the hydrochloric acid this salt yields the chlorine necessary for the liberation of the iodine. Great care must be taken that too much chlorine is not added, as iodine chloride may be formed, and go off as vapour. The clear liquor is then drawn off, and the iodine repeatedly washed by decantation to remove the salts. It is drained in earthen vessels with perforated bottoms, and finally dried on porous tiles. It is then resublimed. This is effected in ordinary earthenware retorts with short necks, and heated in a sand-bath in which they are completely immersed, the iodine being sublimed into earthen receivers. To recover the bromine from the liquor after extraction of the iodine, it is evaporated to dryness, and the residue is distilled in a leaden retort with sulphuric acid and manganese dioxide; it is collected in a receiver under strong sulphuric acid. The production of iodine in France has fallen off considerably; it is all used locally, either resublimed or made into potassium or other iodide, for which purpose the precipitated damp iodine suffices.

In Norway there are now nine or ten works engaged in the extraction of iodine from kelp. In Japan the chief kelp-producing districts are the province of Shima and the island of Hokkaido, but nearly all fishery districts yield a little. The industry is more or less scattered along the coast of Japan and is in the hands of many small producers, from whom the firms of iodine makers procure their supplies.

Iodine from caliche. This mineral, the crude sodium nitrate of Peru and Chile, now forms by far the most important source of iodine. It contains iodine in the form of sodium iodate, which accumulates in the mother liquors from which the sodium nitrate has been crystallised. The proportion of iodine in the caliche varies considerably in the different deposits; in some it is absent altogether, in others it runs as high as 0·17 p.c. or 3·8 lbs. per ton; usually it does not exceed 0·02 p.c.

There are about 157 nitrate factories in Chile, but many of these are old and well worked out, and some are so badly situated as regards position and the raw material is of such a low grade, that they cannot work at a profit, and consequently are closed. At present about 101 factories are in operation, and their production of nitrate amounts to from 2,400,000 to 2,500,000 tons annually. Most of the factories are provided with plant for the extraction of iodine from the mother liquor, but, as their power of production of iodine is largely in excess of the world's power of consumption, the manufacturers have combined to restrict the output. The basis of the power of production of these factories is put down at 115,000 Spanish quintals (about 5,100 tons) per annum, whilst the total quantity consumed is only a fraction of this amount. A certain percentage of the iodine sold in Chile year by year is allotted to each factory, and consequently there are rarely more than a few months in each year during which iodine is made, and there is always a very large stock in hand. The exports are naturally kept as nearly as possible equal to the requirements, but if any large increase in consumption took place there is no doubt that Chile could supply four or five times the quantity at present exported annually. The cost of recovering iodine as a by-product of the sodium nitrate industry is, in many cases, not more than from 1½*d.* to 2*d.* per oz.

It first came over in quantity in 1874, about 497 kegs. In the following year, 900 kegs were exported, and since then the export has continually increased. It was at first a very crude article, containing little over 50 p.c. of iodine, and a good deal was exported in the form of copper iodide. It is now, however, sent over in a pure state.

The following is the analysis of one of the samples of iodine sent from Peru in 1874:

Iodine	52·53
Sodium iodate	1·26
,, nitrate	11·62
Potassium nitrate	2·49
,, sulphate	1·78
Iodine chloride	3·34
Magnesium chloride	0·36
Insoluble matter	1·52
Water	25·20
	100·10

In 1877 the total production of iodine in Scotland was estimated at 1200 kegs; in France at 800 kegs. The present output does not reach these figures.

Japan began to export iodine in 1902, when 35 cwt. were sold. In 1904 the quantity exported was 612 cwt., in 1906 (consequent upon a fall in the price of iodine) only 196 cwt., and in 1907, 305 cwt.

In 1882, the export of iodine from Chile was 4116 cwt., in 1901 it had risen to 5280 cwt., and last year it amounted to 7900 cwt., of a value of about 350,000*l.* This is about four times the present total production of the rest of the world.

The quantity of iodine sold throughout the world in 1887 was 6375 cwt., of which about 1000 cwt. were used in colour making. The present average annual consumption may be taken at nearly 10,000 cwt.

The final mother liquor, or 'aqua vieja,' from which the sodium nitrate has been crystallised, contains sodium iodate, nitrate, chloride, and sulphate, and magnesium sulphate. A good liquor contains about 0·3 p.c. of iodine.

It is run into wooden vats and the iodine is precipitated; the agent employed is sodium bisulphite in solution. The exact amount of iodine in the mother liquor is estimated, and a definite quantity of the solution is added to completely precipitate the iodine. As the bisulphite solution is run into the 'aqua vieja,' the liquid is stirred either by wooden paddle-wheels or by air forced up from perforated pipes at the bottom of the tanks. The latter method is quicker and more efficient, but the air carries away some of the iodine from the solution. The solution is then neutralised by addition of 'sal natron' liquor and again well stirred. After some time, most of the iodine settles to the bottom of the tank; any little that remains floating is removed by a calico bag at the end of a stick. The supernatant liquid is drawn off and used over again with the nitrate liquors.

The iodine is washed with water, and pressed into thick cakes. It then contains 80 to 85 p.c. of iodine and 6 to 10 p.c. of mineral matter, and requires to be purified by resublimation. This is effected in a cast-iron retort, to which eight earthenware condensers or udells are attached in series. The retort is heated by a slow fire, and when the operation is completed the retort is allowed to cool, and the iodine removed from the udells. It is thus obtained pure. The complete plant is shown in the descriptive plans Figs. 2 and 3.

The sodium bisulphite is prepared by passing the fumes of burning native sulphur into a solution of 'sal natron' or sodium carbonate. The sulphur, which is one of the many minerals found in this interesting region, is burned on an iron plate in a plain iron oven, and the fumes drawn by a steam injector into perforated pipes in the solution of sal natron. The manufacture of this substance is also peculiar to the district. It is obtained by burning together 85 parts of crude sodium nitrate, obtained from the 'aqua vieja' tanks, and 15 parts of coal. The mixture is made in the form of a cone 5 feet high, with a space of 2 feet dug out round the base. It is saturated with water and ignited; the sodium carbonate thus formed fuses and runs out into the pit. It is dissolved in water, and the solution is pure enough for use in this process, the impurities consisting of sodium sulphate and chloride, the unburnt coal being left in the residue undissolved.

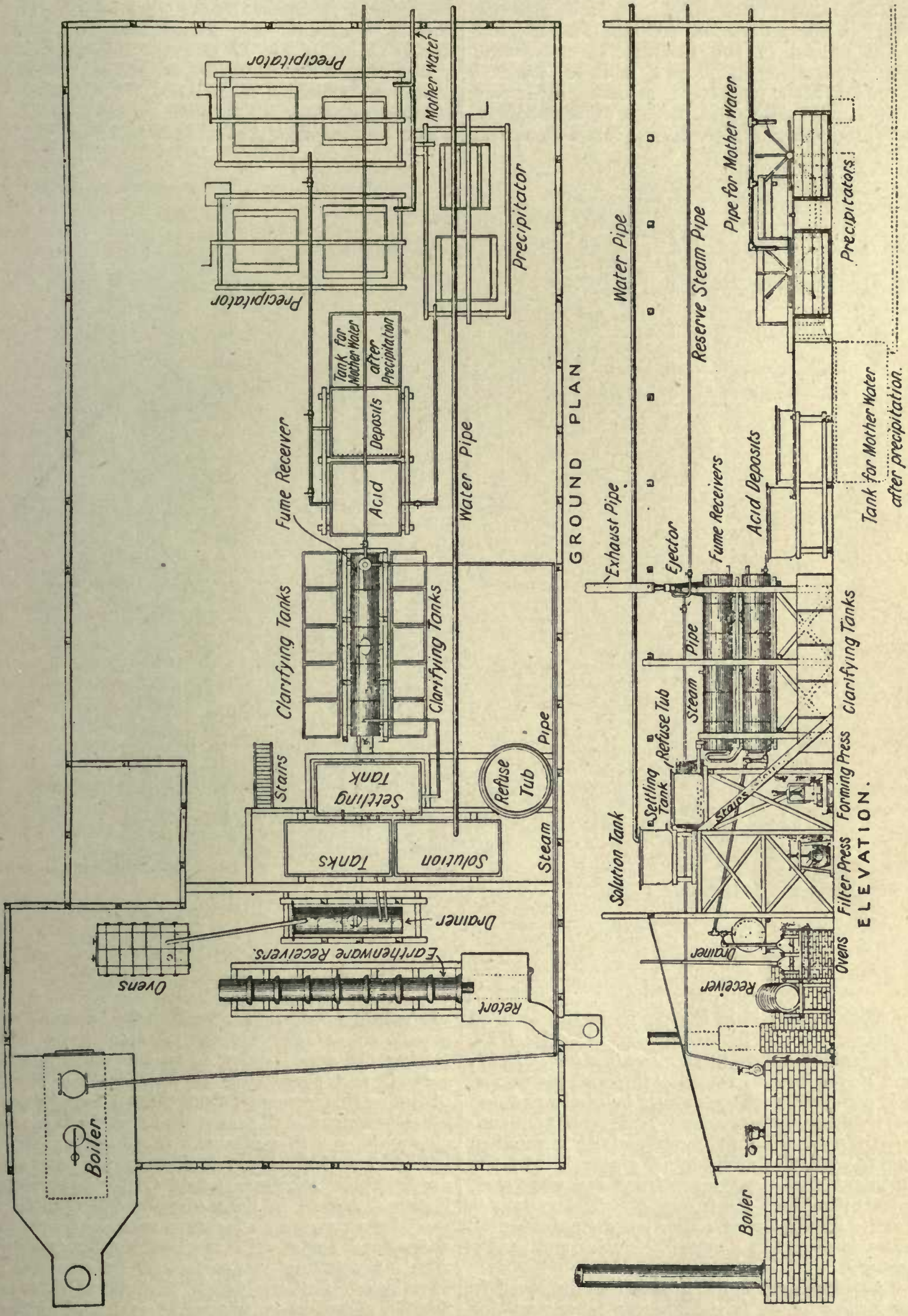
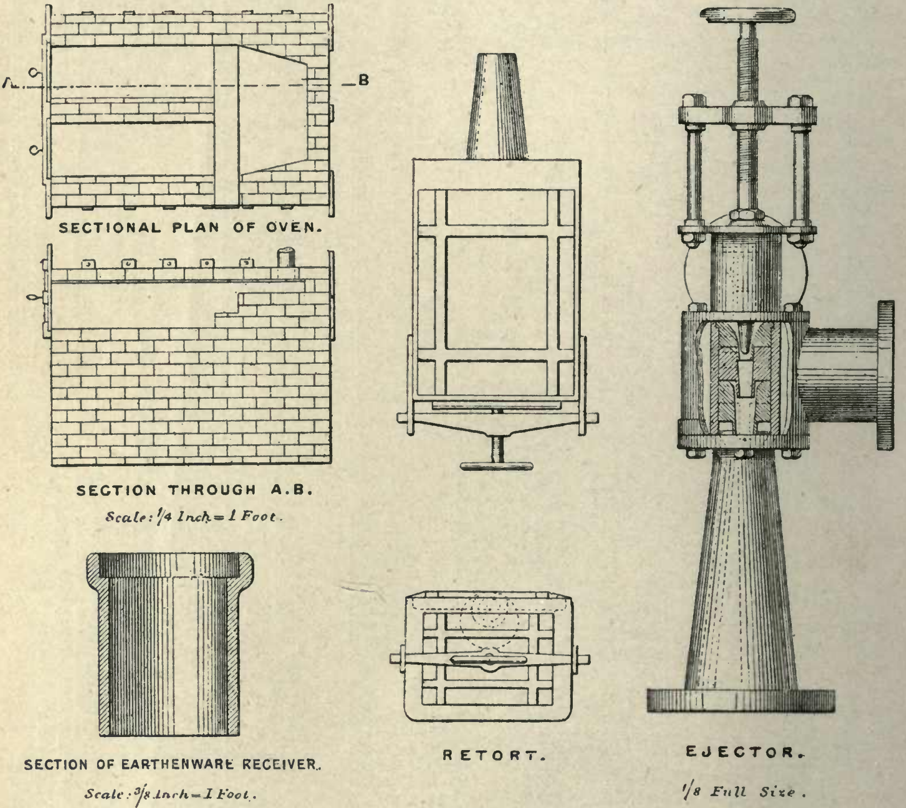


Fig. 2.

Uses of iodine.—About one-fifth of the total consumption of iodine is employed in the manufacture of aniline colours; a good deal of this is recovered and used again. It is principally used in the manufacture of Hofmann violet, and aniline green in the form of methyl iodide; also for making erythrosin and the blue shade eosins, in which iodine is made to react upon fluorescein. Some substitution products are occasionally made, such as the ethylated chrysaniline. A small quantity is used in photography, but the bulk of the iodine of commerce is employed in medicine. Iodine, iodoform, and the iodides of arsenic, iron, lead, mercury (red iodide), potassium, sodium, and sulphur are all official in the British Pharmacopœia; the preparations employed will be referred to under their respective names. Hydriodic acid, ethyl iodide, and iodides of ammonium, cadmium, mercury (green iodide), and starch are also used in medicine, and each will therefore be noticed. Iodine, if pure, should sublime without residue, and the portion subliming first should not include any slender colourless prisms emitting a pungent odour (cyanide). The British Pharmacopœia directs that one gram dissolved in 50 c.c. of water, containing two grams of potassium iodide, should require for complete decolouration at least 78·4 c.c. of the volumetric solution of sodium thiosulphate, which contains 24·8 grams of the salt in 1000 c.c.



SECTIONAL PLAN OF OVEN.

SECTION THROUGH A.B.

Scale: ¼ Inch = 1 Foot.

SECTION OF EARTHENWARE RECEIVER.

Scale: ⅜ Inch = 1 Foot.

RETORT.

EJECTOR.

⅛ Full Size.

FIG. 3.

It is employed in the B. P. in the form of *Tinctura iodi*, 1 in 40, *Liquor iodi*, 1 in 24, *Linimentum iodi*, 1 in 8, *Unguentum iodi*, 1 in 31, and *Vapor iodi*. In the tincture and the liquor, it is dissolved with potassium iodide in rectified spirit and water respectively. The liniment contains the same ingredients dissolved in rectified spirit, with the addition of glycerol. In the ointment the same ingredients are employed, substituting lard for the spirit. The vapour is for the inhalation of iodine; the tincture with water is placed in a suitable inhaler and gently heated.

A volumetric solution of iodine dissolved in potassium iodide is used in the laboratory for titrating solutions of arsenious acid, of sulphurous acid, and sodium thiosulphate. It contains 12·7 grams of iodine in 1000 c.c., and corresponds to 1·7 gram of sulphuretted hydrogen, 3·2 grams of sulphur dioxide, and 4·95 grams of arsenious oxide. Iodine is also used for testing oils, which differ as to the amount absorbed, and some can be distinguished from others by this means (*v.* OILS, FIXED AND FATS).

Other unofficial preparations of iodine are also employed in medicine. *Glycerinum iodi* is iodine dissolved in glycerol, used for external application. *Pigmentum iodi*, Coster's paste, is iodine dissolved in light oil of wood tar, and used for ringworm. *Tinctura iodi decolorata* is a tincture made with rectified spirit, and in which the iodine is decolorised by ammonia. It is used for chilblains. *Collodium iodi* is flexible collodion containing 30 grains of iodine to the ounce, and is very useful for painting on wounds. Carbolised iodine solution is a colourless mixture of tincture of iodine, phenol, and glycerol in hot water; it is used as a gargle or pigment in diphtheria, and internally for Asiatic cholera.

Medicinal properties of iodine.—Iodine was first employed in medicine in the form of burnt sponge, a remedy long used in treating goître. When administered internally it is usually in combination with an alkali; taken alone it is an irritant poison. It is a most powerful alterative, impoverishing the blood and stimulating the absorbents. It is antisyphilitic and antiscrofulic. In syphilis, scrofula, and chronic rheumatism it is largely used, and especially in swellings of the joints and enlarged glands, which are also treated by painting externally with tincture of iodine, in which it acts as a counter-irritant. It has a remarkable power in expelling both mercury and lead from the system. The vapour mixed with steam from hot water is useful in inhalation for many affections of the air passages. Long-continued use may give rise to the depressing nervous train of symptoms known as iodism, and for which belladonna is employed as an antidote. Copious drinks of solution of starch form the antidote in cases of poisoning. Used alone, iodine is a powerful disinfectant and decoloriser, acting in the same way as chlorine. It may be allowed to evaporate spontaneously, but is very apt to colour the sheets, blinds, or anything dressed with starch; it is also used in candles, the burning of which volatilises it.

Hydrogen iodide HI is a colourless gas, very soluble in water and resembling hydrogen chloride; it forms dense white fumes in the air; its sp.gr. is 4·3737. It liquefies under pressure, and solidifies at −55°. It is composed of equal volumes of iodine and hydrogen, and contains 99·2 p.c. of its weight of iodine. The aqueous solution is colourless, but on exposure to air it becomes coloured by the deposition of iodine from oxidation. It is decomposed by sulphuric and nitric acids, and by chlorine and bromine, which set the iodine free.

The following table shows the relative percentage of hydriodic acid at different specific gravities:—

Sp.gr. at 15°	Per cent. of acid
1·708	51·9
1·551	47·2
1·442	39·2
1·297	30·3
1·175	18·5
1·083	5·9

It is usually prepared in solution by passing sulphuretted hydrogen into water in the presence of iodine: $H_2S+I_2=2HI+S$. At first the action is slow on account of the deposition of sulphur covering up the iodine and preventing its solution; the hydriodic acid when formed, however, dissolves an increasing proportion of iodine, and by the gradual addition of iodine and water as the action progresses, large quantities of hydriodic acid may thus be obtained up to a sp.gr. of 1·56.

A modification of this process for very pure acid has been proposed by Winkler. The iodine is dissolved in carbon disulphide, and the solution covered with a stratum of water; when the sulphuretted hydrogen passed into the mixture, the hydriodic acid dissolves in the water, and the sulphur in the carbon disulphide. The aqueous solution only requires boiling for a few minutes to expel the sulphuretted hydrogen, and to obtain the hydriodic acid quite pure. Hydriodic acid is employed in the manufacture of some of the iodides, and is used in medicine in the form of syrup.

Another method was suggested by Kolbe. One part of amorphous phosphorus is added to 15 parts of water in a tubulated retort filled with carbon dioxide, and 20 parts of iodine gradually added. The resulting liquid is allowed to stand and then heated for a short time, cooled, mixed with 4 parts of water and distilled. It yields a colourless acid free from uncombined iodine: $P+5I+4H_2O=5HI+H_3PO_4$.

Iodic acid HIO_3. This acid is usually prepared by boiling iodine in strong nitric acid, free from nitrous acid. Iodic acid is deposited in crystals. When heated it gives off water, and iodine pentoxide I_2O_5 is obtained in small white crystals. It is very soluble in water, and easily decomposed by reducing agents forming hydriodic acid and free iodine.

The iodates have the general formula MIO_3.

Potassium iodate KIO_3 forms small white cubic crystals. Sodium iodate $NaIO_3$ crystallises in small eight-sided prisms. Both salts are poisonous. Both are obtained in considerable quantity in the manufacture of the respective iodides by No. 2 process as described below. The iodates can easily be separated by taking out the first salts deposited on evaporation, as these are less soluble than the iodides. If iodic acid were required on the large scale, it could be easily made as a by-product of the iodide manufacture by crystallising out the iodate before fusion, and precipitating it with barium chloride as barium iodate. This is then decomposed by sulphuric acid. It has, however, no commercial application.

Iodine trichloride ICl_3 is obtained in orange-yellow crystals by passing chlorine into a flask containing iodine vapour sublimed from a small retort. It is a very active disinfectant and germicide in solution of 1 to 1000. It has been used in medicine internally. In contact with organic matter, chlorine and iodine are liberated in a nascent state.

Iodine cyanide, or *Iodide of cyanogen*, CNI. This very poisonous substance is interesting as forming an occasional impurity in commercial iodine; it is very seldom met with now, and ought never to be present if the manufacture is properly carried out. Its occurrence is probably due to an insufficient addition of oil of vitriol to the saturating vat or to the iodine still. It is usually prepared in the laboratory by the distillation of iodine with mercuric cyanide. When present in iodine it presents the appearance of exceedingly fine silky needles, colourless, and very volatile, even at ordinary temperatures, and with a penetrating pungent odour which excites tears. It sublimes without change. It is sparingly soluble in water, easily so in alcohol, and in ether, and also in fixed and volatile oils. The aqueous solution does not give the starch reaction of iodine, nor does it precipitate silver nitrate.

Sulphur iodide S_2I_2 is a dark crystalline substance, obtained by gently heating in a glass flask 1 part of sulphur with 4 parts of iodine until the mixture liquefies; the flask is then broken, and the crystalline mass removed. It is insoluble in water, but soluble in glycerol. It has the odour and staining properties of iodine. It is used in medicine externally in skin diseases applied in an ointment. The official preparation is *Unguentum sulphuris iodidi*, containing 30 grains to 1 ounce.

Arsenious iodide, or *Iodide of arsenic*, AsI_3. This salt forms small orange-coloured crystals, soluble in water and in alcohol; it has a neutral reaction, and gives a yellow precipitate with sulphuretted hydrogen. Heated in a test-tube it almost entirely volatilises, violet vapours of iodine being set free.

It is prepared by direct combination of metallic arsenic and iodine, or by evaporating together to dryness solutions of arsenious and hydriodic acids. The dose is $\frac{1}{30}$ of a grain; and the Pharmacopœia preparation is *Liquor arsenii et hydrargyri iodidi*, about 1 grain in 100.

Nitrogen iodide $N_2H_3I_3$ or $NH_3{\cdot}NI_3$ is a dark brown powder, obtained by adding iodine to excess of solution of ammonia. It is a most violent explosive, but its action is uncontrollable, and it is impossible to keep it in safety. It has therefore found no commercial application, but has been proposed as a chemical photometer on account of the ease with which it is decomposed by light in presence of excess of ammonia (*v.* Guyard, Ann. Chim. Phys. [vi.] 1, 368).

Ammonium iodide NH_4I. This is a white crystalline salt, very deliquescent and becoming yellow on exposure to air. It is prepared by saturating hydriodic acid with ammonia, or by decomposing iodide of iron with ammonium carbonate and filtering off the iron precipitate. The solution in either case is evaporated and set aside to crystallise. It is used in photography, and also in medicine instead of potassium iodide, especially in rheumatism, as causing less depression than the potassium salt. It must be kept from the access of light and air, as iodine is freely given off. It is soluble in alcohol.

Potassium iodide, or '*Hydriodate of potash*,' KI. This is the most important of the iodides, and forms a considerable article of manufacture, as the greater portion of the iodine of commerce goes into consumption in this form. It is a white, colourless, and odourless salt crystallising in large cubes, and permanent in the air. It contains no water of crystallisation, and is very soluble in water, dissolving in two-thirds of its weight. It is also soluble in alcohol. There are three methods employed in the manufacture.

1st. Hydriodic acid is saturated with potassium carbonate, and the solution evaporated and crystallised. This is the most direct method, and there is no loss; it gives a pure product, but it is expensive and tedious.

2nd. Iodine is dissolved in solution of caustic potash. This produces a mixture of potassium iodide and potassium iodate; the reaction is $3I_2+6KOH=5KI+KIO_3+3H_2O$. The solution is evaporated to dryness, a little charcoal is added, and the product fused in an iron pot at a red heat until all the iodate is decomposed, and potassium iodide alone remains. The mass is dissolved in water, the solution filtered and crystallised.

3rd. Iodide of iron is first prepared by the addition of iron borings and iodine to water; the latter must be added gradually to keep down the temperature; the solution is filtered, mixed with potassium carbonate and the iron precipitate washed and filter-pressed. The solution is then evaporated to dryness and the residue redissolved and crystallised.

This process is that most commonly adopted by manufacturers. The crystallisation is performed in enamelled iron pans, surrounded by a steam jacket in brickwork, and very gradually cooled. The best crystals are obtained on fluted glass rods suspended in the liquid.

The second process is that directed by the British Pharmacopœia.

Potassium iodide or '*Hydriodate*,' as it is often called, is used in photography, but medicine is the principal outlet, and requires a large consumption. It is a powerful alterative, diuretic, and absorbent; and is much administered internally, especially in rheumatism and syphilis; the dose is 5 to 10 grains, but doses of 100 grains have been given in some cases. Its properties are similar to those of iodine. As iodine is freely soluble in potassium iodide solution, it presents an excellent form for its internal administration.

It must contain no iodate; this is easily detected by the addition of tartaric acid and starch solution, which sets free hydriodic acid, and if there be any trace of iodate present, free iodine is liberated, as shown by the blue colour of the iodide of starch. Potassium iodide should not contain water, and therefore should not lose weight when heated; it should contain no sulphate, and therefore give no precipitate with barium chloride insoluble in nitric acid. A feeble alkaline reaction from the presence of a slight trace of carbonate, indicated by cloudiness with lime or baryta water, soluble in nitric acid, is allowed by the London Pharmacopœia (but not by the German) as tending to retain the colour of the iodide when long kept. Chlorides of potassium or sodium are a common impurity; the presence of a chloride is shown by precipitating with silver nitrate, and agitating the precipitate with ammonia. The ammonia solution should give no precipitate with nitric acid. One gram requires for complete precipitation 60·2 c.c. of a volumetric solution of silver nitrate containing 17 grams of the salt in 1000 c.c. It is almost impossible to obtain this salt, when made on the large scale, quite free from chloride (the B. P. allows a 'very little') as potassium carbonate cannot be prepared in quantity without it; a good iodide contains:

Potassium iodide . . .	99·4
" chloride . . .	0·2
Water	0·4
	100·0

This salt is officinal in the following preparations; the number of grains in one fluid ounce is given in each case. *Linimentum iodi* 22 grains; *Linimentum potassii iodidi cum Sapone* 54½ grains; *Liquor iodi* 33 grains; *Tinctura iodii* 11 grains; *Unguentum iodi* 16 grains; *Unguentum potassii iodi* 54 grains.

Potassium iodide is sometimes administered in large doses, and it is important medicinally that it should contain no iodate, as this salt is poisonous: it must not be prescribed in mixtures containing potassium chlorate, for this salt decomposes it, forming iodate.

Sodium iodide NaI. This salt is obtained as a deliquescent white crystalline powder, soluble in two-thirds of its weight of water. It may be prepared by the same methods as the corresponding potassium salt; that from ferrous iodide is usually employed, and the solution is simply evaporated to dryness. It crystallises in anhydrous cubes and also in hexagonal plates, having the formula $NaI,2H_2O$. It is used in medicine for the same purposes as potassium iodide, but the principal application is as a precipitant of silver and gold from the weak copper ores of the Tharsis and other copper-extracting companies. The same tests as with the potassium salt may be used for its purity; 1 gram requires 66 c.c. of the volumetric solution of silver nitrate for complete precipitation.

Ferrous iodide, or *Iodide of iron*, FeI_2. This is a crystalline green deliquescent mass. It is only employed in medicine, and more particularly in the form of syrup of iodide of iron, in which it can be better preserved. The official preparations are *Pilula ferri iodidi*, and *Syrupus ferri iodidi*, containing 34·4 grains of the salt in one fluid ounce. It is a tonic alterative useful in anæmia of scrofulous patients, especially children.

A similar syrup of manganese iodide is also sometimes used in medicine.

Zinc iodide ZnI_2. An easily fusible compound which sublimes in needles. It is prepared in the same way as the iron salt, and obtained by evaporation as a white crystalline deliquescent salt. It is sometimes used in photography.

Lead iodide, or *Plumbic iodide*, PbI_2. This is a brilliant yellow powder, made by precipitating a solution of lead nitrate with potassium iodide, and washing and drying the precipitate. By boiling the powder in water, and allowing the solution to cool, it is obtained in bright yellow crystalline scales. It is employed in medicine externally in the form of ointment and plaster. The official preparations are *Emplastrum plumbi iodidi*, 1 part in 9; and *Unguentum plumbi iodidi*, 1 part in 8.

Mercurous iodide HgI, or *Green iodide of mercury*, is a green insoluble powder, which darkens on exposure to light. It is prepared by rubbing together in a porcelain mortar the equivalent proportions of mercury and iodine, and moistening the mixture with alcohol until the metallic globules cease to appear and a green powder is obtained. This must be dried in the air in a dark room, and preserved in a bottle put away from the light. It can be obtained in yellow crystals by sublimation. It is insoluble in water and alcohol. It is employed in medicine in doses of 1 to 3 grains. It is an irritant poison and is used in syphilis.

Mercuric iodide, or *Red iodide of mercury*, HgI_2. This is a brilliant scarlet powder, known as Chinese vermilion. It may be prepared in the same manner as the green iodide, using double the equivalent of iodine; but a better product is obtained by precipitation. A solution of mercuric chloride, or corrosive sublimate, is precipitated with potassium iodide, both salts being dissolved in boiling water; the precipitate is washed and dried over the water-bath. By sublimation it may be obtained in large and beautiful crystals, which when hot are yellow, but reassume their scarlet colour on cooling. It is insoluble in water, but very soluble in solution of potassium iodide. This solution contains a double iodide of mercury and potassium and is used in analysis as a precipitant for alkaloids. It forms a pigment more brilliant than vermilion, but it is not much used for this purpose, as it is easily altered by exposure. It is employed in medicine, especially in syphilis, in doses of a thirty-second to an eighth of a grain, and also externally as an ointment. The official preparations are *Liquor arsenii et hydrargyri iodidi*, containing 1 grain in 100 grain measures, and *Unguentum hydrargyri iodidi rubri*, containing 1 part in 28. It has been recently introduced as a germicide for washing wounds, instead of corrosive sublimate, which is not so effective and is more poisonous. It has also been used as an antifermentive in tanning.

Bismuth iodide BI_3 is a red powder obtained by precipitation from bismuth nitrate by potassium iodide. It has been introduced into medicine as a substitute for iodoform in treating wounds. It has no odour. This iodide is soluble in potassium iodide, forming a double iodide employed in analysis as a precipitant for alkaloids.

Silver iodide AgI. This salt occurs native, in hexagonal crystals, as *iodargyrite* or *iodyrite*. It is obtained by precipitation from a solution of silver nitrate and any soluble iodide. This salt is not employed commercially in this form. It is the active salt of iodine which is used in photography, but it is always produced on the plate or the paper. It is the form in which iodine is often precipitated and weighed. It is almost insoluble in ammonia, but soluble in potassium iodide and cyanide, and in sodium thiosulphate.

Palladium iodide PdI_2. This is a dark-brown powder, interesting as the most insoluble salt of hydriodic acid, and as a form in which it is estimated in analysis.

Cuprous iodide, or *Iodide of copper*, Cu_2I_2. When solutions of potassium iodide and cupric sulphate are mixed, only half the iodine is precipitated as cuprous iodide, the other half being set free, according to the following equation: $2CuSO_4 + 4KI = Cu_2I_2 + I_2 + 2K_2SO_4$. It is necessary, therefore, to add a reducing agent as sulphurous acid or sodium hyposulphite, but ferrous sulphate is usually employed; the whole of the iodine is then thrown down as cuprous iodide

$$2CuSO_4+2FeSO_4+2KI = Cu_2I_2+K_2SO_4+Fe_2(SO_4)_3.$$

The former reaction was proposed by Soubeiran as a method of obtaining iodine from kelp liquors, but it has not been much used.

Cuprous iodide is a white crystalline solid, insoluble in water; on exposure to a red heat it fuses to a brown mass. The iodine can be separated from it by heating it with manganese dioxide or strong sulphuric acid. Or it may be decomposed by boiling with water and zinc, which yields zinc iodide and metallic copper. Or it may be treated with potassium or sodium hydroxides or carbonates, which decompose it, forming cuprous oxide and potassium or sodium iodide. With ammonia it combines, forming ammonio-cuprous iodide $CuI,2NH_3$; a white crystalline powder.

Iodide of starch, or *Iodised starch*, is a dark blue powder obtained by triturating iodine with a little water and adding gradually starch in powder until it assumes a deep and uniform colour, and drying at a low temperature. It is decolorised at 100°. It is used in medicine as a mild form of administering iodine internally, in doses of half a drachm to four drachms. In the form of a paste it is employed to cleanse and heal foul sores and ulcers.

Estimation of iodine.—The violet vapour of free iodine is characteristic, and there are also four very sensitive tests for iodine and iodides: for the former the blue colour test with starch, and the crimson solution in chloroform, benzene, or carbon disulphide; for the latter the precipitation as silver or palladium iodide. All these can be employed in estimating iodine, the colour tests by comparison with standard solutions, and the gravimetric tests by weighing the iodine as silver iodide or palladium iodide. Insoluble iodides must be converted into alkaline iodides before precipitation by silver nitrate or palladium chloride. This may be effected by fusing with sodium carbonate, or preferably by a mixture of this and potassium carbonate. Another method for a metallic iodide is to suspend it in water and pass sulphuretted hydrogen through the mixture; the metal is precipitated as a sulphide, and hydriodic acid formed. Silver iodide is generally heated with zinc and dilute sulphuric acid, the silver is reduced to the metallic state, and zinc iodide remains in solution.

If the iodine exists in the form of a soluble iodate it must be reduced to an iodide by sulphurous acid. With organic iodides it is usual to ignite with pure sodium hydroxide.

In the colour tests, the iodine must be set free by bromine, chlorine, or, preferably, nitro-sulphuric acid. The starch method, owing to the easy decomposition of the iodide of starch, is not generally available, but the separation of the iodine from solution by a solvent forms a process of great accuracy, of easy and rapid execution, and of general application. In estimating the iodine in kelp or seaweed ash, or kelp substitute, the following process is adopted. Kelp is not an easy cargo to sample. There is often great difference in the value of the large masses forming the cargo. Stones and sand are a frequent cause of annoyance; stones are often found fused into the centre of a block of kelp, and forming most of the block. These can only be detected by breaking up all the large pieces. With seaweed ash, or charcoal, or kelp substitute there is no difficulty. Where there is much sand the kelp is more friable. The sand is generally composed of shells, and is mostly carbonate of lime; but it is sometimes quartz, flint, or other form of silica. To insure an accurate sample, about 100 lbs. are carefully picked from a cargo of, say, 100 tons, and ground up. A portion of this is finely powdered and kept as a sample for reference. Of this, 5 grams are taken to estimate the moisture, another 5 grams are taken to estimate the soluble matter, the carbon, and the ash, also the potash and the iodine in the soluble matter. The kelp is treated with about 75 c.c. of hot water, which dissolves little or none of the oxysulphides. This operation is repeated and the residue washed, and the solution made up to 250 c.c. In a portion of this the potash is estimated by platinum tetrachloride. For estimating the iodine, one-tenth part or 25 c.c., equal to 0·5 gram of kelp, is taken. This will not contain more than 5 milligrams of iodine, generally about 2 milligrams, often only 0·5 milligram. If the amount exceeds 5 milligrams, it is advisable to dilute the solution with an equal bulk of water. Five c.c. of carbon disulphide are then added and a few drops (one to three) of nitro-sulphuric acid dropped in. This reagent is prepared by treating starch with nitric acid, and passing the nitrous fumes into sulphuric acid of 1·843 sp.gr. to saturation. The mixture keeps perfectly well. The testings are performed in large even test tubes, and compared with graduated standard solutions of potassium iodide treated in precisely the same manner. By this method $\frac{1}{250000}$th part of iodine is easily detected and measured, and up to $\frac{1}{100000}$th part the estimation is very accurate. It has several advantages over the use of starch, as besides the introduction of an organic substance liable to change, the blue colour of the iodide of starch is distributed over the whole liquid, and when dilute can only be seen by looking down the length of the tube. Moreover, the solution is not transparent, and the indications are not sharp enough for accurate quantitative work, though useful often in testing. The carbon disulphide method is quite as sensitive, and the iodine is removed from the solution and concentrated in a sixth of the volume at the bottom of the tube. The maximum effect, which takes time with the starch, is immediate in this case. The carbon disulphide solution of iodine can be removed, and the iodine recovered from it by an alkali for further experiment if desired, but it is quite unnecessary for accurate results. It is usual to remove it from the disulphide by zinc in the presence of water, so that the reagent can be used over and over again. Many years of experience of this and other processes have shown that this is the only one to be relied on where many such estimations have to be performed daily, especially in kelp and its products, which contain such a small proportion of iodine. If the iodine is to be determined in a seaweed or other organic material, the sample must always be carbonised in a small iron retort or close crucible, and not burnt to ash in an open crucible. The salts are washed out from the charcoal, and the carbon and ash estimated by burning the residue. If this be not done, it is almost impossible to completely burn away the carbon in the presence of so much alkaline salts which at a high temperature fuse and cover it over. If, moreover, a long time is taken, as it must be, over an ordinary Bunsen burner, a large portion of the potash and all the iodine may be easily burnt off. If the salts contain magnesium, as all those from seaweeds do, it is necessary to make sure that there is an excess of alkali present, or the iodine will be rapidly burnt off. In kelp and seaweed there always is sufficient alkali, and this precaution is unnecessary, but where the object is to estimate iodine in organic substances containing it in minute traces, more caustic soda should always be added before carbonising. As all seaweeds also contain soluble sulphates which become reduced to sulphides and oxysulphides when burnt to ash, carbonisation presents another advantage, as it prevents this change.

Palladium chloride is the only reagent which can be relied on for the direct gravimetric estimation of iodine in mixed liquors containing chlorides and bromides. The kelp liquor must be mixed with hydrochloric acid and set aside in a warm place till the sulphur compounds are decomposed, it is then filtered off and precipitated with palladium chloride, and allowed to stand for some time. The black precipitate of palladium iodide may be washed with hot water, and lastly with a little alcohol, dried at a gentle heat, and weighed on a tared filter; 100 parts contain 70·45 parts of iodine. Or it may be ignited in a platinum crucible, and the iodine calculated from the weight of the palladium left; 100 parts of palladium are equal to 238·5 parts of iodine. If chlorine is also to be estimated in the same liquid, palladium nitrate must be substituted for the chloride. If bromine is also present the chloride must be used, or a soluble chloride must be added, or the bromine will be precipitated with the palladium iodide. This method gives discordant results with kelp, on account of the cyanides often present. Free alkalis, chlorine, and bromine also prevent the precipitation.

In 'caliche' the iodine exists as an iodate, and this must be first reduced to an iodide by sulphurous acid or sodium bisulphite. There are several methods of estimating iodine, bromine, and chlorine, directly and indirectly, when present together. A very simple method of separating these elements directly is to distil over the iodine first by boiling with ferric sulphate; it may be condensed in solution of potassium iodide and titrated with sodium thiosulphate. The bromine is then separated from the residue in the retort, which has been allowed to cool, by gently warming the solution after addition of potassium permanganate, and distilling it into solution of ammonia in excess, in which it is titrated with an acid; or estimated gravimetrically by precipitation as silver bromide. The chlorine can be estimated in the residue or by difference from a determination of the total quantity of chlorine, bromine, and iodine in the original substance by precipitation as silver salts. Another method is to distil over the iodine with a concentrated solution of potassium dichromate; after the iodine is removed the addition of a little sulphuric acid to the retort will set free the bromine, the chlorine can then be determined as in the last process.

Field's method of separating these three halogens is to divide a solution into three equal parts; each portion is precipitated by silver nitrate. No. 1 is washed, dried, and weighed. No. 2 is digested with potassium bromide, then washed, dried, and weighed. No. 3 is digested with potassium iodide, then washed, dried, and weighed. No. 1 contains the silver chloride, bromide, and iodide. No. 2 contains only silver bromide and iodide, the chloride having been by this process converted into bromide. No. 3 contains silver iodide only, the chloride and bromide having been both converted into iodide. The exact quantities of each in the solution can therefore be easily calculated. The valuation of commercial iodine has been alluded to already; the sodium thiosulphate is usually standardised by titrating it with a potassium iodide solution of pure iodine. 100 c.c.=2·48 grams ($\frac{1}{100}$th of $Na_2S_2O_3,5H_2O$) and is equal to 1·27 grams of iodine ($\frac{1}{100}$th of atomic weight in grams). Another method of volumetrically estimating the strength of an iodine solution is to pass sulphuretted hydrogen into it until decolorised; the hydriodic acid formed is then titrated with decinormal soda, using methyl orange as an indicator.

Commercial iodine seldom contains any impurity but moisture; it is almost impossible to estimate the water by drying in the ordinary way. An easy method is to rub it up with five times its weight of pure dry mercury, adding a little alcohol. It is then dried for 12 hours, or until it ceases to lose weight, over sulphuric acid in a desiccator. This process is accurate to about 0·1 p.c., but most suitable for very damp iodine. Another method is to add a weighed quantity (about double the weight of the iodine) of zinc sheet in small pieces in a tared capsule, along with a little water, when the iodine is all converted into zinc iodide; the contents of the capsule are gradually evaporated to dryness and weighed, the weight then includes that of the dry iodine. It is better, however, in all cases to estimate the iodine by titration. The same may be said of the valuation of potassium iodide; but in this case it is often also necessary to estimate a small quantity of chloride which is always present; and silver nitrate is the best reagent for this purpose, as the chloride ought to represent so small a percentage as to be difficult of detection. Bromine as a rule need not be looked for. Should it be present, however, some other process must be employed. It is necessary to take at least 3 grams of the potassium iodide, and add to it not less than 3·1 grams of pure silver nitrate, the precipitate is digested in strong ammonia, then filtered off, washed, dried, and fused with the usual precautions. The solution is concentrated by evaporation, and the silver chloride precipitated by nitric acid. This gives accurate results, even when the potassium chloride is under 0·5 p.c.

For the determination of small proportions of chlorine and bromine in iodine, the following process is recommended by Tatlock and Thomson (J. Soc. Chem. Ind. 1905, 24, 187). 10 grams of the sample are triturated with 100 c.c. of water, and finely granulated zinc, or zinc dust, is added in small portions, with agitation, until all the iodine is converted into zinc iodide. The temperature of the solution must not be allowed to rise sensibly during the process. The solution is now filtered, the residue washed two or three times, and to the filtrate 7 grams of pure sodium nitrite are added. The solution is carefully acidified with dilute sulphuric acid, the precipitated iodine is collected and washed two or three times with cold water, and the filtrate is agitated with benzene in a small separator. The aqueous layer is run into another small separator, mixed with a little more sodium nitrite and dilute sulphuric acid, and again shaken with benzene. To the aqueous solution excess of silver nitrate and some nitric acid are added, the liquid is heated to boiling, and the precipitate is collected on a weighed filter and well washed with hot water. A solution containing 2 grams of silver nitrate, 90 c.c. of water, and 10 c.c. of ammonia of sp.gr. 0·88 is prepared. About 60 c.c. of this solution are poured back and forward through the filter containing the precipitate, and the latter is finally washed with the remaining 40 c.c. The silver bromide on the filter is now washed with warm dilute nitric acid and with hot water, dried, and weighed. The ammoniacal filtrate is acidified with dilute nitric acid, and the precipitate of silver chloride is collected as usual. G. G. H.

IODIPIN, IODIVAL, IODLECITHIN, *v.* SYNTHETIC DRUGS.

IODOCAFFEIN *v.* SYNTHETIC DRUGS.

IODOETHYLFORMIN $C_6H_{12}N_4(C_2H_5I)_2$ is obtained by the action of ethyl iodide on a weak alcoholic solution of hexamethylene-tetramine. Crystallises in long needles, tasteless, soluble in water, sparingly soluble in alcohol, insoluble in ether and chloroform. Decomposed by sodium carbonate and strong acids with liberation of formaldehyde; used internally as a substitute for alkaline iodide.

IODOFORM *Tri-iodomethane* CHI_3. Iodoform was discovered in 1822 by Serullas (Ann. Chim. Phys. [ii.] 20, 165; 22, 172; 25, 311; 29, 225; 39, 230), and Dumas in 1834 (*ibid.* [ii.] 56, 122) determined its exact composition. Serullas obtained it by acting on alcohol with iodine in presence of caustic or carbonated alkalis. The reaction may be stated thus:

$$CH_3{\cdot}CH_2{\cdot}OH+4I_2+6KOH$$
$$=CHI_3+HCOOK+5KI+5H_2O.$$

Numerous other compounds have been suggested as substitutes for alcohol in this reaction, by Serullas, Bouchardat (J. Pharm. Chim. [ii.] 23, 1; [iii.] 3, 18), Lefort (Compt. rend. 23, 229), Millon (*ibid.* 21, 828), and others; but Lieben (Annalen Suppl. 7, 218 and 377) has shown that many of these, such as ether, chloroform, methyl alcohol, formic and acetic acids, phenol and probably the carbohydrates, when properly purified, do not yield iodoform. The reaction, however, takes place with ethyl ethers, which first break up by the action of water into alcohol and acid; with aldehyde, acetone, and generally with the higher normal alcohols of the fatty series and their corresponding aldehydes; also with lactic acid, turpentine, methyl benzene, and some other compounds. This reaction serves in many instances as a very delicate and reliable test for the presence of alcohol. It may be obtained in dilute solutions (Lieben, Annalen Suppl. 7, 236). In the reaction with turpentine, Guyot (J. Pharm. Chim. [iv.] 13, 313) and Chautaud (*ibid.* [iv.] 14, 19) employ iodated lime. When iodine is made to act on sodium ethoxide, instead of on alcohol and alkali, methylene iodide is formed together with only small proportions of iodoform (Butlerow, Annalen, 107, 110; Mulder, Rec. trav. chim. 7, 310). Iodoform was observed by Erlenmeyer (J. 1861, 668) among the products of the action of hydriodic acid on glycerol, and Rice (Pharm. J. [iii.] 6, 765) notes that a mixture of 'white precipitate,' alcohol, and iodine does not explode from the formation of nitrogen iodide when phenol is present, but that nitrogen and iodoform are formed. Iodoform may also be extracted from the product of the action of coal gas on iodine (Johnston, Phil. Mag. 17, 1). Acetylene mercuric chloride, silver and cuprous acetylides, and a solution of acetylene in concentrated sulphuric acid all yield iodoform when treated with iodine and dilute sodium hydroxide solution (Le Comte, J. Pharm. Chim. [vi.] 16, 297).

To prepare iodoform, Filhol (J. Pharm. Chim. [iii.] 7, 267) adds 1 part of alcohol to a solution of 2 parts of crystallised sodium carbonate in 10 parts of water and raises the temperature to 60°–80°. 1 part of iodine is then gradually added, and when the liquid has become colourless, iodoform slowly forms and sinks to the bottom and may be removed by filtration. The filtrate is heated as before, another portion of sodium carbonate and alcohol added, and chlorine is led into the mixture to liberate iodine which has combined with the alkali. Another deposit of iodoform occurs, and the process may be repeated until the product represents nearly half the iodine employed. Another plan, suggested by Rother (Pharm. J. [iii.] 4, 594), is to warm the following mixture until it becomes colourless: iodine 32 parts, potassium carbonate 32 parts, 95 p.c. alcohol 16 parts, water 80 parts. The iodoform which is deposited is removed, and to the clear solution a mixture of potassium dichromate 2 to 3 parts, and hydrochloric acid 16 to 24 parts, is added to liberate iodine. After neutralising the solution with potassium carbonate, 32 parts more of that salt are added, together with 6 parts of iodine and 16 parts of alcohol, and the heat being maintained a second quantity of iodoform precipitates. This may be removed and the operation repeated several times (*cf.* Cornelius and Gille, J. Pharm. Chim. [iii.] 22, 196; Smith, Pharm. J. [iii.] 5, 211; Bell, *ibid.* [iii.] 12, 786; Günther, Arch. Pharm. [iii.] 25, 373). Iodoform can be prepared by the electrolysis of a solution of an iodide in the presence of alcohol, aldehyde, or acetone (Dingl. poly. J. 255, 88; J. Soc. Chem. Ind. 1885, 243; Foerster and Meyes, J. pr. Chem. [ii.] 56, 353; Elbs and Herz, Zeitsch. Elektrochem. 4, 113; Abbot, J. Phys. Chem. 1903, 84; Teeple, Amer. Chem. J. 26, 170). According to Suilliot and Raynaud (Bull. Soc. chim. [iii.] 1, 3) almost the whole of the iodine employed is obtained as iodoform when acetone is acted upon by what is possibly nascent potassium hypoiodite produced by treating potassium iodide with sodium hypochlorite. A slight excess of dilute solution of sodium hypochlorite is added to a mixture of potassium iodide 50 parts, acetone 6 parts, and sodium hydroxide 2 parts, dissolved in 1 to 2 parts of water. The reaction probably takes place thus:

$$(1)\ KI+NaClO=KIO+NaCl.$$

$$(2)\ CH_3{\cdot}CO{\cdot}CH_3+3KIO$$
$$=CHI_3+CH_3COOK+2KHO.$$

This process has been applied to the working of kelp, and is said to produce iodoform of a very high degree of purity (Pharm. J. [iii.] 20, 423).

Iodoform crystallises in lemon-yellow hexagonal plates (Rammelsberg and Kokscharow, J. 1857, 431) which melt at 119°, volatilise when heated (*cf.* Dott, Pharm. J. [iii.] 16, 299; 17, 282), or better in a current of steam. It has a persistent and disagreeable odour. It is nearly insoluble in water, benzene, or light petroleum, but dissolves in ether, alcohol, and volatile oils (*cf.* Vulpius, Arch. Pharm. [iii.] 20, 44). Crystalline form (Pope, Chem. Soc. Trans. 75, 46). Lowering of the freezing-point in benzene solution (Paternò, Ber. 22, 465). In the dry state iodoform is not acted on by sunlight; but in solution, with access of oxygen, it rapidly liberates free iodine (Humbert, J. Pharm. Chim. [iii.] 29, 352; Hebeler, Pharm. J. [iii.] 16, 1088; Daccomo, Gazz. chim. ital. 16, 247; Neuss and Schmidt, Pharm. J. [iii.] 19, 247; Fischer, Pharm. Zeit. 34, 31; Bougault, J. Pharm. Chim. [vi.] 8, 213). Iodoform has been much used in medicine and surgery as an antiseptic, but its value in this respect has often been questioned. It would appear, however, that while outside the system it exerts no antiseptic power, it acts differently in presence of pus at the temperature of the body. Iodine is, in this case, liberated which combines with ptomaïnes to render them innocuous (De Ruyter, Med. Press Cir. 1887, 403; *cf.* Riedlin, Arch. Hygiene, 7, 309, and Ber. 22, Ref. 66; also Altenberg, Chem. Zentr. 1901, ii. 1212; Mulzer, *ibid.* 1905, i. 1174). Numerous attempts have been made to mask the odour of iodoform in its pharmaceutical preparations (Pharm. J. [iii.] 8, 439; 11, 111 and 895; 12, 439 and 703; 16, 288; 17, 556; 18, 249). For iodoform gauze *v.* Daux, J. Pharm. Chim. [5] 16, 201.

When iodoform is heated in closed tubes to 150°, methylene iodide is formed (Hofmann, Chem. Soc. Trans. 13, 65). The zinc-copper couple reduces it to acetylene (Gladstone and Tribe, *ibid.* 28, 512). Bromine converts it into bromoform (Löscher, Ber. 21, 410), and phosphorus pentachloride into chloroform. Finely divided silver, even in the cold, reduces iodoform, acetylene and silver iodide being formed. Other metals act in the same way, but in the case of iron in the presence of water the products are methyl and methylene iodides (Cazeneuve, Compt. rend. 97, 1371; 98, 369). With sodium ethoxide, methylene iodide, acrylic acid, and ethyl lactic acid are produced (Butlerow, Annalen, 107, 110; 114, 204; 118, 325). Methylene iodide is also formed by the action of potassium hydroxide on a solution of iodoform in acetone (Willgerodt and Muller, Chem. Zentr. 1884, 808). Iodoform reacts with certain mercury and silver salts. Mercuric acetate is reduced to mercurous acetate with evolution of carbon dioxide (Cotton, J. Pharm. Chim. [v.] 16, 481); mercurous chloride is converted into mercurous iodide and chloroform (Drescher, Pharm. J. [iii.] 17, 882), the reaction being similar to that between iodoform and phosphorus pentachloride; and dry silver nitrate is decomposed with explosive violence, silver iodide, nitrogen peroxide, nitric acid, and carbonic acid being probably formed (Pharm. J. [iii.] 20, 62). The last-mentioned reaction has been made the basis of a method for the volumetric estimation of iodoform (Greshoff, Rec. trav. chim. 7, 342). A crystalline but unstable compound of iodoform with strychnine is described by Lextrait (Compt. rend. 92, 1057). A reaction, which has been employed as a test, is obtained when a few drops of an alcoholic solution of iodoform are added to a small quantity of a mixture of phenol and solution of caustic potash, and the mixture gently warmed. A red precipitate is formed which, dissolved in a small quantity of alcohol, exhibits a carmine red colour (Lustgarten, Monatsh. 3, 717). Detection of adulteration (Kremel, Ph. Post, 21, 213). Assay of iodoform (Meillère, Chem. Zentr. 1898, ii. 140). A. S.

IODOFORMAL *v.* Synthetic drugs.

IODOFORMIN $C_8H_{12}N_4I_4$ is prepared by adding an alcoholic solution of iodine to ammonia and formaldehyde mixed in molecular proportions when iodoformin falls as a brown pulverulent precipitate (*v.* Synthetic drugs).

IODOFORMOGEN *v.* Synthetic drugs.

IODOKOL *v.* Synthetic drugs.

IODOLE *Tetraiodopyrrole* C_4I_4NH. Iodole is an antiseptic, similar in its action to iodoform. It is less energetic, but is free from the disagreeable smell which characterises that compound. References to communications on the physiological action of iodole and its application in therapeutics are given by Ciamician (Gazz. chim. ital. 16, 543). *Cf.* Trousseau (Pharm. J. [iii.] 17, 265); and Robinson (Chem. Zeit. 1887, 222).

Ciamician and Dennstedt, who first prepared iodole, obtained it by acting on potassium pyrrole, C_4H_4NK, with iodine in ethereal solution (Ber. 15, 2582). It is formed, even in the cold, when iodine is brought in contact with pyrrole, in presence of such indifferent solvents as alcohol, wood spirit, chloroform, acetone, carbon disulphide, or ethyl acetate. The reaction may be explained thus: $C_4H_4NH+8I=C_4I_4NH+4HI$. It is, however, better to add some agent to remove the hydriodic acid as it is formed, such as alkalis or their carbonates; or to oxidise it with such substances as ferric chloride, cupric sulphate, chlorine or bromine, oxide of manganese, &c., and thereby utilise the whole of the iodine (Ciamician and Silber, Ber. 18, 1766, 19, Ref. 327). Iodole may also be obtained from the corresponding chlorine or bromine derivatives of pyrrole by the action of metallic iodides (Patent, Ber. 20, Ref. 123).

Iodole crystallises from alcohol in light yellow microscopic needles. Heated at 140°–150° it decomposes without melting. It is insoluble in water but easily dissolves in ether, in hot alcohol or glacial acetic acid, or in alcoholic potash. The alcoholic solution with nitric acid gives an intense red colour, and a green colour is obtained when the crystals are heated with sulphuric acid. Acted upon by zinc-dust and potassium hydroxide, iodole is converted into pyrrole (Ciamician and Silber, Ber. 19, 3027) (*v.* Synthetic drugs). A. S.

IODOLEN, IODOLIN, IODOGALLICIN, IODOPHENIN, IODOTHYRINE, IODOZOL, *v.* Synthetic drugs.

IODOMENIN *v.* Synthetic drugs.

IODOMETRY *v.* Analysis, Volumetric.

IODOPYRINE. A pharmaceutical preparation made by adding a solution of iodine in potassium iodide to an aqueous solution of antipyrine containing sodium acetate.

IODOTHEOBROMIN, IODOTHYRIN, IODYLIN, IODYLOFORM, *v.* Synthetic drugs.

IODOTHION *v.* Synthetic drugs.

IODYRITE, or Iodargyrite. A mineral composed of silver iodide (AgI) crystallising in the rhombohedral system. Distinctly developed crystals are small and comparatively rare; they possess a perfect cleavage parallel to the basal plane, on which the lustre is pearly, and are very soft (H. = 1) and readily distorted. Their pale sulphur-yellow is not darkened by exposure to sunlight. Sp.gr. 5·51. At a temperature of 146°, the material becomes optically isotropic and cubic, reverting on cooling into the birefringent rhombohedral form.

The mineral occurs in the upper oxidised zones of certain silver-bearing veins, and when found in quantity, as at Broken Hill in New South Wales, in Chile and Mexico, it is an important ore of silver (Ag, 45·97 p.c.). Some of the silver-ore formerly mined at Broken Hill consisted of white kaolin enclosing films and specks of iodyrite.

Miersite is a rare cubic form of silver iodide with copper iodide (4AgI·CuI) from Broken Hill, New South Wales (L. J. Spencer, Min. Mag. 1901, 13, 41; G. T. Prior, *l.c.* 188). L. J. S.

IONIUM. A radioactive element, discovered by Boltwood in uranium minerals (Boltwood, Amer. J. Sci. 1907, 24, 370; *cf.* Hahn, Ber. 1907, 40, 4415). The results obtained by Boltwood and Hahn were confirmed by Marckwald and Keetman (Ber. 1908, 41, 49), who were unable to separate ionium from thorium, an element which it closely resembles. Ionium occurs, however, associated with actinium, in many of the uranium group of minerals in the absence of thorium (Szilárd, Le Radium, 1909, 6, 80).

Highly active preparations of ionium may be obtained from carnotite as follows (Boltwood, Amer. J. Sci. 1908, 25, 365). The ore is dissolved in hydrochloric acid and several grams of the chlorides of the cerite earths added. The earths are separated as oxalates, converted into chlorides, and precipitated with sodium thiosulphate. The latter procedure is repeated several times, when a product is obtained having a radioactivity several thousand times as great as that of an equal weight of pure uranium.

The residues obtained in working up uranium ores containing little thorium may be precipitated in strongly acid solution with hydrofluoric acid. The precipitated fluorides are converted into sulphates, and from the aqueous solution of these, ionium and thorium are quantitatively precipitated by adding zinc hydroxide. The precipitate is dissolved in hydrochloric acid and the solution precipitated with oxalic acid. The oxalate thus obtained contains the ionium, and has an activity 200 times as large as that of metallic uranium (Keetman, Jahrb. Radioaktiv. Elektronik. 1909, 6, 265).

Ionium emits α-rays, which have a range in air of only 2·8 cms.; it also emits β-rays. It produces no emanation. The life of ionium is at least as long as that of radium.

According to Boltwood, ionium is the direct parent of radium, and according to Keetman (*l.c.*), does not change directly into actinium.

Thorium-ionium oxalate has a very high and constant activity, and may with advantage be utilised in testing the constancy of electrometers and for determining capacities (Keetman, *l.c.*).

IONONES *v.* KETONES.

IPECACUANHA. *Ipecacuanha Root. Racine d'Ipecacuanha*, Fr.; *Brechwurzel*, Ger. Ipecacuanha occurs in commerce as a dusky grey root, with a thick bark, transversely corrugated or ringed, the corrugations often penetrating to the woody interior, and minutely wrinkled longitudinally. The root attains a diameter in some cases of $\frac{2}{10}$ to $\frac{3}{10}$ of an inch, and as many as twenty rings may be counted to the inch in length. It has a short friable, not fibrous, fracture, and the bark, which constitutes some three-fourths of the root, separates easily from the wood. (*Cf.* Flück. a. Hanb. 373; Tschirch and Lüdtke, Arch. Pharm. 1888, 432.)

The drug was first introduced into Europe from Brazil about the close of the 17th century as a remedy for dysentery, and since that period it has always retained a place among articles of *materia medica.* Its employment has, however, been mainly as an expectorant and emetic, but it has frequently been used in the treatment of intestinal diseases, and its historic reputation as a remedy for dysentery has been somewhat revived in India. Applied locally the powdered root is an irritant, and in large doses it is poisonous. (*Cf.* Pereira, Mat. Med. 1853, 2, 1591; Flück. a. Hanb. 370.) It is administered either in the state of powder—for instance, admixed with opium and potassium sulphate in the well-known Dover's Powder—or made into pills, or in vinous solution. The mode of preparation of the drug for use in medicine has been much studied by pharmacists (*v.* indexes Ph. and Year-Bk. Ph.).

The root is derived from the *Uragoga Ipecacuanha* [Willd. (Baill.)], a low shrub found for the most part between 8° and 22° S. latitude, in Brazil and also to some extent in the adjoining portions of New Granada and Bolivia. The plant grows in shady forests, in valleys, but not actually in swamps. According to Balfour the plant exists in two varieties, one having a woody and the other an herbaceous stem (*cf.* Bentl. a. Trim. 145; Flück. a. Hanb. 374; Pocklington, Pharm. J. [iii.] 2, 841, 921).

The most important constituent of ipecacuanha is the alkaloid *emetine*, first obtained in an impure state by Pelletier and Magendie in 1817 (Ann. Chim. Phys. [ii.] 4, 172), and further studied by Pelletier (J. Pharm. Chim. [ii.] 3, 145; 14, 200), Pelletier and Dumas (Ann. Chim. Phys. [2] 24, 180), Merck (Neues Jour. Trommsdorf. 20, 1, 134), Buchner (Rep. Pharm. 7, 289), Landerer (*ibid.* 52, 211), Reich (Arch. Pharm. [2] 113, 193), Lefort (J. Pharm. Chim. [iv.] 9, 241), Pander (J. 1871, 373), Glénard (J. Pharm. Chim. 22, 178; Compt. rend. 81, 100), Lefort and F. Würtz (*ibid.* 84, 1299), Power (Pharm. J. [iii.] 8, 344), Kunz-Krause (Arch. Pharm. [3] 25, 461; 232, 466) and Podwyssotzky (Pharm. J. [iii.] 10, 642); Kremel (Arch. Pharm. [iii.] 26, 419).

The emetine of the earlier investigators has been shown by Paul and Cownley (Pharm. J. 53, 61; [iii.] 25, 111) to be a mixture of at least two different alkaloids; one, a base insoluble in caustic alkalis, for which it is proposed to retain the name of *emetine*; the other, *cephæline*, is soluble in caustic alkalis. These were separated from ipecacuanha by extraction with alcohol, precipitation with basic lead acetate, evaporation of the filtrate to dryness, and treatment of the residue with dilute acid; the solution was mixed with ether, ammonia added in slight excess, and shaken, and from the separated ethereal solution, dilute sulphuric acid took up the emetine, which was precipitated by adding caustic soda solution and treated further in order to entirely remove the other base. The alkaline solution when acidified and then shaken with ether and ammonia yielded cephæline. Emetine $C_{15}H_{22}NO_2$ melts at 68°, is amorphous, strongly alkaline and colourless, but turns yellow when exposed to light. It is soluble in alcohol, ether, chloroform, or benzene, but only sparingly so in hot light petroleum or in water. Cephæline $C_{14}H_{22}NO_2$ is colourless, but, like emetine, is turned yellow by exposure to light. It is less soluble in ether than emetine. It melts at 119° when all the solvent has been driven off (Frerichs and Tapis, Arch. Pharm. 240, 390).

A third alkaloid, *psychotrine*, has been isolated from ipecacuanha (Paul and Cownley, Pharm. J. [iii.] 25, 690). It exists in relatively small proportion, is characterised by its very sparing solubility in ether, and remains in the ammoniacal liquor from which emetine and cephæline have been extracted by ether. Psychotrine forms pale yellow crystals which melt at about 138°. The proportions of these alkaloids in Brazilian, Columbian, and Indian ipecacuanha are given by Paul and Cownley (Pharm. J. [iv.] 2, 321; 15, 256). Allen and Scott-Smith (Analyst, 27, 345) give a table comparing the colour reactions of emetine, cephæline, and psychotrine.

To determine the value of ipecacuanha or its pharmaceutical preparations, an estimation of the alkaloidal content is made. This is done either by a process similar to one of those given for the extraction of the alkaloid (*v.* Kremel, Pharm. Post, 21, 151) or, having obtained a suitable solution, by titration with Mayer's reagent (*cf.* Zinoffsky, Pharm. J. [iii.] 3, 342; Dragendorff, Werthbestimmung einiger starkwirkender Droguen, 1874, 37; Stewart, Amer. J. Pharm. 1876, 359; Naylor, Pharm. J. [iii.] 16, 507; Lyons, *ibid.* [iii.] 16, 627; Zeitsch. anal. Chem. 28, 258; Flückiger, Pharm. J. [iii.] 16, 643; Jones, *ibid.* [iii.] 17, 277; Alcock, *ibid.* [iii.] 16, 680; Ransom, *ibid.* [iii.] 18, 241, 400; Cripps and Whitby, *ibid.* [iii.] 19, 721; Braithwaite and J. C. Umney, *ibid.* [iii.] 20, 252, 253; Arndt, Pharm. Zeit. 1889, 585; Keller, Chem. Zentr. 1893, i. 235, 322; 1894, i. 236; J. Pharm. Chim. [v.] 27, 465; Frerichs and Tapis, Arch. Pharm. 240, 390).

Besides emetine, ipecacuanha contains a compound *ipecacuanhic acid* $C_{14}H_{18}O_7$ (Willigt, Sitz. Ber. K. Akad. Wien. 5, 192) which was thought by Pelletier (Ann. Chim. Phys. [ii.] 4, 172) to be gallic acid. It is a reddish-brown amorphous mass, with a bitter taste and very hygroscopic. It is soluble in water or alcohol, but less so in ether. With ferric chloride it gives a green colour. It reduces salts of silver and mercury, and is not precipitated by neutral lead acetate. Kunz found the root to contain *choline*. The colouring matter of ipecacuanha was examined by Podwyssotzky. It forms purple-red compounds with alkalis. From its combination with barium an acid was obtained, *erythrocephaleïn*, which crystallises from chloroform in straw-coloured needles. When the root is distilled with sodium carbonate and a little ferric chloride, a distillate is obtained from which a crystalline fluorescent *volatile alkaloid* may be isolated (Arndt, Chem. Zentr. 1889, 433; Pharm. Zeit. 1889, 585). It is present to the extent of 0·3 p.c. It forms compounds with most alkaloidal reagents, and gives a *hydrochloride* which crystallises in fluorescent octahedrons. No trace of this volatile alkaloid, however, could be found by Cripps (Pharm. J. [iv.] i. 159). Ipecacuanha also contains *gum* (Willigt), *starch*, 30 p.c. in the cortica and 7 p.c. in the woody portion (Flück. a. Hanb.), and other constituents usually found in plants. It yields about 3 p.c. of ash (Mumms, Pharm. J. [iii.] 17, 898).

For characters of allied plants, such as striated ipecacuanha, *Psychotria emetica* (Linn.), and undulated ipecacuanha, *Richardsonia grandiflora* (Cham. et Schlecht.), and others sometimes substituted for *Uragoga*, *cf.* Flück. a. Hanb. 375; Attfield (Pharm. J. [ii.] 11, 140); Planchon (J. Pharm. Chim. [iv.] 16, 404; 17, 19); Power (Pharm. J. [iii.] 8, 344); Kirkby (*ibid.* [iii.] 16, 126); Hooper (*ibid.* [iii.] 18, 317); and Ransom (*ibid.* [iii.] 18, 787). A. S.

IRETOL *v.* PHENOL AND ITS HOMOLOGUES.

IRIDIN *v.* GLUCOSIDES.

IRIDIUM. Sym. Ir. At.wt. 193·1.

The occurrence of this metal and the properties of its principal alloys with platinum will be described under PLATINUM. Its principal source is the osmiridium which is left after treatment of crude platinum with *aqua regia.*

The osmiridium is first freed from sand and certain other admixed metals by lixiviation with water, after which it is brought into a fine state of division by melting it with its own weight of lead, and once or twice its own weight of oxide of lead. The mixture is kept at red heat for half an hour, treated successively with nitric acid, and with *aqua regia*, and then sifted through fine silk. The division of the mineral may also be brought about by melting it with zinc and then removing the latter by means of hydrochloric acid or by volatilisation.

The finely-divided mineral may now be fused with barium or sodium peroxide, with sodium chloride, or with a mixture of nitre and potash, after which the mass is taken up with water containing alcohol, then with hydrochloric acid which converts the metals into chlorides. These are transformed into double chlorides by the potassium chloride, and the metals are finally separated as nitrites.

The solution of the chlorides, after standing for 24 hours, is filtered, and the filtrate treated with sodium nitrite, iron is precipitated as sesquioxide and gold (if present) as metal; on addition of soda any remaining lead, copper, and bismuth are precipitated. The solution is now made alkaline with soda and treated with chlorine at 50°–60°, whereby osmium and ruthenium oxides are volatilised. The residue is acidified with hydrochloric acid, and the iridium and rhodium are precipitated as ammonium double nitrites by means of sodium nitrite and ammonium chloride. The precipitate is filtered off, dissolved in warm hydrochloric acid, and again treated with ammonium chloride, whereupon iridium separates as ammonium iridochloride, whilst the rhodium remains in solution (Deville and Debray, Compt. rend. 1874, 78, 1502; Leidié, *ibid.* 1899, 129, 214; *ibid.* 1900, 131, 888; Quenessen, *ibid.* 1905, 141, 258; Leidié, Bull. Soc. chim. 1901, [iii.] 25, 9; *ibid.* 1902, [iii.] 27, 179; *ibid.* 1903, [iii.] 29, 801; Gibbs, J. pr. Chem. 1864, 91, 175).

The mineral may also be fused with potash and potassium chlorate; on treating the mass with water, the osmium and ruthenium are dissolved, whilst the iridium mixed with some platinum remains as a blue-black powder, which is attacked by acids, and from which the platinum may be removed by means of sulphuretted hydrogen, the iridium remaining behind as a sesquichloride.

Iridium may be separated from gold by heating the mixture in a clay crucible. The fused gold is poured off and the iridium silicate remaining is reduced (Mietzschki, J. Pharm. Chim. 1902, 15, 68).

The metal may be isolated by heating iridium ammonium chloride with reducing agents at a dull red heat (U.S. Pat. 805316, 1905).

Another method of separating iridium sometimes employed, is to mix the finely-divided osmiridium with sodium chloride in a porcelain tube and pass a current of chlorine through it. This converts the metals into chloride, and the iridium can then be separated by means of sulphuretted hydrogen (Schneider, Annalen, 1867, Suppl. 5, 267).

On account of their extreme hardness, the native grains of osmiridium are employed as such for tipping the points of gold nibs, but only a small proportion even of the few grains which occur with ordinary crude platinum are suitable for the purpose. A small quantity of osmiridium is used for pivots, &c., of watches and scientific instruments, but practically the whole is worked up for the production of iridium, which is mainly employed in alloy with platinum for the manufacture of crucibles and for many other purposes. Owing to its extreme hardness and to its power of retaining its temper and edge under conditions where steel requires constant sharpening, iridium has been employed in preference to that metal, for wire-drawing, jewellers' tools, points for compasses and watches, and for edging cutters for rubber, celluloid, &c. If the metal could be produced in quantity, it would find extended use in place of platinum for crucibles. Such crucibles possess the hardness of steel and show no alteration in weight on strong ignition, although they become bluish at a red heat from superficial oxidation, which disappears on stronger heating. With a badly regulated gas flame, a deposit of carbon is produced upon the crucible, but this readily burns off and leaves no ill effect as regards weight, appearance, or brittleness. Boiling with *aqua regia*, fusion of phosphates in presence of carbon, the heating of silica or silicates with a reducing agent, or even fusion of metallic lead or zinc in the crucibles, is without apparent action. Prolonged fusion of copper in iridium makes it brittle when hot, but if the heat be raised sufficiently to volatilise the copper, the iridium shows no ill effect.

Iridium is a white metal as bright as steel, having a sp.gr. of 22·39 (G. Matthey), and melting at about 1950°; 2150°–2250° (J. Ind. Eng. Chem. 1911, 3, 354).

Under ordinary conditions, iridium is not attacked by any acid, not even by *aqua regia*.

At a dull red heat it combines with fluorine, chlorine, or oxygen. It also combines with sulphur when heated, and gives a readily fusible compound with phosphorus, which is decomposed at a white heat.

Colloidal iridium may be obtained by mixing iridium chloride with lysalbic acid and concentrated soda, and subsequently dialysing the mixture (Paal and Amberger, Ber. 1904, 37, 124); or by reducing iridium chloride with hydrazine hydrate in the presence of gum arabic solution (Gutbier and Hoffmeier, J. pr. Chem. 1905, [ii.] 71, 452). It is a catalyst, but is not as powerful as colloidal platinum.

Iridium black is a complex mixture containing varying proportions of the metal and its oxides, obtained by reducing iridium salts with alcohol, formic acid, or formaldehyde. The black powder thus formed is washed with water and dried *in vacuô* (Böttger, J. pr. Chem. 1834, 3, 276).

It has properties similar to, but more powerful than, those of platinum black. It absorbs gases and has the property of inducing chemical action, as, for instance, the combustion of hydrogen and of alcohol, the transformation of chlorine, iodine, or bromine water into halogen acid and oxygen, the decomposition of hypochlorites, and so forth (Schönbein, Ann. Chim. Phys. 1866, [iv.] 7, 103, 113). It dissolves in *aqua regia*, as does also iridium in alloy with platinum.

Although the black iridium oxide is a valued pigment for china, the commercial use of iridium for that or other purposes other than as metal or in alloys, is practically *nil*, as the demand for the metal as such exceeds the supply. For the same reason, none of the large variety of salts which iridium forms, are of technological interest.

Iridium Compounds.

According to Wöhler and Witzmann (Zeitsch. anorg. Chem. 1908, 57, 323; *see* also Zeitsch. Elektrochem. 1908, 14, 97), the oxide IrO does not exist under ordinary conditions.

Iridium dioxide IrO_2 is best prepared by the action of alkali on a hot solution of sodium iridichloride Na_2IrCl_6, the sesquioxide first formed being oxidised to dioxide by a current of oxygen. The oxide is then dried in a current of carbon dioxide at 200°, after which it is boiled with alkali and then with sulphuric acid. The anhydrous dioxide and also the one containing 2 mols. H_2O is black. When freshly precipitated it is more readily soluble in acids and alkalis than when dried.

The solution obtained by the action of potash or sodium iridichloride in the cold, ultimately becomes violet in colour and contains the dioxide in colloidal form; after a time a violet modification of the dioxide separates, and on boiling, the solution becomes blue. The blue and green solutions of the dioxide in hydrochloric acid also contain the dioxide in colloidal solution.

Iridium sesquioxide Ir_2O_3 is obtained by mixing air-free hot solutions of sodium iridium sesquichloride $Ir_2Cl_6,6NaCl,24H_2O$, and potash in a current of carbon dioxide. The mixture is evaporated to dryness and heated to redness in a current of the same gas, after which it is purified in the same way as the dioxide. With hydrochloric acid this oxide also gives a colloidal solution. Like the dioxide, its properties depend on the proportion of water it contains. The sesquioxide imparts a fine black colour to porcelain after firing, and when mixed with zinc oxide it yields a grey tint.

Iridium trioxide is so unstable that it has not been obtained pure.

Iridium trihydroxide $Ir(OH)_3$ is a yellowish-green substance which dissolves in alkalis and oxidises rapidly in the air, forming

Iridium tetrahydroxide $Ir(OH)_4$, a heavy indigo blue powder, which becomes green, then brown on heating (Joly and Leidié, Compt. rend. 1895, 120, 1341; Gutbier and Riess, Ber. 1909, 42, 3905).

Iridous chloride $IrCl_2$ is a green, insoluble mass, formed when chlorine is passed over spongy iridium or when the tetrachloride is heated.

Iridium trichloride $IrCl_3$ is a light, insoluble, olive-green powder prepared by heating one of its double salts with sulphuric acid, and also by other methods (Antony, Gazz. chim. ital. 1893, 23, i. 184). It forms complex compounds with the chlorides of phosphorus and arsenic (Geisenheimer, Compt. rend. 1890, 110, 1004, 1336), and double salts with metallic chlorides of the type $M_3IrCl_69H_2O$.

Iridium tetrachloride $IrCl_4$ may be obtained by heating ammonium iridichloride in chlorine, or by dissolving the finely-divided metal in *aqua regia*, or the blue hydroxide in hydrochloric acid. It forms double chlorides of the type M_2IrCl_6 and with alkyl amines (Rimbach and Korten, Zeitsch. anorg. Chem. 1907, 52, 406; Delépine, Compt. rend. 1909, 149, 1072; *ibid.* 1908, 146, 1267; Vézes, *ibid.* 1392; Gutbier, Zeitsch. physikal. Chem. 1909, 69, 304; Gutbier and Riess, *l.c.*). The iridichlorides, when reduced, yield the iridiochlorides. Similar bromides and iodides of iridium also exist.

Iridium forms ammonium or ammine derivatives similar in constitution to the platinum compounds and corresponding to the chlorides $IrCl_2$, $IrCl_4$; also a series of compounds corresponding to $IrCl_3$, and analogous to the cobaltic, chromic, and rhodic compounds, thus:

When iridium chloride is treated with ammonia, double salts $Ir(NH_3)_3Cl_3$,

$$Ir(NH_3)_4,Cl_3,H_2O,$$

and $Ir(NH_3)_5Cl_3,H_2O$ are formed. Iridium ammonia chlorohydroxide, sulphate, thionate, oxalate, nitrate, and a number of halide derivatives are also known (Palmaer, Zeitsch. anorg. Chem. 1895, 10, 320; *ibid.* 1896, 13, 211; *see* also Mylius and Dietz, Ber. 1898, 31, 3187).

Complex iridium nitrites and their chloro and oxalic acid derivatives have been prepared (Joly and Leidié, Compt. rend. 1895, 120, 1341; Leidié, *ibid.* 1902, 134, 1582; Bull. Soc. chim. 1902, [iii.] 27, 936; Vézes and Duffour, *ibid.* 1910, [iv.] 7, 507, 512; Miolati and Gialdini, Atti. R. Accad. Lincei, 1902, [v.] 11, ii. 151; Werner and Vries, Annalen, 1908, 364, 77).

Iridicyanides resemble the ferricyanides and are described by Martius (*ibid.* 1861, 117, 357; *see* also Rimbach and Korten, Zeitsch. anorg. Chem. 1907, 52, 406).

Iridium sulphides IrS, Ir_2S_3, IrS_2 (Antony, Gazz. chim. ital. 1893, 23, i. 184, 190), and the ammonium pentadecasulphide $(NH_4)_3IrS_{15}$ (Hofmann and Höchtlen, Ber. 1904, 37, 245) are known.

Iridium sulphate $Ir(SO_4)_2$ is a yellow-brown mass which when warmed with sulphuric acid is reduced, giving a green solution of the sesquisulphate $Ir_2(SO_4)_3,6H_2O$ (Rimbach and Korten, *l.c.*).

Iridium sesquisulphate forms alums with ammonium, thallium, and the alkali metals, of the type $Ir_2(SO_4)_3\cdot M_2SO_4,24H_2O$ (Marino, Zeitsch. anorg. Chem. 1904, 42, 213; Rimbach and Korten, *l.c.*; Delépine, Compt. rend. 1906, 142, 631). It also forms sulphates of the type

$$Ir(SO_4M')_3,H_2O\ (?)\ \text{or}\ Ir_2(SO_4)_3\cdot 3M_2SO_4,H_2O$$

which are bluish-green in colour, and are decomposed by ammonia and alkali hydroxides with precipitation of a violet oxide of iridium. The contained sulphuric acid is not precipitated by barium (Delépine, Compt. rend. 1906, 142, 1525).

According to Delépine iridium forms two series of disulphates: (1) green salts, generally acidic, derived from the acid

$$H_2[Ir(SO_4)_2(OH)H_2O];$$

(2) reddish-brown basic salts derived from the acid $H_3[Ir(SO_4)_2(OH)_2]$ (Compt. rend. 1909, 149, 785).

He has also obtained green pyridine derivatives (*ibid.* 1910, 151, 878).

Double salts of *iridous sulphite* have been described by Seubert (Ber. 1898, 11, 1761).

Iridium selenide (Chabrié and Bouchonnet, Compt. rend. 1903, 137, 1059); *oxalates* (Gialdini, Atti. R. Accad. Lincei, 1907, [v.] 16, ii. 551, 648; Vézes and Duffour, Bull. Soc. chim. 1907, [iv.] 5, 869, 872); *phosphor halides* (Strecker and Schurigin, Ber. 1909, 42, 1768); and *mercaptide* (Hofmann and Rabe, Zeitsch. anorg. Chem. 1897, 14, 293) are known.

IRIS BLUE *v.* OXAZINE COLOURING MATTERS.

IRIS GREEN. *Sap Green* (*v.* PIGMENTS).

IRISH MOSS GUM *v.* GUMS.

IRON. Sym. Fe. At.wt. 55·84. *History.*—Iron has been known and prized from the very earliest historical period, articles of the metal having been found among the contents of the Great Pryamid of Egypt, where they are believed to have remained for 5000 years. Iron was also used in Nineveh in considerable quantities, and in the British Museum are picks, hammers, and saws made of iron, found by Layard in the ruins of Nineveh, and which are believed to be of a date not later than 880 B.C. Iron is frequently mentioned in the earlier books of the Bible; it was much prized by the Greeks, and was discovered by Schliemann in the ruins of Mycenæ, which was destroyed B.C. 561. The Chinese were acquainted with the use of iron at a very early period, and it was also highly valued and much worked by the Romans. The metal employed in all the above instances was obtained by direct reduction from the ore, by methods very closely resembling those still in use by semi-barbarous peoples in various parts of the world. In England iron was largely worked by the Romans, and in the Forest of Dean there are still to be seen remains of these old Roman workings, whilst the partly reduced slags left by the Romans were in more modern times employed for many years in the blast furnaces of that district as a source of iron. At the Norman invasion Gloucester possessed a considerable trade in iron, but until the introduction of coal Sussex was the chief seat of the manufacture in this country. The exact date at which the blast furnace was introduced is not known, and it was probably the result of a gradual development of the more primitive hearths formerly in use. Cast iron was, however, known to Agricola, who died in 1555, and it was employed for cannon in this country in the year 1516. At this period small blast furnaces were employed which were capable of producing about 7–10 tons of metal per week, the fuel used being charcoal. The resulting pig iron was afterwards converted into wrought iron in a finery, or small hearth, not unlike the smith's fire. The large quantities of wood employed for the production of charcoal for this manufacture led to the introduction of various Acts of Parliament during the 16th century, which had for their object the restriction of the industry to certain districts, and a diminution of the waste of valuable timber. In the early part of the 17th century Dud Dudley succeeded in 'charring' coal or producing a coke suitable for use in the blast furnace, but the use of coal did not become general until after Abraham Darby had again succeeded in the manufacture of coke at Colebrook Dale about 1730. The introduction of the steam engine by Watt led to the use of more powerful blowing machinery, and gave increased yields, which again were much improved upon by the application of hot blast in 1829, by subsequent alteration in the shape of the interior, and by the considerable increase in the size and the capacity of the furnaces. Various other improvements have from time to time been adopted, such as the utilisation of the gases from the furnace, the use of regenerative hot blast stoves, and the introduction of improved methods of calcining the ore, so that the present output of the best furnaces is about 400 times that of the blast furnaces of 200 years ago, whilst the consumption of fuel has been reduced to about one-fifth of that formerly employed. In connection with the manufacture of steel, the cementation process is in various forms of very great antiquity, but a notable improvement was effected by Huntsman, about 1740, by the introduction of cast steel, while a further advance was made in 1839, when Heath introduced the use of manganese in steel melting. As before mentioned, wrought iron was originally prepared directly from the ore, and at a subsequent date was obtained from cast iron by the use of the open-hearth finery. In 1784 Cort patented the puddling process, and in so doing laid the foundation of much of the prosperity of England during the century that followed. But in recent years the whole system of the manufacture of wrought iron has been revolutionised by the magnificent inventions of Bessemer and Siemens, by which the decarburised iron is obtained in the fluid condition. The metal then is commonly known as 'mild steel,' and has met with such a variety of applications that for rails, girders, guns, shipbuilding, bridge construction, and many other uses, it has gradually replaced the iron obtained by the puddling process.

Chief iron ores. Iron is occasionally found native, either in the form of meteorites also containing nickel, or as metal which, by the action of heat and reducing agents, has been naturally separated from the ore. These sources are, however, unimportant, except for savage tribes, who are in some instances largely dependent upon such methods of supply. Iron is very widely distributed throughout the crust of the earth in various forms. On account of its cheapness, and the readiness with which it combines with various elements, such as sulphur, phosphorus, or arsenic, which, if present in the metal, would injuriously affect its mechanical properties, comparatively few ferruginous compounds are practically available as sources of iron. It is necessary if an iron ore is to be profitably employed that the working expenses and carriage should be small, that the ore should be rich and readily reduced, and that it should be free from sulphur, phosphorus, arsenic, or other impurities which seriously deteriorate the quality of the iron. Such ores are practically either oxides or carbonates.

Oxides of iron. These may be divided into three classes.

1. *Magnetites.* Magnetic oxide of iron (Fe_3O_4) is the richest oxide of iron which occurs in nature; if pure, it would contain 72·4 p.c. of metallic iron. Its colour varies from brownish-grey to iron-black; it is brittle, magnetic, and produces a black streak. It crystallises in the cubic system, but is generally found massive. It occurs in immense quantities of remarkable purity in Sweden and on the shores of Lake Superior. The Swedish iron, which has so long been famed, is made from this ore. *Ilmenite* is an impure magnetite containing titanium, which occurs in Norway. *Franklinite*, which occurs in New Jersey, may be regarded as a magnetite in which the ferrous oxide is more or less replaced by oxide of zinc; and *Chrome Iron Ore* is a magnetite in which the ferric oxide is replaced by oxide of chromium.

2. *Red hæmatites.* Ferric oxide (Fe_2O_3) occurs in a number of forms which possess different physical characters, such as *Micaceous iron ore*, *Specular iron ore*, *Kidney iron stone*, &c. These forms differ in hardness, density, and colour, but each gives a red streak. Red hæmatite is generally very free from phosphorus, and is found in Cumberland, where it is employed in the preparation of a pig iron low in phosphorus, suitable for the ordinary, or acid, Bessemer process. In the United States a deposit of phosphoric red fossil (hæmatite) ore runs from Clinton in the State of New York to Birmingham in Alabama. Many of the ores of Spain and of the Lake Superior district, such as those of Vermillion, are also red hæmatites.

3. *Brown hæmatites.* Ferric oxide occurs associated with a variable amount of combined water in the different varieties of brown hæmatites. In colour these vary from light to dark brown, and they give a brown streak. A specially rich, pure, and easily reducible variety is now imported in large quantities from Spain, and a pure variety was formerly worked in the Forest of Dean. In Northamptonshire, Lincolnshire, &c., a brown hæmatite is employed which contains about 10 p.c. of silica and over 0·5 p.c. of phosphorus. The *minette* ores of

France and Northern Germany, in the vicinity of the Rhine, although phosphoric, and containing only about 30 p.c. of iron, are of this class, and are among the most important iron ore deposits of the world. Brown ores are also met with in considerable quantities in the United States. *Limonite, Bog iron ores,* and *Lake ores* are other examples of hydrated oxides of iron occurring in various localities.

Carbonates. These consist essentially of ferrous carbonate ($FeCO_3$), the important differences in character observed in various ores depending chiefly upon the amount and character of the impurities present. These ores are widely distributed and of great importance.

Spathic iron ore is the purest form in which ferrous carbonate occurs; it has a pearly lustre, and is generally light brown in colour. There are very extensive deposits of this ore in various parts of Europe, notably at Erzberg in Styria; the ore is usually free from phosphorus, but contains much manganese.

Clay iron stone is a less pure variety of ferrous carbonate which contains clayey matter, and was for many years the most important ore of this country; it usually occurs in the coal measures. The ore is generally dark in colour, and contains from 30 to 40 p.c. of metallic iron, associated with less manganese and more phosphorus than in the purer spathic ores.

Cleveland iron stone is a variety of clay iron stone met with in the North Riding of Yorkshire. It is generally uniform in character and contains about 33 p.c. of metallic iron; it contains little manganese, but the percentage of phosphorus is higher than in either of the ores previously mentioned, except, perhaps, in the case of the impure brown hæmatites.

Black band iron stone is an ore which occurs chiefly in Scotland and North Staffordshire. It contains a variable amount of bituminous matter which imparts a characteristic black colour, and which frequently enables the ore to be calcined without the addition of any extra fuel. In other respects black band very closely resembles clay iron stone.

In addition to the ores previously enumerated, several other materials are employed for the production of iron, such as 'tap-cinder,' which is essentially ferrous silicate, and is produced in the puddling process. In this case the product obtained is a common variety of iron known as cinder pig. Tap-cinder is only met with in quantities suitable for the requirements of blast furnaces in those districts where puddling has been conducted for a considerable period. The residue from Spanish pyrites, after the extraction of sulphur and copper, is commonly known as 'purple ore,' and has been made into bricks and used in the blast furnace. It is often used as a fettling in the puddling process.

The following table will illustrate the approximate composition of the various ores of iron. It will be understood, of course, that such materials are subject to considerable variations in character, and it has been thought better to give approximate values deduced from a number of analyses, than to introduce a mass of figures detailing actual results obtained.

APPROXIMATE COMPOSITION OF IRON ORES.

—	Magnetite	Red hæmatite	Brown hæmatite		Carbonate ores			
			Lake Superior ore (Mesabi)	Northampton	Spathic	Clay band	Cleveland	Black band
Ferric oxide (Fe_2O_3)	65	90	85	65	—	0·5	3	3
Ferrous oxide (FeO)	25	—		—	50	47	40	41
Manganous oxide (MnO)	—	—	—	0·5	10	2	1	1
Carbon dioxide (CO_2)	—	—	—	—	38	30	25	26
Silica (SiO_2)	10	6	6	13	2	10	8	7
Alumina (Al_2O_3)	—	1	2·5	3	—	5	7	3
Lime (CaO)	—	1	0·75	variable	—	2	7	2
Magnesia (MgO)	—	—	0·5	—	—	2	4	1
Phosphorus pentoxide (P_2O_5)	trace	trace	0·22	1·3	trace	0·6	1·5	0·6
Water	—	—	5	14	—	1	2	1
Organic matter	—	—	—	—	—	trace	trace	15

Preparation of iron ores.—The greater part of the iron ores now raised are charged into the blast furnace without any special preparation. Anhydrous oxides, such as Lake Superior ores, do not require calcination, except in some cases, to remove sulphur. The chief European ores are, however, treated before smelting. The mechanical preparation of iron ores is very simple, and consists of a rough assortment of the size of the materials to be employed. In some cases the larger pieces are broken by hand or suitable crushing machinery, whilst in other instances the very fine ore is separated by riddles and used for other purposes, as it would be apt to choke up the blast furnace. Poor ores, such as those of Cleveland, are charged in larger pieces than the richer hæmatities or magnetites. Non-calcareous ores, which contain iron pyrites, are frequently weathered for a few months, and the sulphur becoming oxidised, passes away in solution as ferrous sulphate. Shale is also removed by weathering.

Calcination.—Many iron ores are calcined before being used in the blast furnace, the object being to remove volatile substances such as sulphur, water, carbon dioxide, arsenic, &c., and to concentrate the iron in the residue. Two other important objects are also gained by calcination; in the first place the iron is oxidised from the ferrous to the ferric condition, which prevents the formation of scouring slags, rich in ferrous silicate, during reduction in the blast furnace; and further, the material is rendered much more porous so that it is more readily acted upon by the gases of the furnace. From the above remarks it will be evident that some ores, such as red hæmatites, do not require calcination. Ores which are in a state of fine division, such as much of the ore from the Lake Superior district, are not calcined. Fine ores are frequently briquetted, and the briquettes are generally calcined before use in the blast furnace. When calcining, it is necessary to regulate the temperature as carefully as possible; with low temperatures the ore is insufficiently calcined, whilst if the heat be too great, or too much fuel is employed, the materials clot together and much of the benefit otherwise obtained is thus lost. Calcination is often conducted in open heaps, or between rectangular walls, exactly as in the case of many ores of other metals; but these methods are costly in fuel, space, and labour, and are apt to give irregular results, so are chiefly used for roasting tap-cinder in Staffordshire, or the black bands of North Staffordshire and Scotland, in which latter case the ore itself contains the necessary fuel. Kilns are now very generally employed for calcining, and in the Cleveland district the use of large circular kilns, constructed of iron lined with firebrick, is almost universal. In such kilns the ore and fuel are charged in at the top, and the calcined material removed from the bottom, the operation being continuous; in such kilns calcination is well under control, fuel is economised, and labour is saved. Rectangular kilns, fired with surplus gas from the blast furnace, have been introduced both in the United Kingdom and elsewhere.

Production of pig iron.—The ore, having if necessary been prepared as before described, is now *smelted* in the *blast furnace* to produce pig iron. For this purpose it is introduced at the top of the furnace together with the *flux* necessary to form a fluid slag (or 'cinder') with the gangue of the ore; *fuel* is also added in sufficient quantity to melt the materials and to reduce the iron. The air necessary for combustion is introduced near the bottom of the furnace, having been blown, and usually also heated, by suitable appliances. The operation is continuous, a furnace frequently working without any important stoppage for a number of years. The whole of the materials introduced into the furnace have either to be melted and flow off from the bottom as iron and cinder, or to be converted into vapour and pass off as 'waste gases' from the top.

The blast furnace.—The earliest form of blast furnace is shown in Fig. 1, which represents a form employed on the Continent for the production of wrought iron about 500 years ago. After the furnace had been heated, ore and fuel were introduced at the top, and blast from below; the result was the production of a bloom of wrought iron, which, owing to the low temperatures of such furnaces, was never melted, but was removed by taking down the brickwork at the front of the furnace. Doubtless in some of the larger furnaces of this description cast iron would sometimes be accidentally obtained, and as the value of this material for castings, and for the direct production of wrought iron by means of the finery came to be recognised, cast iron would be regularly made. This change was probably introduced early in the 16th century, and the furnaces gradually increased in size until they were capable of producing about 20 tons of pig iron per week, using charcoal for fuel. About 180 years ago coke was introduced as fuel in the blast furnace, and the size and production were slightly increased. Since this period enormous changes have been introduced, commencing with the use of coke about 1735; of hot blast in Scotland in 1829; the adoption of round and larger hearths in South Staffordshire about 1835; the utilisation of the waste gases; the largely increased height and capacity adopted in the Cleveland district shortly after 1860, and the use of hot blast stoves on the regenerative principle. A remarkable development took place in West Pennsylvania about 1890, and as a result of easily reducible ores, smaller and steeper furnaces, higher blast pressure, and increased engine power, a weekly production of nearly 5000 tons of pig iron per furnace has been attained. Fig. 2 represents a Cleveland blast furnace, the height of which would be about 80 feet, its capacity about 25,500 cub. ft., and the weekly production of pig iron varying from 500 to about 1000 tons, according to the character of the ore used, the temperature and pressure of the blast, and other circumstances. Such a furnace is closed at the top by means of the 'cup and cone' arrangement, into which the materials are charged, and delivered into the furnace at suitable intervals by lowering the moveable cone. The combustible gases are conducted by means of suitable pipes to the regenerative stoves employed for heating the blast, or to the boilers required for raising steam for the works. A portion of the gases is carefully cleaned from dust and used for power purposes in gas engines. The furnace itself is very light in construction for so large an erection, which

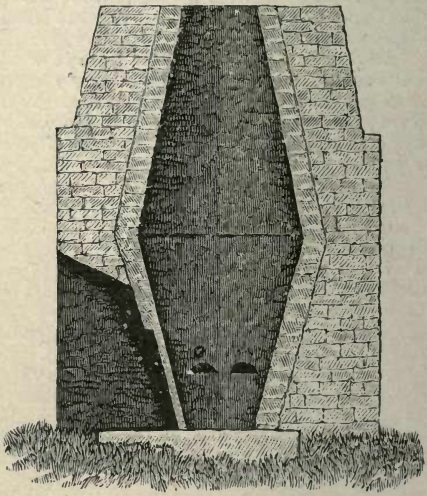


FIG. 1.

is intended to contain a great weight and to resist a very high temperature. The outer casing is of iron plates riveted together, and the furnace is lined with refractory firebrick. The blast is delivered into the furnace by about six twyers, which are connected with the hot blast main, and which are water-jacketed where they enter the furnace to prevent them being rapidly destroyed by the high temperature. The following summary will illustrate the nature of the products, and the approximate weight of the charges employed for the production of 1 ton of No. 3 Ormesby (Cleveland) hot blast pig iron :

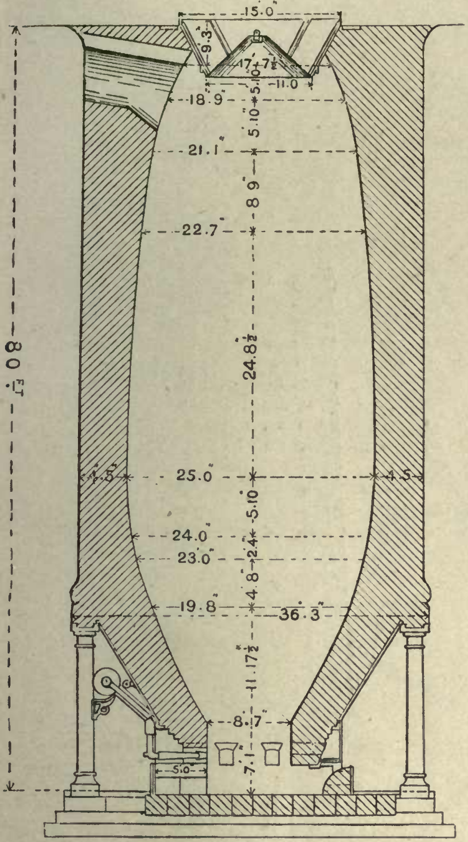


FIG. 2.

Charge	cwt.	Products	cwt.
Calcined iron stone	48	Iron . . .	20
Limestone . .	12	Slag . . .	30
Hard Durham coke	20		
Blast . .	100	Waste gases .	130
	9 tons		9 tons

In working richer ores, such as hæmatites the amount of limestone and ore employed would be less than the quantities required in the Cleveland district, and the weight of slag would be proportionately diminished. To prepare a No. 1 pig iron the quantity of fuel used would be somewhat greater, whilst with a No. 4, or a white iron, rather less fuel would be required ; the weight of the blast and of the waste gases would vary correspondingly. Usually the only material added as a flux is limestone, which is sometimes burnt before being charged into the furnace. Other fluxes are often indirectly added in the form of iron ores rich in argillaceous or aluminous matter, as mixtures of ore are frequently made to obtain a more fusible cinder. The fuel most generally used is hard coke, free from sulphur, and with as little ash as possible. Raw bituminous coal is used in Scotland and North Staffordshire and in parts of the United States, though lower furnaces are necessary as the fuel is more friable. Mixtures of coal and coke are not uncommon, and anthracite is employed in Eastern Pennyslvania. Charcoal is still used on the Continent in Sweden and in some parts of America (particularly Michigan) for the production of a superior class of iron where coal is scarce.

Any moisture which is present in the blast is decomposed in the furnace hearth, with the formation of hydrogen and carbon monoxide, and absorption of heat. Hence blast furnaces work better and more economically in cold dry weather. Gayley has successfully introduced a method of drying the blast, by refrigeration, before it is passed into the hot blast stoves. With large installations this leads to greater regularity of composition, increased output, and lower fuel consumption.

The chief changes which take place in the blast furnace may be briefly summarised as follows. The ore in the first part of its descent is rapidly heated to low redness, at which temperature the carbon monoxide, which at this point forms about 36 p.c. of the furnace gases, reduces the ferric oxide to metallic iron ; thus

$$Fe_2O_3+3CO=Fe_2+3CO_2.$$

The iron is not melted at this low temperature, but remains as a metallic sponge, which if brought in contact with the air would rapidly burn, and so reproduce ferric oxide. At a part of the furnace slightly lower than that at which reduction is chiefly accomplished the limestone is decomposed, carbon dioxide being evolved and lime produced ; thus $CaCO_3=CaO+CO_2$. During the next stage of the process, which occupies more time than either of the others, the materials gradually descend to the boshes of the furnace, and in so doing absorb heat from the ascending gases. Carbon in a state of minute subdivision produced by the reduction of carbon monoxide, is also deposited in the pores of the spongy iron, which becomes more and more carburised as it descends to the hotter parts of the furnace where fusion takes place. In passing from the boshes to the hearth the temperature is sufficiently high to cause the combination of the silica in the gangue with the lime, alumina, and other bases in the charge, and thus to form a fluid cinder, which separates from the now molten iron, the latter sinking to the bottom of the hearth, while the slag, on account of its relative lightness, floats on the top. The cinder is either tapped off at intervals, or is allowed to flow regularly off through what is known as the 'slagging hole.' The iron is allowed to accumulate, and is then tapped off from a lower point, usually at intervals of about 12 hours, into moulds roughly made in sand. The product is cast iron, but on account of its being cast in long pieces of section, which are called 'pigs,' and which generally weigh about 1 cwt. each, this variety of cast iron is commercially known as pig iron.

Chemical Properties of Cast Iron.

The metal obtained as just described is by no means pure metallic iron, but usually contains at least 5 p.c. of other materials, such as carbon, silicon, sulphur, phosphorus, manganese, chromium, &c., &c. The element which imparts the characteristic properties to cast iron is *carbon*, which is present to the extent of at least 1·5 p.c. Under ordinary conditions the maximum amount of carbon found in pig iron is 4·25 p.c., but in the presence of much manganese this amount may be considerably exceeded. The carbon is present in cast iron in two distinct conditions, known respectively as 'graphitic' and 'combined.'

Iron and carbon unite to form a definite carbide Fe_3C, and it is probable that in molten cast iron the carbon exists in solution in this form. This carbide is retained in solution if the metal is rapidly cooled, but on slow cooling, or conversely by long heating to a temperature of 900°, the carbide decomposes into the more stable condition of iron and graphite. Silicon assists the decomposition of the carbide. The graphite is of two kinds, primary and secondary. Primary graphite is formed at about 1050°, and occurs in relatively large flakes; it causes the iron to be soft and weak. Secondary graphite or 'temper carbon' is produced by decomposition of the residue of the carbide at a lower temperature (700°–800°). It is smaller, more evenly distributed, and the metal is soft but strong. The carbide may exist in solid cast iron in two forms, one of which separates at about 680° (the recalescence point), and can be seen by the microscope. The other is retained in solution at the ordinary temperature, and hence cannot be seen in micro-sections. The latter is sometimes called 'missing' carbon, as it is not determined in the ordinary Eggertz colour test.

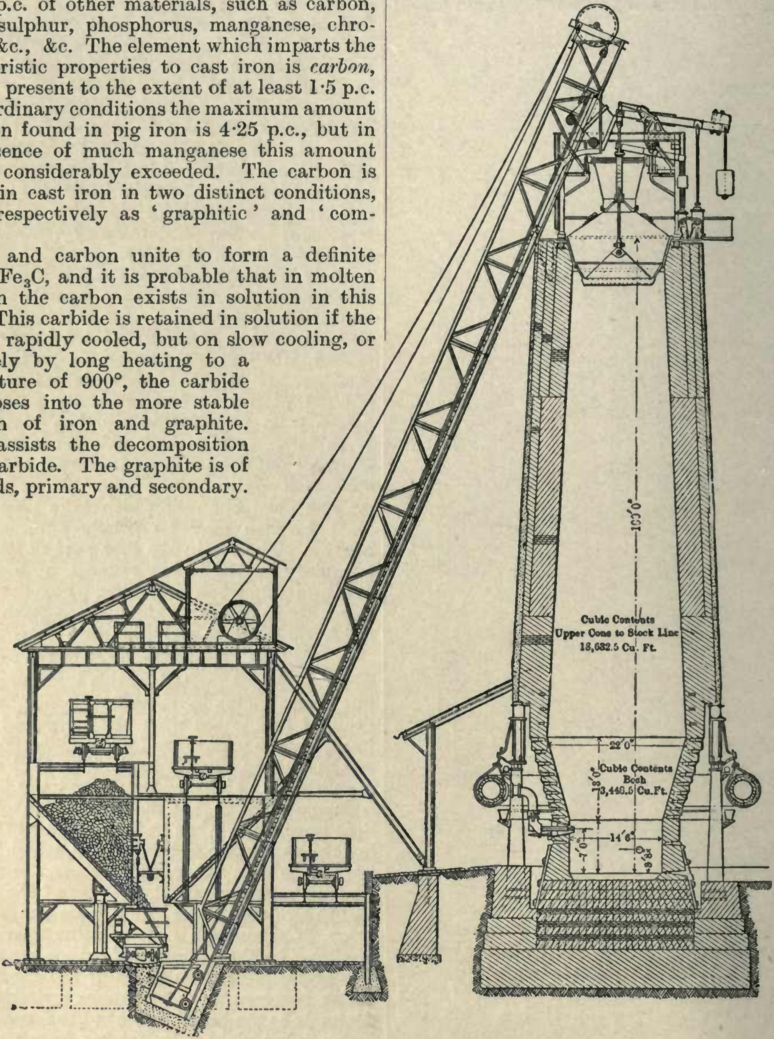


Fig. 3.—Modern American Blast Furnace with Mechanical Charging.

Graphitic carbon renders the iron *grey* in fracture, soft to the tool, and capable of taking a sharp impression of a mould. Combined carbon gives a *white* fracture, the metal is very hard, it melts at a lower temperature, but is never so fluid as in the case of grey iron. Graphitic carbon may be separated from the metal either by mechanical or chemical processes, and may be obtained in either of these ways in a state of great purity. Combined carbon, on the other hand, cannot be mechanically separated from cast iron; whilst if white iron be treated with an acid, such as hydrochloric or sulphuric, the carbon passes off in the gaseous condition, with the hydrogen evolved, in the form of badly smelling hydrocarbons. The graphitic carbon, on the other hand, would in a similar case be left behind in the insoluble residue. Iron which contains combined and graphitic carbon in nearly equal proportions has a characteristic fracture, and on this account is called 'mottled' iron. Slow cooling produces grey iron, while rapid cooling, or 'chilling,' produces white iron.

Silicon is always present in cast iron, the amount varying from about 0·2 p.c. in specially pure Swedish iron, to upwards of 18 p.c. in some varieties of 'silicon pig,' which are specially prepared for certain purposes. The average is probably from 1 to 4 p.c. When present in large proportions silicon renders the pig hard, weak, and brittle; it is also quite unsuitable for use in the puddling furnace on account of the waste of time and the injury to the lining of the furnace. Silicon, however, renders cast iron soft, strong, and grey when present in suitable proportions; and silicious irons have been largely used in the foundry on this account, as they allow of the use of larger quantities of foundry scrap, which is white and hard. They also allow in many cases of the employment of cheaper irons in foundry mixtures (Turner, Chem. Soc. Trans. 1885, 577, 902; 1886, 130). For such purposes the amount of silicon should vary from about 0·8 to 3·5 p.c., according to the size and character of the work; the lower value would be employed for chilled rolls or other purposes where crushing strength is desired, whilst the higher value would be preferred where fluidity and softness are necessary. In the blast furnace high temperatures and silicious slags favour the absorption of silicon.

Sulphur is generally present only in very small quantities in good cast iron. With much sulphur the metal is white, hard, and unsound in the foundry; and if converted into wrought iron or steel the product is red-short, and useless. In the blast furnace hot working, a slag rich in lime, and the presence of either silicon or manganese in the metal, prevents the absorption of sulphur.

Manganese is always present in pig iron; its reduction is favoured by hot working and basic slags. *Spiegel-eisen* is a white iron, containing upwards of 5 p.c. of manganese. With 20 p.c. of manganese or upwards, the metal is known as *ferro-manganese*; it frequently contains as much as 86 p.c. of metallic manganese. Both spiegel-eisen and ferro-manganese are used in steel-making, as additions at the end of the operation, the object being to add a little manganese to the bath of metal to prevent red-shortness.

Pig iron, which contains manganese, is generally low in sulphur; this fact has been applied to the production of a special pig for use in the basic process, where both sulphur and silicon are required to be present in small quantity.

Sulphur is removed from fluid cast iron for steel making by the use of 'metal mixers,' which are large vessels or furnaces capable of holding about 250 tons of fluid metal. If the iron does not already contain sufficient manganese that element is added, and manganese sulphide separates and passes into the slag. The desulphurised metal is drawn off as required and fresh iron added, so that the process is simple and continuous. Metal mixers also equalise the content of silicon, and this element may be considerably reduced in quantity by adding oxides of iron to the mixer slag.

Phosphorus varies from 0·02 in best Swedish or hæmatite iron to upwards of 3 p.c. in common cinder pig. In the case of each of the elements previously considered only a portion of that which is present in the blast furnace charge passes into the metal, but with phosphorus practically the whole of that which is present in the materials used passes into the pig iron. For foundry and forge purposes probably a little phosphorus is actually beneficial in cast iron; but in the case of wrought iron or steel its presence is highly prejudicial, as it produces remarkable brittleness in the metal when cold. Hence in the manufacture by the ordinary or 'acid' process, of either Bessemer or Siemens steel, only such pig iron as is free from phosphorus may be employed, since by the acid process no phosphorus is removed. For irons containing phosphorus the 'basic' process must be employed if they are to be converted into steel (*v. infra*, p. 171). A selection of representative analyses of cast iron will be found in Tables at the end of this article.

Grades of pig iron.—For a great number of uses pig iron is sold by the appearance on fracture. A pig which is very grey, with large crystals, is called No. 1; if the fracture shows smaller crystals it is called No. 2; with still closer grain it would be sold as No. 3 or 4. If white and grey are mixed it is called mottled; when graphitic carbon almost entirely disappears it is called white. On account of their softness and fluidity Nos. 1, 2, and 3 are chiefly employed for foundry purposes, and usually command a somewhat higher price. No. 4 is largely used in the puddling process, and would be called a forge or 'strong' iron. No. 4 is also employed in mixtures in the foundry when heavy castings are required, or when the metal is to be chilled —*i.e.* when the surface is to be rendered white and hard by cooling in contact with a mass of metal, technically known as a 'chill.' Mottled and white irons are chiefly used in mixtures of pig iron to give hardness, strength, or density.

Foundry practice.—The ironfounder commonly employs a mixture of irons, and it is the custom to mix not merely different grades of iron, but also metal from different localities. This originated at first from the results of practical experience, but it has since been shown in many cases to be in accordance with scientific knowledge, as the best foundry iron for any particular purpose contains a certain proportion of combined and graphitic carbon, silicon, phosphorus, &c. (Turner, Journ. Iron and Steel Inst. 1886), and these constituents can usually be best regulated by mixing together the irons obtained from different localities. If special strength is required the silicon should not exceed about 2 p.c., and the phosphorus should be somewhat less than half that quantity. But if softness and fluidity are specially desired these amounts may frequently be nearly doubled without serious injury. The metal is melted in a small blast furnace called a cupola, which is constructed of iron plates, lined with firebrick or ganister; it is circular in section, and is driven with a low-pressure cold blast, introduced through twyers near the bottom. The metal is charged from the top, the fuel used being hard coke free from sulphur; the weight of coke varies from about 5 to 15 p.c. of the metal used, being higher with smaller outputs. A small quantity of limestone is added to act as a flux. The metal on melting runs down, accumulating in the bottom of the cupola below the twyers, and is then tapped off at intervals into suitable ladles. For special qualities of castings, melting is sometimes performed in a reverberatory furnace; this is more expensive, but gives a cleaner and more uniform metal, which can, if necessary, be tested before use. For the majority of purposes 'green sand moulding' is adopted, a pattern being first prepared and an impression obtained in fine sand, which has been previously mixed with a small proportion of carbonaceous matter, such as coke dust. For special work, or intricate forms, other varieties of moulds are prepared, which are often of loam; these are supported by masonry, and braced with tie rods, &c., as may be found necessary. Such moulds are carefully dried before being used; in some cases drying is performed in stoves at a low red heat, in other instances by means of a fire which is placed inside the mould. In the latter case gaseous fuel is commonly employed. Green sand moulds are not dried before use; where they can be employed they have the advantages of rapidity and economy.

Iron, when remelted in the foundry, becomes harder, owing to the elimination of silicon and the absorption of sulphur. Hence in some cases, when the metal is originally too soft, a great improvement is noticed on remelting several times; but in other cases no improvement is observed, and frequently deterioration results. Many observers, among them Sir W. Fairbairn (Brit. Assoc. Report, 1853, 87), have stated that iron is improved by remelting a certain number of times, and that afterwards by further melting it again deteriorates. But the experiments of various observers gave very conflicting results in this direction, some recommending very few meltings, others a larger number. It has been shown by Turner (Chem. Soc. Trans. 1886, 493) that the effect formerly attributed to the operation of remelting is really due to the chemical changes which take place during that operation, and that the chemical composition of the product, when rightly understood, gives an indication of its mechanical properties.

Production of wrought iron.—It has already been mentioned that by the earlier processes wrought iron was produced directly from the ore. Similar processes are still carried on by semi-civilised races in various parts of the world, and in an improved form direct reduction is still practised in parts of America where charcoal is cheap, and where no ready means of transit exist. Many attempts in the same direction have also been made in various parts of Europe. In several instances great expectations have been raised in connection with these suggested improvements, but none of them has met with much commercial success. In these methods of reducing the iron ore the temperature employed is usually not sufficiently high to melt the metal obtained; the phosphorus present in the ore remains in a great measure in the slag, which is rich in oxide of iron, and the wrought iron obtained even from moderately phosphoric ores, is still sufficiently pure to be useful. The direct method is usually extravagant both in fuel and labour, whilst the slags produced frequently contain sufficient iron to make them valuable for use in the blast furnace.

Wrought iron is now generally prepared by an indirect process, cast iron being produced as an intermediate product between the ore and the finished metal. The impurities of the crude pig iron are then removed by oxidation, and pass away either in the form of gas, as with carbon, or, like phosphorus, silicon, and manganese, remain in the slag. This purification was originally performed in small hearths called 'fineries,' and for the production of specially selected metal these have survived in isolated places to the present day. But a most important change was introduced in 1784, when Cort patented the puddling process, in which the operation of purification is conducted in a reverberatory furnace. In Cort's original furnace the working bottom was made of sand, and white pig iron was employed; the iron never became perfectly fluid, and from the pasty character of the metal the 'puddling' process derived its name. This original form of the process has now almost entirely given way to what is known as 'pig boiling,' in distinction from the earlier 'dry process.' Pig boiling was introduced by Joseph Hall, of Tipton, Staffordshire, about 1820. In principle the operation is exactly the same in either case; in practice the chief differences are in the construction of the furnace, the materials forming the bottom, and the kind of cast iron employed. In the more modern process (which, however, is gradually being replaced by the use of 'mild steel') the furnace bottom is constructed of cast-iron plates, and the bridge is internally cooled either by air or water; the cast-iron bottom plates are covered with a layer of oxide of iron about 3 inches thick, which forms the working bottom of the furnace; the sides are formed of fettling, also consisting essentially of oxide of iron; the metal used is a grey iron, usually what is known as a No. 4 forge quality. The result of these changes is that the furnace works with fewer repairs; that, owing to the use of oxidising fettling, the operation is conducted more rapidly, and larger charges can be employed; whilst, as grey iron is used, the metal is perfectly fluid when melted, and 'boils' vigorously during the elimination of the carbon. A sketch of the furnace is given in Fig. 4.

The operation is conducted as follows. The furnace being at a red heat from the previous charge, the fettling is repaired, as necessary, by the addition of 'bull-dog,' pottery mine, hæmatite, or other forms of oxide of iron. About 4 or 4½ cwts. of pig iron are then charged on to the bed of the furnace, the door being closed and the temperature raised while melting proceeds. After about 30 minutes the iron is generally melted, and is then kept fluid and well rabbled for about 10 minutes, the length of time depending very much on the composition of the metal employed. By this time practically the whole of the silicon will have been removed, and much of the manganese. The temperature is then lowered somewhat, by regulating the damper, and a violent reaction ensues between the oxygen of the fettling and the carbon in the metal. The iron boils vigorously owing to the escape of carbon monoxide, which burns in jets at the surface, and a quantity of slag, called tap cinder, is removed, part of this being allowed to boil over the fore plate of the furnace, and the remainder being tapped out at the end of the operation. The phosphorus gradually passes out during the process, being eliminated most rapidly at this stage, and passing into the tap cinder. After the boiling stage is over the metal 'drops' and 'comes to nature'—*i.e.* granules of malleable iron gradually separate, and the whole becomes quite pasty. In this condition it is 'balled up' by the puddler into blooms, each of which is somewhat under 100 lbs. in weight. These are then hammered and rolled, forming 'puddled bar,' which is not yet fit to be sent into commerce. The whole operation of puddling usually occupies about 70 minutes. Analyses of forge irons, puddled bar, &c., are given in Tables at the end of this article. The puddled bar is cut up into lengths and made into suitable bundles called 'piles,' which are reheated in a furnace, which is larger but otherwise very similar in construction to that in which the puddling operation is conducted. The piles are withdrawn at a welding heat, and hammered or rolled to produce merchant iron, best iron, best best iron, &c., according to the quality and the amount of work expended on the material. A number of attempts have been made to introduce mechanical contrivances to replace the laborious process of puddling; but, after numerous trials, these have been almost entirely abandoned in this country, though a revolving furnace invented by Danks was successfully used in America. Wrought iron was formerly used for ship building, bridge construction, rails, armour plates, and similar purposes, for which it has since been replaced by steel. Wrought iron is now chiefly employed for purposes which require a reliable metal which can be easily welded or otherwise worked by the smith. It is also used for tubes, wire, sheets, and fittings which are exposed to atmospheric oxidation.

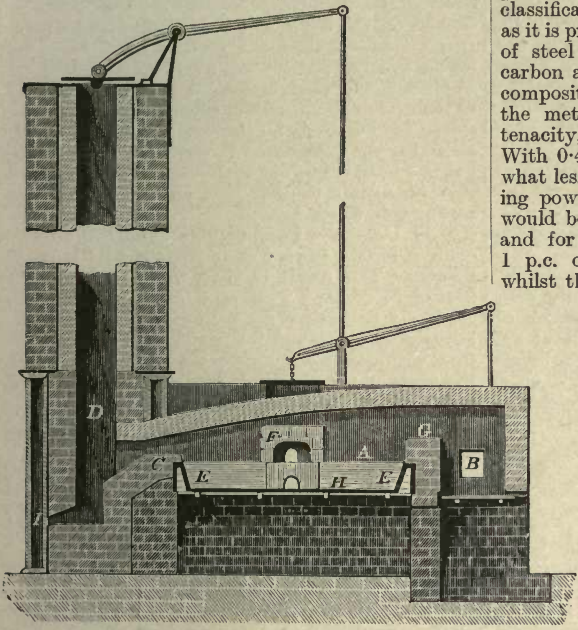


FIG. 4.—THE PUDDLING FURNACE.

A, Furnace bed; B, Firing hole; C, Flue; D, Chimney; E, Fettling; F, Working door; G, Fire bridge; H, Cast-iron bottom plate.

Steel. Steel was formerly defined as a variety of iron which contained from 0·5 to 1·5 p.c. of carbon, and which was capable of being hardened and tempered. This definition, however, has now to be extended so as to include various forms of 'mild steel' which contain under 0·5 p.c. of carbon, and which cannot be hardened. We therefore include under the designation of 'steel' all metal which, though containing under 0·5 p.c. of carbon, has been produced in the molten condition. In such a classification wrought iron is obviously excluded, as it is produced in a pasty form. The characters of steel depend largely on the proportion of carbon and other elements which enter into its composition. With low percentages of carbon the metal possesses great ductility, moderate tenacity, and very slight power of hardening. With 0·45 p.c. of carbon the ductility is somewhat less, the tenacity greater, whilst its hardening power is quite appreciable. Such a metal would be employed in the manufacture of rails and for similar purposes. With from 0·6 to 1 p.c. of carbon the ductility is still lower, whilst the tenacity reaches upwards of 40 tons per square inch of section, and a metal is obtained which can be readily hardened and tempered. This class of steel is largely used for cutting tools, drills, dies, &c., and for best purposes is still usually produced in crucibles. With carbon from 1 to 1·5 p.c. a steel is obtained which is suitable for the hardest tools, and which requires to be very skilfully hardened and tempered. As the proportion of carbon increases, the steel requires to be worked at a somewhat lower temperature. With upwards of 1·5 p.c. of carbon the metal is brittle, is no longer capable of being hardened, it is more fusible, and thus gradually passes into cast iron. Hardening increases the tenacity of steel, but diminishes its ductility. The tenacity of steel, like that of wrought iron, is also increased by the amount of work done in rolling or in drawing out the metal into wire, and certain varieties of steel wire are prepared which have a tensile strength of upwards of 100 tons per square inch. The presence of manganese in steel increases its tenacity; in suitable proportions it also very materially improves the working properties of the metal, and on this account is employed both in crucible steel making and in the Bessemer and Siemens processes. In large quantities manganese renders steel permanently harder, and also causes it to be unmagnetisable (Hadfield). 'Manganese steel' contains about 10 p.c. of manganese. It is permanently hard, and is used chiefly in the form of castings for tramway points, stamp batteries, and many similar purposes. Phosphorus renders steel cold-short, and should on this account not exceed 0·1 p.c., whilst crucible steel of special quality usually contains not more than 0·04 p.c. of phosphorus.

Sulphur renders steel red-short, and should never exceed a few hundredths per cent. Silicon in the absence of any reducing agent forms silica, which renders mild steel red-short and brittle, although the presence of manganese very much modifies these effects, so that with about 0·5 p.c. of manganese several tenths per cent. of silicon may be present without injury. In steel castings about 0·3 p.c. of silicon is frequently added to promote soundness. Arsenic renders steel both hot- and cold-short; practically the whole of the arsenic present in the blast furnace charge passes into the pig iron, and is not removed during conversion into steel (*v.* Stead, also Harbord & Tucker, Jour. Iron & Steel Inst. 1888, part 1). Chromium in small quantities gives increased tenacity, and on this account is frequently added to basic or other very mild steel so as to impart greater strength. With considerable proportions of chromium the welding power of steel is much reduced. Chromium is added to steel shells as the penetrating power is thereby greatly increased. Aluminium is frequently used for addition to fluid steel for deoxidising purposes. It assists in the production of solid ingots, and prevents segregation of the impurities. The amount of aluminium left in the steel is, however, so small as to be with difficulty estimated by analysis. Nickel is added to mild steel for shipbuilding and constructional purposes, usually to about the extent of 3·5 p.c., as it imparts increased tenacity with unusual ductility. With higher proportions of nickel hard non-magnetic alloys are obtained, which are only used for certain special purposes. In recent years tungsten has been used on a very considerable scale for the production of self-hardening and other 'special' steels. Usually about 6 or 7 p.c. of tungsten is added; the steels are made in crucibles, and contain from 1 to 2 p.c. of carbon. Vanadium is also added to mild steels with marked advantage, a very small percentage giving improved physical properties. Much attention is now being devoted to the production of special alloy steels for a variety of purposes.

Manufacture of steel.—A variety of steel, or more correctly steely iron, was obtained by the earlier processes used for the production of wrought iron directly from the ore, when the process was modified by altering the amount of blast used, and the angle at which it was introduced, together with a slight increase in the quantity of fuel employed. By these means the metal prepared contained sufficient carbon to impart steely properties, although when obtained by such methods the steel is never of uniform quality. A steely iron was also frequently prepared in the puddling furnace when the process was carried on in such a manner as to remove the metal before the carbon was completely eliminated. But for some centuries at least the best varieties of steel have been prepared by what is known as the 'cementation' process. For this purpose, bar iron of the best quality is cut up in suitable lengths and placed in charcoal in the cementation furnace. This furnace consists essentially of two rectangular chambers which are constructed of firebrick, and are arranged to contain the iron and charcoal. The charge of iron used in one operation is generally about 15 tons. A fireplace under the chambers supplies the necessary heat, whilst the whole is contained in the base of a large conical chimney stack. The iron is carefully arranged and surrounded with charcoal, the rectangular chests, which are open at the top, being covered with 'swarf' to protect the contents, as far as possible, from oxidation. The heat is continued for about 7 days, although the time will vary somewhat with the temper required and other circumstances. The progress of the operation is judged by the appearance of the fracture of trial bars, which are removed and examined from time to time. The product is known as 'blister' steel, the name being derived from the characteristic appearance of the surface. Percy has shown that this is probably due to carbon monoxide evolved at a high temperature by the action of carbon on the oxygen of the intermingled slag. In good blister steel the protuberances should be as evenly distributed as possible. When fractured, the blister steel is generally found to consist of an outer crystalline layer of steel surrounding an inner portion of less altered iron. The exact theory of cementation has not been made out with certainty, although Roberts-Austen showed that pure iron became carburised when heated with a diamond *in vacuô*; but under usual conditions carbon monoxide is known to play an important part in the process. The result is that the metal, when heated in contact with solid carbon, becomes gradually carburised on the outside, and if the heating be continued for a sufficient length of time, carburisation gradually extends throughout the whole of the mass. Blister steel, when piled and reheated, is known as 'shear' steel, and gains considerably in uniformity by the treatment. The name is derived from the fact that shears used for cutting woollen cloth were formerly made of this variety of steel. But for best steel for tools and other purposes it is usual to employ 'cast steel,' the best qualities of which are prepared by melting blister steel in clay or plumbago crucibles. The charges usually weigh somewhat less than 100 lbs., a little glass or other flux is employed, and the crucible is kept covered while melting proceeds. Heating is conducted usually in wind furnaces, using coke as fuel, though gaseous fuel has also been employed. It is contended that gaseous fuel has the advantage of being more under control; it is also economical in working, and enables the process to be carried on continuously, whilst the wind furnace 'clinkers' up and has to be stopped for cleaning. Cast steel is also prepared in crucibles from materials other than blister steel, but the product is usually of an inferior character. It is found advantageous (especially with cheaper mixtures) to introduce a little manganese in the production of crucible steel, as the metal then possesses better working qualities. The 'body,' which is so characteristic of good steel, appears to be closely connected with its chemical composition, and is associated with special freedom from phosphorus and similar impurities. Crucible steel contains a few hundredths per cent. of silicon, which is reduced from the silicious material of the crucible during the melting, and which appears to play an important part in producing solid castings. For special purposes, in recent years, considerable quantities of manganese, chromium, tungsten, and of other elements have been added to steel produced in the crucible, and the 'special' steel industry has become important both in this country and abroad.

Bessemer steel. The method of producing steel with which the name of Bessemer will always be connected, and which has done so much to revolutionise the iron trade of the world, was described and patented in 1856. At first great incredulity was manifested by ironmasters, and the product was inferior; but when it came to be recognised that only iron free from phosphorus could be employed in this process, and that the red shortness which at first had been so difficult to overcome could be removed by the addition of manganese before tapping the metal, the success of the process was assured. The iron now used in the ordinary, or as it has come to be called the 'acid' Bessemer process, is of special quality, and is made from ores of hæmatite quality. It should contain only a few hundredths p.c. of phosphorus, and about 1-3 p.c. of silicon. With rapid working, as in the large American works, the silicon is about 1 p.c. lower than is the custom where fewer charges are run in the same time as in England. The metal is either remelted in a cupola or is run in the fluid state from the blast furnace, or the metal mixer, according to circumstances, but in any case is introduced in the molten condition into an egg-shaped vessel known as a 'converter,' and which has been heated either by a previous charge or by lighting a fire inside. The converter is constructed externally of iron plates, and is arranged so as to rotate on trunnions which are fixed on either side a little below the middle of the vessel. By this arrangement the converter can be readily manipulated as required during the process. At the lower part of the vessel is a moveable bottom, fitted with a blast box into which air is admitted during the 'blow' at a pressure of about 20 lbs. to the square inch. From the blast box the air enters the vessel through a number of holes passing through a fireclay or ganister bottom lining. The sides of the converter are generally lined by means of ganister (a silicious or 'acid' material) which is generally rammed into position. At the top of the converter, a little on one side, is an opening which serves for the introduction of the metal in the first place, then for the escape of waste gases during the blow, and lastly for the tapping of the metal and slag when the operation is concluded. The charge of pig iron, which weighs from about 8 to 12 tons, is introduced while the vessel is in a horizontal position, in order to avoid closing the twyers at the bottom; the blast is then turned on and the vessel rotated so as to cause the blast to rise through the bath of metal. The silicon present is rapidly oxidised and passes into the slag, at the same time producing sufficient heat, not merely to maintain the fluidity of the metal, but actually to very much increase its temperature. After the silicon has in this manner been removed, which generally occupies about 10 minutes, the carbon is attacked, and this is rendered evident by a marked increase in the size and luminosity of the flame produced. This flame continues for rather more than 10 minutes, and then, when the carbon has been burned out, suddenly 'drops,' *i.e.* becomes much smaller and less luminous, showing that the operation is concluded. During the whole of the blow the metal remains molten, and the temperature produced by the combustion of the carbon and silicon is so great that the resulting decarburised metal can be readily poured into suitable ingot moulds. But if used in this form, when it is almost perfectly freed from carbon and manganese, the metal would be red-short, and would also be too soft for many purposes. It is usual, therefore, after the flame has dropped, to add a quantity of spiegeleisen or ferro-manganese in order to counteract this red-shortness and to introduce the required amount of carbon. After the requisite addition has been made the metal is allowed to stand a few minutes so as to some extent to mix the constituents; it is then 'teemed' into the ladle and thence cast into ingots.

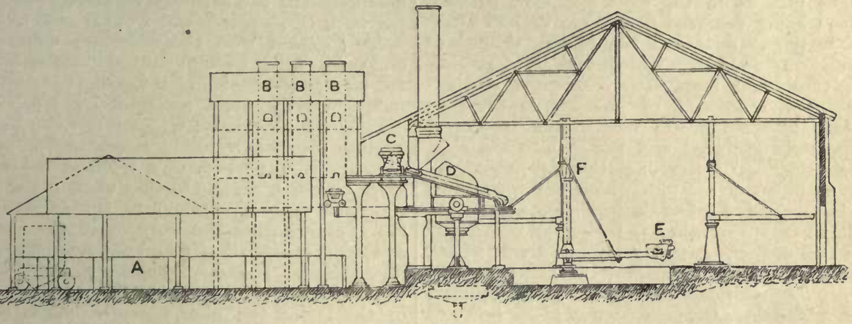


FIG. 5.

A, Shop for preparing Basic Lining; B, Cupolas for calcining Dolomite and remelting Iron; C, Ladle for Cast Iron; D, Bessemer Converter; E, Steel Ladle; F, Ladle Crane.

The basic Bessemer process.—It will be noticed that in the original Bessemer process the vessel is lined with silicious or acid materials, and only cast iron free from phosphorus can be employed, as practically none of this element is removed during the blow. But a modification of the process was introduced by Messrs. Thomas and Gilchrist, which most successfully solved the problem of the treatment of phosphoric iron. Fig. 5 (after A. Holley) shows the general arrangement of a basic Bessemer works. The mechanical arrangements of the plant and general principles involved in the two processes are exactly alike, with the exception that the lining used in the basic process is a mixture of lime and magnesia, obtained by calcining dolomite. This is mixed with dry tar in suitable proportions so as to make it bind, and is then either rammed into shape with hot tools, or pressed into bricks and baked as may be most convenient. The cast iron used should be as low in silicon as possible, on account of the injurious action of a silicious slag on the basic material of which the lining is composed. The phosphorus, on the other hand, may be as high as 3 p.c. without exerting any injurious effect on the finished product. To ensure low sulphur while the silicon is also low, about 1·5 p.c. of manganese is usually introduced into the iron. In modern works the proportions both of silicon and of sulphur are reduced and rendered more uniform by the use of a metal mixer. The 'blow' is conducted in the early stages just as in the acid Bessemer process, silicon being removed first while carbon afterwards passes out, and the flame 'drops' as before. Lime is then added, and an after-blow is given, which lasts some 5 minutes, depending on the amount of phosphorus present; during this stage the phosphorus is almost completely removed and passes into the slag. The progress of the operation is judged by means of small samples which are withdrawn and examined at intervals during the after-blow. When ready, the metal is tapped as usual, and the product is a specially mild and soft metal. The slag is used, when ground to fine powder, as a phosphatic manure; it has also been used as a material for the construction of the bottoms of reheating furnaces (Harbord and Tucker's patent). The basic Bessemer process is applied on a large scale in this country, but is used still more extensively on the Continent, especially in the large steel works in the district around Düsseldorf on the Rhine.

In Bessemer's earlier experiments small converters were employed; some of which were moveable, whilst others were fixed. Both of these forms have been recently reintroduced, and small converters have met with considerable favour for special purposes, particularly for the production of steel castings.

Siemens steel. Numerous attempts have been made to prepare steel by decarburising cast iron by some method other than that previously described; but the only successful rival to the Bessemer process was originated by the late Sir William Siemens. The invention of the Siemens furnace, with the accompanying gas producers and regenerators, placed in the hands of the practical man the successful application of a beautiful scientific principle which has been largely used in many branches of manufacture, such as the production of glass, porcelain, and pottery; for the reheating of iron and steel, and for numerous other purposes. Space will not here allow of the description of the apparatus, and it will only be necessary to mention that by this means a temperature can be easily and economically obtained, which is amply sufficient to melt wrought iron, and to enable it to be readily poured when melted. Apart from the method used in heating the furnace, the Siemens-Martin process (which was invented by Siemens, and rendered commercially successful by Martin) closely resembles in principle the original puddling process. The furnace is of the same general shape as the puddling furnace, but is capable of working a charge of from 5 to upwards of 50 tons. The external portions are of cast iron lined with very refractory silicious firebrick, while the working bottom is of refractory sand. The pig iron to be used is charged first, and the malleable iron and iron ores which are added to decarburise the pig iron are introduced at suitable intervals during the operation, which generally lasts about 8–10 hours. Several modifications of the process have been introduced, it being convenient sometimes to omit either the malleable iron or the ore, whilst in some cases malleable iron or steel scrap only has been used (Martin's process). In any case, so long as a silicious lining is employed, the materials used must be as free as possible from phosphorus. The *basic process* is also conducted in the Siemens furnace, phosphoric pig iron, or similar metal from a mixer, being used, together with the necessary steel scrap and ore or other ferruginous oxidising materials. In larger establishments hand charging has now generally been replaced by mechanical appliances. For basic working the chief modification introduced is the substitution, for the ordinary silicious bed, of a working bottom of basic material, similar to that used in the basic Bessemer process. Quicklime is also added to the charge during the working of the heat so as to ensure a basic slag and the removal of the phosphorus. The open hearth process differs from the Bessemer basic process in that while in the latter the phosphorus remains in the fluid metal until practically all the carbon has been eliminated, in the open-hearth process, on the other hand, much of the phosphorus is removed during the earlier stages of the operation. If the acid Siemens furnace may be regarded as a large puddling furnace with gaseous fuel, working on Cort's original lines, except that the temperature used is sufficiently high to melt the resulting malleable iron and so produce mild steel, then we may consider the basic Siemens process as closely resembling the 'pig boiling' of more recent times, except that, as in the previous case, the operation is on a much larger scale and the product is in a molten condition.

As compared with the Bessemer process the Siemens, or as it is frequently called, the 'open hearth' process, possesses the advantage that it is more under control, and for this reason is frequently preferred when work of a specially uniform character is required; it is also more in favour for steel castings. Further, it permits of the use of considerable quantities of scrap, which is relatively cheap, and would otherwise be a drug on the market. It also gives a greater yield per ton of metal used. This extra yield often more than pays for the cost of fuel used. The Bessemer plant, on the other hand, gives more rapid working, and hence is preferred for large outputs. There is little doubt that equally good steel may be produced by either of the processes, though the pneumatic method requires very careful attention when special uniformity is desired. In the United

Kingdom the acid Siemens process is most important; in Germany the basic Bessemer is chiefly used; in America the two processes employed are the acid Bessemer for rails, &c., and the basic open hearth for structural materials. From the metal which is slightly too phosphoric to be used in the acid process an excellent steel is made in the basic open hearth furnace.

The Talbot process. In this important modification of the open hearth basic process a large tilting furnace of cylindrical form is heated at either end by gaseous fuel and regenerators. The vessel, which holds about 150 tons of fluid metal, is basic lined and a slag rich in molten oxides of iron is maintained. Some 20 tons of metal is added to the contents of the furnace and a reaction is set up as a result of which silicon, carbon, and phosphorus are removed, and fluid steel remains. Metal is run off into the ladle as required for the rolling mills, and fresh iron poured in from time to time. The process is thus continuous, and the furnace works from week to week without stopping. The fuel consumption is low, the yield good, repairs are diminished, whilst steel of excellent quality can be produced from phosphoric ores.

Malleable cast iron. For many purposes where a complex form is necessary, and only moderate strength is required, the articles are cast in green sand in the ordinary way, but a special variety of pig iron is used, low in silicon, phosphorus, and manganese. The castings so prepared are white, hard, and brittle; but when heated, in contact with oxide of iron, in covered cast-iron boxes, to a cherry-red heat for about 48 hours, they become grey and soft. The softness so developed is accompanied with considerable malleability, so that the articles can be readily worked under the tool and punched, planed, &c., as required. Malleable cast iron, however, will not weld like ordinary malleable iron. This process is chiefly conducted in this country in the Midlands, particularly at Walsall and Birmingham, and the heating in contact with oxide of iron is known technically as 'annealing.' A portion of the graphite is removed by oxidation, and the rest, having been thrown out of solution at about 900°, exists as secondary graphite, or 'temper' carbon. In recent years the malleable cast iron industry has reached very large proportions in the United States, the output being now about ten times as great as that of the United Kingdom. The castings are generally produced from metal low in sulphur and melted in the hearth of an acid Siemens furnace. The annealing occupies a shorter time, less graphite is removed by oxidation, and the product is known as 'black heart' castings.

Tin plates. In order to protect iron from oxidation it is frequently covered with a thin layer of metallic tin. This is chiefly applied to the protection of thin plates of iron, which are first rolled in the ordinary way, and, after a preparation (including 'pickling' in dilute sulphuric acid, annealing, and cold rolling) in order to obtain a suitable surface, the plates are immersed in a bath of molten tin which is kept covered with grease. In this way a thin coating of tin adheres to the surface of the iron and protects it from oxidation so long as the iron is completely covered. In case the tin is removed from any part of the surface, however, oxidation takes place more readily than in the original metal. For this reason galvanised iron is to be

ANALYSES OF PIG IRON.

Ore	Red hæmatite		Red mountain. Alabama		Northants. Brown hæmatite		South Staffordshire All Mine (clay iron stone, cold blast)							Clay, iron stone (Dowlais)
Analyst . .	Greenwood		Leutscher		Henry	Turner	Tucker							Riley
Variety . .	No. 1	No. 2	No. 1	Grey forge	Grey	Grey	No. 1	No. 2	No. 3	No. 4	No. 5	No. 6	White	No. 3 Cold blast
Graphitic carbon	3·045	2·579	3·49	3·00	1·150	2·65	3·30	2·68	2·55	2·14	1·90	0·55	0·20	3·10
Combined carbon	0·704	1·175	0·07	0·57	0·554	0·08	0·40	0·45	0·40	0·50	0·56	1·70	2·00	0·04
Silicon . .	2·003	1·758	3·15	1·50	1·900	2·95	1·88	1·72	1·92	1·33	0·97	0·89	0·71	2·16
Manganese .	0·309	0·130	0·25	0·19	0·414	0·40	0·40	0·54	0·40	0·25	0·52	0·46	0·50	0·50
Phosphorus .	0·037	0·038	0·68	0·64	1·807	1·84	0·71	0·68	0·52	0·56	0·51	0·48	0·47	0·63
Sulphur . .	0·008	0·014	0·005	0·06	0·395	0·06	0·02	0·04	0·07	0·09	0·12	0·16	0·19	0·11
Metallic iron .	93·800	94·304	—	—	93·780	92·02	93·29	93·89	94·13	95·13	95·42	95·76	95 93	93·46

Ore	Carron Black band	Cleveland iron stone			Cinder	Dannemora magnetite	—	Mixed	Spanish	Cleveland	Carbonaceous
Analyst . .	M'Alley	Stead			Tucker	Henry	Tookey	Turner	Turner	Stead	Fleming
Variety . .	No. 1	No. 3	Forge	Mottled	Soft grey	White	Spiegeleisen	Silicon spiegel	Silicon pig	Silicon pig	Ohio softener
Graphitic carbon	3·00	3·70	3·40	2·90	2·90	—	} 5·04	1·71 {	1·12	3·15	2·85
Combined carbon	0·50	0·30	0·25	0·75	0·25	4·20			0·69	0·01	0·30
Silicon . .	1·96	2·50	2·10	1·00	2·84	0·08	0·41	8·72	9·80	4·48	5·90
Manganese . .	1·71	0·72	0·50	0·47	0·44	0·10	7·57	16·92	1·95	0·72	1·00
Phosphorus .	0·69	1·50	1·60	1·60	2·80	0·05	0·16	—	0·21	1·97	1·10
Sulphur . .	0·04	0·04	0·06	0·15	0·05	trace	0·08	—	0·04	0·01	0·02
Metallic iron .	92·10	92·00	92·28	92·75	90·72	95·57	86·74	71·87	86·19	89·66	88·83

Analyses of Wrought Iron, Steel, &c.

Description	Special strong foundry iron	Refined iron	Puddled bar	Wrought iron	Basic Bessemer metal, end of blow	Bessemer soft steel	Mushet steel, self hardening
Locality . .	—	Bromford	S. Stafford	S. Stafford	S. Stafford	Neuberg	Sheffield
Authority. .	Turner	Dick	Turner	Turner	Walton	Greenwood	Hadfield
Carbon (combined)	0·47	3·07	0·10	0·06	0·02	0·126	2·00
Silicon . .	1·43	0·63	0·13	0·04	0·01	0·135	1·60
Manganese .	1·04	trace	0·08	0·08	0·06	0·158	1·72
Phosphorus .	0·58	0·73	0·35	0·20	0·04	0·060	—
Tungsten . .	—	—	—	—	—	—	8·22
Sulphur . .	0·07	0·16	0·05	0·05	0·04	0·014	0·02
Iron . .	—	95·14	99·29	99·57	99·83	—	—

Description	Siemens soft steel	Bessemer steel rails	Siemens steel tyres	Silicon cast steel	Crucible steel for forgings	Hard tool steel
Locality . .	—	—	Sheffield	Terre Noire	—	—
Authority .	Greenwood	Greenwood	Turner	Pourcel	Greenwood	Greenwood
Carbon . .	0·167	0·21	0·58	0·61	0·36	1·144
Silicon . .	0·023	0·047	0·23	0·23	0·02	0·166
Manganese .	0·044	0·36	0·64	0·70	0·30	0·104
Phosphorus .	0·062	0·035	0·03	0·12	0·03	—
Sulphur . .	0·013	0·052	0·03	0·05	0·02	—
Iron . .	—	—	98·49	—	—	—

Analyses of Various Slags.

Material	Blast furnace cinders			Refinery slag	Tap cinder	Mill cinder	Bessemer slag, end of blow
	With white iron	Grey iron	Cold blast grey iron				
Locality . . .	Dowlais	Cleveland	South Stafford	Dowlais	Dowlais	Dowlais	—
Authority . . .	Riley	Bell	Percy	Riley	Riley	Riley	Snelus
Silica	43·07	29·92	39·52	25·77	7·71	28·71	46·75
Alumina . . .	14·85	21·70	15·11	3·60	1·63	2·47	2·80
Ferrous oxide . .	2·53	0·32	2·02	65·52	66·32	66·01	16·86
Ferric oxide . .	—	—	—	—	8·27	—	—
Manganous oxide . .	1·37	0·80	2·89	1·57	1·29	0·19	32·23
Lime	28·92	38·72	32·52	0·45	3·91	0·81	1·19
Magnesia . . .	5·87	6·10	3·49	1·28	0·34	0·27	0·52
Potash	1·84	—	1·06	—	—	—	—
Calcium sulphide . .	1·90	—	2·15	—	—	—	—
Phosphorus pentoxide .	—	0·07	—	1·37	8·07	1·22	0·01
Sulphur . . .	—	1·61	—	0·23	1·78	0·11	trace

preferred for purposes where iron has to be exposed to atmospheric action, and where there is no chance of articles of food coming in contact with the zinc. Tin plates are largely manufactured in South Wales, and were formerly made from an iron possessing special malleability, and which was prepared in the old-fashioned open hearth. At present tin plates are prepared from mild steel, chiefly that produced by the Siemens process. (For details of preparation *v.* Tin plates.)

Galvanised iron. Iron which has to be exposed to the weather or other oxidising agencies is frequently galvanised, *i.e.* covered with a thin coating of metallic zinc. In this case the metal is previously cleaned from scale, &c., by being 'pickled' in hydrochloric acid, and after cleansing the article is immersed for a few moments in a bath of molten zinc, which is kept covered with a little ammonium chloride. By this means a uniform covering of zinc is obtained, which protects the iron underneath, not merely so long as the coating is perfect, but also when zinc has been partly removed. Galvanised iron, however, cannot be used in contact with either mineral or vegetable acids, and hence is not employed for cooking utensils, nor for the cans in which food is preserved.

Iron can also be coated with zinc by heating at a moderate temperature with zinc-dust; this process is known as 'sherardising.' (For further details *v.* ZINC.)

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T. T.

COMPOUNDS OF IRON.

Oxides. Three oxides of iron are known:—

Ferrous oxide or iron monoxide FeO;

Ferric oxide or iron sesquioxide Fe_2O_3;

Ferroso-ferric oxide or magnetic oxide of iron Fe_3O_4.

The trioxide FeO_3, which may be considered to exist in the ferrates, has not been isolated.

Iron monoxide or **ferrous oxide** FeO is a strong base. It may be prepared by the reduction of the sesquioxide in a current of hydrogen at 300°. On exposure to air it oxidises with incandescence, but loses this property when allowed to remain for 12 hours in an atmosphere of hydrogen. It is also obtained as a black, velvety powder by adding ferrous oxalate to boiling caustic potash solution; when washed with water in air it takes up oxygen. Ferrous oxide is also formed by the action of nitrous oxide on metallic iron at 200° (Sabatier and Senderens, Compt. rend. 1892, 114, 1429).

The hydrated oxide $Fe(OH)_2$ is precipitated on addition of caustic soda to a ferrous salt in absence of air. When absolutely pure the precipitate is white, but it rapidly absorbs oxygen, acquiring a greenish hue and becoming ultimately converted into the red sesquioxide. It crystallises from a strong caustic soda solution in flat, pale green prisms (de Schulten, Compt. rend. 1889, 109, 266).

Ferrous oxide absorbs carbon dioxide with avidity. It dissolves in about 150,000 parts of water. It is used to impart a green colour to glass, which at the same time becomes athermanous, transmitting but little heat (Zsigmondy, Dingl. poly. J. 287, 17 *et seq*).

Ferroso-ferric oxide, *Magnetic oxide, Black oxide* $FeO{\cdot}Fe_2O_3$ or Fe_3O_4, occurs in nature as *magnetite* (*magnetic iron ore* or *lodestone* (*q.v.*)) in most parts of the world, and constitutes one of the most important ores of iron. It is always attracted by the magnet, but does not always possess the property of attracting iron. It may be prepared by passing steam or carbon dioxide over red-hot iron. It is probably a coating of this oxide which renders iron 'passive,' or unacted upon by concentrated nitric acid or water. This property is taken advantage of in the Bower-Barff process for preventing the rusting of iron, in which the metal is heated to redness and subjected to the action of steam.

When pure this oxide is an iron-black substance having a sub-metallic lustre. Its sp.gr. is 5·18, and its melting-point is 1527° (Kohlmeyer, Metallurgie, 1909, 6, 323).

The oxide is soluble in strong acids, the solutions containing a mixture of ferrous and ferric salts. By adding caustic alkali to such a solution or to a mixture of ferrous and ferric chlorides in proper proportions, a black precipitate of *ferroso-ferric hydroxide* is obtained, which, on drying in air, yields a brown-black, brittle mass, stable in air, which is magnetic, and may thus be separated from admixed ferrous and ferric oxides. It has the composition $Fe(OH)_2{\cdot}Fe_2O_3$.

Iron-scale is a compound of ferrous and ferric oxides in varying proportions. The inner layers are not magnetic, and approximate in composition to $6FeO,Fe_2O_3$; the outer layers of the scale are magnetic, and contain a larger proportion of ferrous oxide.

Iron sesquioxide or **ferric oxide** Fe_2O_3 occurs anhydrous as *hæmatite*, sp.gr. 5·19–5·25, *specular iron ore*, *kidney ore*, and *micaceous iron ore*, and, in the hydrated condition, as the yellow or brownish *limonite* $2Fe_2O_3,3H_2O$, of which *bog iron ore*, *pea iron ore*, and certain *clay iron stones* are earthy varieties. *Göthite* Fe_2O_3,H_2O and *targite* $2Fe_2O_3,H_2O$ are other forms in which the hydrated oxide occurs. The earthy varieties of hæmatite are known as *reddle* or *raddle*, and as *red ochre*, and are used as pigments; the earthy varieties of limonite being similarly used under the names *yellow* and *brown ochre*.

The anhydrous oxide may be obtained by heating the hydrated oxide or a ferrous or ferric salt containing a volatile acid. The latter method is the one principally used for the preparation of the commercial oxide, the salts most used being the sulphate or the chloride obtained from the 'pickling' of iron in the process of galvanising.

It may be prepared in small crystals by passing the vapour of ferric chloride over heated lime. The ignited or native oxide is slowly soluble in acids, the best solvent being a mixture of 8 parts sulphuric acid and 3 parts water.

Ferric oxide crystallises in tabular rhombohedral scales of sp.gr. 5·17, having a steely lustre. At the edges the crystals transmit light of a ruby-red colour. The solidifying-point of the molten oxide is 1562°–1565° (Kohlmeyer, Metallurgie, 1909, 6, 323).

Heated in the electric furnace or in the oxyhydrogen flame it yields the magnetic oxide (Moissan, Compt. rend. 1892, 115, 1034; Read, Chem. Soc. Trans. 1894, 314). Usually it is very slightly paramagnetic, but it is more strongly magnetic if prepared by the oxidation of ferrous hydroxide (Malaguti, Compt. rend. 1862, 55, 350). Walden states that at 1350° the dissociation pressure of the oxide is about equal to that of the oxygen in the air (J. Amer. Chem. Soc. 1908, 39, 1350).

The residue obtained in the manufacture of Nordhausen sulphuric acid by distillation of ferrous sulphate consists of this oxide, and is known as *colcothar*, and is largely used as a pigment. On account of the absence of grit it is used as polishing *rouge*; the parts which are of a scarlet colour—*i.e.* which have not been strongly heated—being preferred for glass polishing and for jewellery, &c., whilst the more strongly heated parts, which possess a bluish tint, are employed under the term *crocus* for polishing metals. It has been shown that these variations in colour are due to the varying size of the grains (Wohler and Condrea, Zeitsch. angew. Chem. 1908, 21, 481).

Ferric oxide acts as a catalyst in promoting the combination of sulphur dioxide and oxygen, and a process for the preparation of sulphuric acid has been based upon this reaction (Lunge and Reinhardt, Zeitsch. angew. Chem. 1904, 17, 1041; *see* also Keppeler, d'Ans, Sundell, and Kaiser, *ibid.* 1908, 21, 532, 577; Keppeler and d'Ans, Zeitsch. physikal. Chem. 1908, 62, 89). This oxide is also used in some forms of accumulator (*see e.g.* D. R. PP. 180672 and 190236; also Peters, Chem. Zentr. 1908, i. 213).

The use of ferric oxide for standardising solutions of permanganate has been proposed by Brandt, who describes a method for the preparation of the pure substance (Chem. Zeit. 1908, 32, 812 *et seq*).

Ferric oxide is invariably present in considerable quantities in *copper paint* (*v.* COPPER OXIDES).

This oxide may be combined with the monoxides of calcium, magnesium, zinc, copper, and other metals. The resultant oxides, which are prepared usually by fusing the mixed oxides, are always magnetic, and correspond in composition with the magnetic iron oxide. The oxide containing magnesium $Fe_2O_3 \cdot MgO$ occurs naturally as *magnoferrite*, and that containing zinc and manganese is found as *Franklinite* (*see* Percy, Phil. Mag. 1873, [iv.] 45, 455; and List, Ber. 1878, 11, 1512).

Solutions of alkali ferrites are obtained by boiling solutions of the ferrates or by boiling ferric hydroxide in strong caustic alkali solution (Haber and Pick, Zeitsch. Elektrochem. 1900, 7, 215; 1901, 7, 724).

The hydrated oxide is best prepared by precipitating a solution of ferric chloride with excess of ammonia. It forms a bulky, brown, slimy precipitate, which shrinks considerably in drying. It slowly gives up its water at 320°, and if heated to dull redness when anhydrous, suddenly contracts and glows brightly, becoming much less soluble in acids; this is probably due to an allotropic change which is known to take place at 640° (Keppeler and d'Ans, Zeitsch. physikal. Chem. 1908, 62, 89; *see* also *ibid.* 641).

Freshly precipitated ferric hydroxide when heated with water under a pressure of 5000 atmospheres gives the following products:—

At 30°–42·5° limonite,

At 42·5°–62·5° göthite,

And above 62·5° targite or hydrohæmatite (Ruff, Ber. 1901, 34, 3417).

A 'yellow hydrate,' which, under these conditions is unchanged between 40° and 70°, can be obtained by the oxidation of moist ferrous hydroxide or carbonate (Muck, Zeitsch. Chem. 1868, [ii.] 4, 41; Tommasi, Ber. 1879, 12, 1299, 2334).

When the hydrated oxide is merely allowed to remain for some months under water, a crystalline powder containing $Fe_2O_3(OH)_6$ is obtained which corresponds to the native limonite. This hydrate is the colouring ingredient of yellow clays, &c., and constitutes the precipitate from chalybeate streams. It may also be obtained by precipitation from a cold solution of a ferric salt and drying, without the aid of heat, over sulphuric acid.

The freshly precipitated oxide is readily soluble in acids and in concentrated solutions of ferric salts. The solution in ferric chloride, when containing excess of oxide, may be slowly dialysed with separation of a dark red liquid in which the ratio of chlorine to iron corresponds to the composition $82Fe(OH)_3 : FeCl_3$ (Linder and Picton, Chem. Soc. Trans. 1905, 1920). A similar solution containing a small amount of acetate is prepared by dialysing ferric acetate, and is used medicinally as *dialysed iron* or *liquor ferri dialysati.*

A colloidal solution of pure ferric hydroxide may be obtained from the dialysed solution containing chlorine by electrolysis under special conditions (Tribot and Chrétien, Compt. rend. 1905, 140, 144). The solution is gelatinised by alkalis and by many acids and salts, even in very small amounts (*see* also Gilotti, Gazz. chim. ital. 1908, 38, ii. 252).

Soluble metaferric hydroxide $Fe_2O_4H_2$ is obtained by heating a solution of ferric nitrate to 100° for 3 days, and then adding a few drops of hydrochloric acid. The hydroxide is thus precipitated, and when dried on a porous tile forms black scales, which dissolve in water to a tasteless red liquid (Péan de St. Gilles, Ann. Chim. Phys. 1856, [iii.] 46, 47; Scheurer-Kestner, *ibid.* 1859, [iii.] 57, 23; Debray, Compt. rend. 1869, 68, 913).

The hydrated oxide combines with sugar, forming a soluble compound, thus lowering the percentage of crystalline sugar obtained from the pans and raising the proportion of molasses. On this account raw sugar is soon injured by contact with iron vessels, and even the clearing 'char' should be as free as possible from iron. According to Schachtrupp and Spunt (Pharm. Centralhalle, 1893, 11, 148) the hydroxide is soluble only in solutions of invert sugar, and cannot itself cause inversion, though this may be brought about by anhydrous ferric oxide.

The hydrated oxide is largely used for removing sulphuretted hydrogen from coal gas. A hydrated sulphide is thus produced with evolution of water. When the oxide ceases to absorb the gas, it is exposed to a current of air, care being taken to prevent great rise of temperature, and the oxide is reproduced with separation of free sulphur. The large quantity of Prussian blue contained in the spent 'oxide' is now used for the production of cyanides (*q.v.*).

A yellowish-brown hydrated sesquioxide, precipitated on calico by the action of caustic soda on ferrous sulphate, is known as *chamois* or *rouille.*

Iron rust when completely oxidised has a composition approximating to that of limonite, but when freshly formed contains much hydrated ferrous oxide and carbonate (Moody, Chem. Soc. Trans. 1906, 720).

Ferric acid H_2FeO_4 is only known in combination. The potassium salt is produced with evolution of considerable heat by heating the sesquioxide with potassium nitrate or hydroxide, or with a mixture of the two substances (Fremy, J. Pharm. Chim. 1841, 27, 97; Hofmann, Ber. 1869, 2, 239).

It may be prepared by the electrolytic oxidation of iron in caustic potash solution (Haber and Pick, Zeitsch. Elektrochem. 1900, 7, 215), or by passing chlorine through a suspension of ferric hydroxide in caustic potash.

Barium ferrate is the most stable salt of ferric acid, and is obtained as a dark red powder by precipitating a solution of sodium ferrate with barium chloride (Baschieri, Gazz. chim. ital. 1906, 36, ii. 282).

Ferrous sulphide FeS is found in certain meteorites. It may be considered to exist in combination with the sesquisulphide in *pyrrhotine* or *magnetic pyrites*, and in combination with other sulphides in other minerals. It is found in considerable quantities in the black deposit in cesspools, &c., being produced by the action of organic matter on ferruginous bodies or iron oxide in presence of sulphates. In meteorites it occurs as the mineral *triolite*.

It may be prepared by heating a mixture of iron filings and sulphur, or of ferrous sulphate and charcoal; by stirring a white-hot rod of wrought iron in melted sulphur; by heating other iron sulphides to bright redness in hydrogen, or by precipitating ferrous salts with alkaline sulphides or sulphuretted hydrogen. In the compact state, ferrous sulphide is a very hard, metallic-looking black, or nearly black crystalline solid of sp.gr. 4·69. It has a metallic lustre with a yellowish reflex, and sometimes occurs in hexagonal prisms. It is not magnetic, is permanent in air, and fusible at a full red heat. The precipitated sulphide, however, is readily oxidised to sulphate in air, especially when moist.

It is decomposed by acids with evolution of sulphuretted hydrogen, and is usually employed for the preparation of that gas.

Ferrous sulphide forms the main constituent of *iron lute* (*v.* LUTES).

Ferroso-ferric sulphide $FeS{\cdot}Fe_2S_3$ forms one of the varieties of *pyrrhotine*: it is obtained when iron pyrites is heated out of contact with air for the production of sulphur. *Magnetic pyrites* $5FeS{\cdot}Fe_2S_3$ or $6FeS{\cdot}Fe_2S_3$ occurs in hexagonal plates of a brassy colour. It is attracted by the magnet and has sp.gr. 4·4–4·7.

Ferric sulphide Fe_2S_3 is obtained by gently heating a mixture of iron and sulphur or by the action of sulphuretted hydrogen on the sesquioxide below 100°, and may be prepared by pouring a solution of ferric salt into excess of ammonium sulphide. By the latter reaction it is formed in the purification of coal gas (Gedel, J. Gasbel. 1905, 48, 400; Stokes, J. Amer. Chem. Soc. 1907, 29, 304). It combines with other sulphides of iron, and with the sulphides of silver, potassium, and sodium.

Potassium ferric sulphide $K_2Fe_2S_4$ is obtained when iron filings, potassium carbonate, and sulphur are heated together and the mass extracted with water. It is thus obtained in purple-coloured, needle-shaped crystals of sp.gr. 2·863, which burn when heated in air.

Sodium ferric sulphide $Na_2Fe_2S_4,4H_2O$ is obtained in a similar way and forms brown microscopic needles. It occurs in the 'black-ash liquors' of the Leblanc process.

Cuprous ferric sulphide $Cu_2S{\cdot}Fe_2S_3$ occurs native as '*copper pyrites.*'

Iron disulphide FeS_2 occurs in immense quantities as *iron pyrites* or *mundic* in hard, yellow, brassy cubes, sp.gr. 5·185; or in other forms of the regular system, and in masses of various shapes, frequently known as 'thunderbolts.' This mineral, as well as *marcasite* or *white iron pyrites* (sp.gr. 4·68–4·85), and other minerals of the same composition, but crystallising in the rhombic system, is produced in nature by the reduction of ferrous sulphate by organic matter, and is therefore often found forming fossils in peat, chalk, &c., and in clay, containing much organic matter. Marcasite may be prepared artificially by heating ferrous sulphide with sulphur; by passing hydrogen sulphide over the oxides or chlorides of iron at a red heat; by the action of carbon disulphide vapour on heated ferric oxide or by heating ferric chloride with phosphorus pentasulphide (Glatzel, Ber. 1890, 23, 37).

Pyrites is quite permanent in air, but marcasite slowly becomes oxidised and disintegrated on exposure. Iron pyrites is largely employed as a source of sulphur in the manufacture of sulphuric acid, ferrous sulphate, &c. (*v.* SULPHURIC ACID; SULPHUR; *Ferrous sulphate*).

By heating iron disulphide with aluminium powder in a stream of hydrogen sulphide the compound Al_2FeS_4 is obtained (Houdard, Compt. rend. 1907, 144, 801; *see* also Ditz, Metallurgie, 1907, 4, 786).

Iron sub-sulphide Fe_4S_3 is obtained when iron is heated in the vapour of carbon disulphide. It forms a crystalline mass of sp.gr. 6·957, and dissolves in dilute acids with evolution of hydrogen and hydrogen sulphide (Gautier and Hallopeau, Compt. rend. 1889, 108, 806).

Ferric arsenide occurs in nature as *lölingite* $FeAs_2$, and with sulphur as *mispickel* or *arsenical pyrites* Fe_2AsS, from which the greater part of the arsenic of commerce is obtained (*v.* ARSENIC). Arsenic combines directly with iron.

Compounds of carbon, phosphorus, silicon, and nitrogen with iron are also known. The effects produced on the properties of iron and steel by the three first-named elements are described under the manufacture of iron.

Iron nitride Fe_2N (Stahlschmidt, Pogg. Annalen, 1864, 125, 37) is obtained by the action of excess of ammonia at 420° on ferrous chloride or bromide, reduced iron, or iron amalgam, as a dull grey powder (Fowler, Chem. Soc. Trans. 1901, 285).

It may be prepared in the compact state by heating iron wire or rod to a bright red heat in a large excess of ammonia. The product is so brittle that it can be powdered, and has sp.gr. 6·0–6·5. When heated in air it is oxidised, and it ignites when warmed in chlorine. Dilute acids dissolve it with the formation of ferrous and ammonium salts (Beilby and Henderson, Chem. Soc. Trans. 1901, 1249; Guntz, Compt. rend. 1902, 135, 738).

Phosphides of iron. A phosphide Fe_2P is produced by heating a mixture of ferrous or ferric phosphate under common salt or by heating iron filings with cuprous phosphide in the electric furnace. It forms lustrous grey crystals, probably hexagonal in form; sp.gr. 6·56; m.p. 1290° (Maronneau, Compt. rend. 1900, 130, 656; Le Chatelier and Wologdine, *ibid.* 1909, 149, 709). Heated in air it forms the basic phosphate $2Fe_2O_3,P_2O_5$.

When iron is heated in phosphorus vapour, or the monosulphide is heated in hydrogen phosphide gas, the phosphide FeP is formed. It is a dark grey powder of sp.gr. 5·76.

Another phosphide Fe_2P_3 is formed by strongly heating phosphorus and ferric chloride vapours in a current of carbon dioxide (Granger, Compt. rend. 1896, 122, 936); or by the action of the vapour of phosphorus iodide on finely divided iron. It forms hard, non-magnetic, steel-grey crystals; sp.gr. 4·5.

A phosphide Fe_3P of sp.gr. 6·74 and m.p. 1110° has also been described (Le Chatelier and Wologdine, *l.c.*).

Iron borides. Two borides of iron have been described:

Fe_2B forms steel-grey prisms; sp.gr. 7·37 at 18°. It is oxidised by dry air at a red-heat and by moist air at the ordinary temperature.

FeB_2 has not been obtained pure, but has sp.gr. *circa* 5, and is extremely hard (Binet du Jassonneix, Compt. rend. 1907, 145, 121).

Iron silicide $SiFe_2$ (ferro-silicon) is produced by heating iron with silicon, or with silica and carbon, in the electric furnace (Moissan, Compt. rend. 1895, 121, 621; Bertolus, Fr. Pat. 393, 818, 1908). It forms grey magnetic prisms of sp.gr. 7, and is readily attacked by acids.

Under certain circumstances commercial ferro-silicon may evolve the gaseous hydrides of arsenic and phosphorus (present as impurities) with very bad effect on human beings (*e.g. see* J. Soc. Chem. Ind. 1909, 25).

Iron carbide (*see* CEMENTITE and STEEL).

FERROUS SALTS.

Anhydrous ferrous salts are usually colourless; the hydrated salts are greenish or blue. The solutions are sweet and astringent and ink-like in taste, and form powerful reducing agents.

Ferrous chloride $FeCl_2$ may be prepared by passing dry hydrogen chloride over red-hot iron or by reducing ferric chloride in a current of hydrogen, when the anhydrous salt is deposited in colourless shining scales, sp.gr. 2·528, which are very deliquescent and easily soluble in water and alcohol. It fuses at a red-heat, and volatilises at a yellow-heat, the V.D. being 6·4–6·6 (V. Meyer, Ber. 1884, 17, 1335). At 1300°–1500° the V.D. is normal=4·3 (Nilson and Pettersson, Chem. Soc. Trans. 1888, 827).

In solution it is obtained by dissolving iron in hydrochloric acid. It crystallises in deliquescent, bluish-green, monoclinic crystals, sp.gr. 1·93, containing 4 molecules of water.

The anhydrous salt absorbs ammonia to form the compound $FeCl_2{\cdot}6NH_3$, which gives off ammonia at 100°, and at higher temperatures yields ammonium chloride, nitrogen, and iron nitride (Fowler, Chem. Soc. Trans. 1901, 288). It combines with bromine to form the unstable compound $FeCl_2Br$ (Lenormand, Compt. rend. 1893, 116, 820).

Ferrous bromide $FeBr_2$ is obtained as a yellowish crystalline solid by the union of its elements. The hydrated bromide crystallises in bluish-green rhombic tablets with 6 molecules of water.

Ferrous iodide FeI_2 is obtained by heating iron with iodine as a grey lamino-crystalline mass; m.p. 177° (Carius and Wanklyn, Annalen, 1861, 120, 69).

Ferrous sulphite $FeSO_3$. Iron dissolves in aqueous sulphurous acid in absence of air, with formation of ferrous sulphite and thiosulphate. The latter salt is very soluble, but the sulphite is deposited in greenish crystals.

Ferrous sulphate, green vitriol, or **copperas,** $FeSO_4,7H_2O$, occurs as *melanterite*, being derived from the decomposition of the native sulphide, especially of marcasite, and is manufactured in large quantities in South Lancashire by the oxidation of pyrites by air and rain.

The pure salt is prepared by heating an excess of iron wire or 1½ parts of precipitated ferrous sulphide in 1½ parts of sulphuric acid diluted with four times its weight of water. The solution is acidified if necessary, and is filtered quickly. Bluish-green monoclinic crystals containing $FeSO_4,7H_2O$, and having a sp.gr. of 1·889 at 4° (Joule and Playfair), are thus produced.

Large quantities of this sulphate are obtained in the manufacture of copper sulphate (*v.* COPPER), and small quantities in the preparation of sulphuretted hydrogen for precipitating arsenic from sulphuric acid. It is prepared on the large scale by dissolving scrap iron in warm sulphuric acid of 1·150 sp.gr., and concentrating the nearly neutral solution. The liquid is settled, quickly drawn off, allowed to clear for 24 hours, and run into crystallising tanks, in which strings, straws, or wooden laths are suspended to induce crystallisation. The crystals are washed with a minimum quantity of water and dried.

When sulphur is distilled from iron pyrites, the residue, known as *sulphur waste*, is laid upon inclined shelves in contact with air to oxidise. The weathered mass is levigated, and the ferrous sulphate is crystallised out.

Ferrous sulphate is obtained at Fahlun during the extraction of copper sulphate from mine water, and also from the runnings of other mines.

The *Salzburg vitriol* prepared at Buxweiler contains ferrous and copper sulphates (*v.* COPPER). The copper may be separated as metal and any excess of acid converted into sulphate by the addition of scrap iron to the liquid.

Crude ferrous sulphate always contains ferric sulphate, which gives the crystals a more decided green colour; they are frequently coated with a yellow deposit due to oxidation. By washing with absolute alcohol, this deposit, being soluble, is removed, and the crystals are rendered more permanent.

The pure salt may be obtained in the most permanent condition by precipitating a concentrated aqueous solution by addition of excess of alcohol and washing the precipitated crystals with nearly absolute alcohol. The presence of even a trace of ferric salt increases the liability of the crystals to oxidation. The crystals usually contain 7 molecules of water and are monoclinic, of sp.gr. 1·889 at 4°. Another hydrate contains $5H_2O$ and crystallises in the triclinic system, being isomorphous with $CuSO_4,5H_2O$. The monohydrate is obtained when the heptahydrate is allowed to effloresce over conc. sulphuric acid, or when it is melted in its water of crystallisation and allowed to solidify (Etard, Compt. rend. 1878, 87, 502;

Scott, Chem. Soc. Trans. 1897, 564). Ferrous sulphate may be obtained in rhombic prisms containing 4 molecules of water, isomorphous with zinc sulphate. Crystals may also be produced containing 3 and 2 molecules of water.

Ferrous sulphate is insoluble in absolute alcohol. Its solubility in 100 parts of water is:

10°	15°	25°	32·5°	46°	60°	90°	100°
61	70	115	151	227	263	370	333

The reduced solubility at 100° may be attributed to partial dehydration or dissociation.

The aqueous solution slowly oxidises on exposure to air, and deposits a yellowish, highly basic ferric sulphate, leaving the normal ferric sulphate in solution. The acid finally becomes divided between the precipitated salt and that in solution, rendering the former less basic but still insoluble, and converting the normal salt into a soluble basic sulphate. Ferrous sulphate, like the chloride, absorbs nitric oxide in solution. The gas is given off in a vacuum, or when the solution is heated, but it probably forms the compound $FeSO_4 \cdot NO$. When such a solution is mixed with sulphuric acid and cooled a purple-red colour is produced, which is used in the well-known ring test for nitrates (*see* also Machot and Zechentmacher, Annalen, 1906, 350, 368).

On account of its reducing power, it precipitates gold and palladium from solution, and reduces indigo to the leuco compound.

When gradually heated to 140° *in vacuô* it loses 6 molecules of water and becomes colourless, but the remaining molecule is not removed at 260°, and, except when heated in small quantities, it is impossible to render the salt anhydrous without loss of acid. At a red heat a basic sulphate is produced, with evolution of sulphur trioxide, and, at higher temperatures, ferric oxide is left. A complete investigation of the dissociation of ferrous sulphate has been made by L. Wöhler, Plüddemann, and P. Wöhler (Ber. 1908, 41, 703).

Ferrous sulphate is largely used in dyeing and tanning, and in the manufacture of inks (*v.* INK), Prussian blue, and other pigments, Nordhausen sulphuric acid, red oxide of iron, &c. In weak solution it is said to promote the growth of certain plants, especially of roots. When added to excremental matters it absorbs ammonia and other volatile substances, and renders the matter almost odourless. It is largely used for the treatment of sewage (*see e.g.* Pochin and Richardson, Eng. Pats. 15239 and 17976, 1908).

In dyeing textiles, leather, wood, &c., it is largely used for the production of various shades of black, grey, lilac, and brown. It is used as a mordant for the production of Prussian blue in calico-printing, and is the raw material from which acetates, nitrosulphates, and other iron mordants are prepared.

Ferrous disulphate FeS_2O_7 is separated as a white powder on addition of excess of concentrated sulphuric acid to a concentrated aqueous solution of the normal sulphate. On addition of water, it is decomposed into the normal salt and free acid (Bolas, Chem. Soc. Trans. 1874, 212).

With ammonium and potassium sulphates, ferrous sulphate produces double salts containing 6 molecules of water and of great stability and fine crystalline form.

Ferrous ammonium sulphate

$FeSO_4,(NH_4)_2SO_4,6H_2O$

is prepared by dissolving molecular proportions of the two sulphates in the minimum quantity of hot water, filtering hot, and crystallising. It forms fine bluish-green monoclinic crystals of sp.gr. 1·813, of which 100 parts of water dissolves 21·6 parts at 20° and 56·7 parts at 75°.

The double salt is permanent in air, particularly when precipitated by addition of alcohol to the concentrated aqueous solution and washed with absolute alcohol, and is used by chemists in place of ferrous sulphate, especially for standardising solutions.

Ferrous phosphate $Fe_3(PO_4)_2,8H_2O$ occurs as *Vivianite* or *blue iron earth*, sometimes mixed with clay and peat or associated with bog iron ore. It may be produced by addition of sodium phosphate to ferrous sulphate. The fresh precipitate is used medicinally. When quite pure it is colourless, but it rapidly becomes bluish or green from oxidation. When iron is dissolved in phosphoric acid the solution deposits colourless needles of $Fe(H_2PO_4)_2,2H_2O$, which rapidly alter in air (Erlenmeyer, Annalen, 1878, 194, 182).

Ferrous arsenate prepared from ferrous sulphate and sodium arsenate has been proposed for use as an insecticide, for which purpose it has many advantages over Scheele's green (Vermorel and Dantony, Compt. rend. 1909, 148, 302).

Ferrous carbonate $FeCO_3$ occurs as *spathic iron ore*, together with the carbonates of lime, magnesia, and manganese. *Clay iron stone* is an argillaceous ferrous carbonate.

Ferrous carbonate dissolves in water containing free carbonic acid, the acid salt so produced being the essential constituent of chalybeate waters. The solution is decomposed rapidly on boiling and slowly on exposure to air, with precipitation of an ochreous deposit of the hydrated oxide, which, in the case of mineral waters, frequently contains organic matter and ferric arsenate, and is occasionally found to contain antimony.

Spathic iron ore can be obtained artificially in microscopic rhombohedra by precipitating ferrous sulphate with sodium hydrogen carbonate and heating the solution for 12–36 hours at 150°. When sodium carbonate solution is added to ferrous sulphate solution a flocculent white precipitate is obtained which rapidly becomes green, and is ultimately completely converted into ferric hydroxide.

Ferrous nitrate $Fe(NO_3)_2,6H_2O$ is prepared by dissolving ferrous sulphide in dilute nitric acid, or, preferably, by addition of barium nitrate to ferrous sulphate solution.

The solid salt is very soluble in water and very unstable, changing to ferric nitrate. The action between iron and dilute nitric acid does not result in the formation of ferrous nitrate, and is extremely complicated (Montemartini, Chem. Soc. Abstr. 1892, 1278).

Cyanogen compounds of iron (*see* CYANIDES).

FERRIC SALTS.

Are usually of yellowish or reddish brown colour. In solution they are reduced to the ferrous condition by zinc, or, with precipitation of sulphur, by sulphuretted hydrogen. Potassium or other soluble thiocyanate imparts an intense blood-red colour to a neutral or acid solution of a ferric salt.

Ferric chloride $FeCl_3$ or Fe_2Cl_6 may be obtained in the anhydrous condition by passing excess of chlorine gas over red-hot iron or by passing hydrogen chloride over the heated sesquioxide, and thus occurs not infrequently in the craters of volcanos. Thus prepared, it forms iridescent iron-black scales which are dichroic, appearing red by transmitted and green by reflected light.

In solution it may be prepared by dissolving the precipitated sesquioxide in hydrochloric acid, and driving off the excess of acid by heat; or, preferably, by dissolving iron in hydrochloric acid and passing chlorine through the liquid until saturated with that gas, finally entirely removing the chlorine by passage of a current of carbon dioxide through the warm liquid. A commercial method for the preparation of ferric chloride from native phosphate of iron and aluminium has been described by Schröder (D. R. P. 192591).

Ferric chloride readily volatilises at 448°, and the V.D. is then less than that required for Fe_2Cl_6. It is, therefore, probable that the molecular formula is $FeCl_3$ (Grünewald and V. Meyer, Ber. 1888, 21, 687). In boiling alcohol or ether it also appears to have the molecular formula $FeCl_3$ (Müller, Compt. rend. 1894, 118, 641). At the ordinary temperature it forms unstable compounds with nitric oxide, but at higher temperatures it is reduced by that gas to ferrous chloride (Besson, Compt. rend. 1889, 108, 1012; Thomas, *ibid.* 1895, 120, 447; 121, 128).

Ferric chloride is very deliquescent, and dissolves in alcohol and ether. The concentrated aqueous solution is dark brown and oily; if diluted it becomes of a pale yellow colour. In dilute solution the salt may exist as $Fe_2Cl_4{\cdot}Cl_2$ (Tufereff, Zeitsch. anorg. Chem. 1908, 59, 82).

There are four hydrates of ferric chloride, $FeCl_3,6H_2O$, m.p. 37°; $2FeCl_3,7H_2O$, m.p. 32·5°; $2FeCl_3,5H_2O$, m.p. 56°; and $FeCl_3,2H_2O$, m.p. 73·5°. Solutions which contain more of the chloride than corresponds with the composition $FeCl_3,2H_2O$ deposit the anhydrous salt when heated above 66° (Roozeboom, Zeitsch. physikal. Chem. 1892, 10, 477).

Compounds of the formulæ $FeCl_3,HCl,2H_2O$, $FeCl_3,HCl,4H_2O$, and $FeCl_3,HCl,6H_2O$ are known (Sabatier, Bull. Soc. chim. 1881, [ii.] 36, 197; Roozeboom and Schreinemacker, Zeitsch. physikal. Chem. 1894, 15, 588).

Ferric chloride is partly hydrolysed by water with the formation of many complex colloid bodies (Malfitano and Michel, Compt. rend. 1907, 145, 185, and 1275; Michel, *ibid.* 1908, 147, 1052, and 1288).

Ferric chloride forms compounds with alkaloids, most of which have definite melting-points. The use of these substances has been suggested for the identification of the alkaloids (Scholtz, Chem. Soc. Abstr. 1908, i. 202, from Ber. Deut. pharm. Ges. 1908, 18, 44).

Solutions of ferric chloride in methyl alcohol are reduced by light, which acts, not as a catalyst, but as the source of the energy required to bring about the reaction (Benrath, J. pr. Chem. 1909, [ii.] 80, 283).

Ferric chloride is sometimes used as a disinfectant. It deodorises sewage with partial reduction to ferrous chloride.

With potassium chloride it produces a finely crystallised garnet-coloured double chloride $Fe_2Cl_6,4KCl,2H_2O$ decomposed by water. A similar garnet-coloured salt crystallising in cubes is formed with ammonium chloride and is used medicinally as *ammonio-chloride of iron*. The salt used, however, does not correspond to the potassium salt, but usually contains less than 2 p.c. of iron. It is very deliquescent and may be considered as formed by the combination of the normal salt $FeCl_6,4NH_4Cl,2H_2O$ with variable proportions of ammonium chloride.

Soluble and insoluble *oxychlorides* of iron are known, but are unimportant.

Ferric sulphate $Fe_2(SO_4)_3$ occurs in Chile as *coquimbite* in white silky pyramids containing $Fe_2(SO_4)_3,9H_2O$. It is usually prepared by mixing one equivalent of concentrated sulphuric acid with a solution of two equivalents of ferrous sulphate, concentrated nitric acid being added in portions to the hot solution until red fumes cease to be evolved. On concentrating the solution to a syrup colourless crystals are obtained.

Several hydrated basic sulphates are prepared artificially, or occur in nature.

Ferric sulphate is used to a slight extent in dyeing cotton, but not in printing. The basic sulphates are used for dyeing cotton, for the production of buffs, or, in combination with logwood and sumach, for blacks. The iron mordant prepared by treating ferrous sulphate with nitric acid is sold as *nitrosulphate* or *nitrate of iron*, and is used in dyeing, but not in printing cotton.

With alkaline sulphates ferric sulphate forms double salts, resembling and corresponding in composition to alum.

The potassium salt, *potassium iron alum* $Fe_2(SO_4)_3,K_2SO_4,24H_2O$, is prepared by mixing molecular proportions of ferric and potassium sulphates and concentrating the solution spontaneously. It forms fine violet octahedra very liable to decompose into a brown, gummy, deliquescent mass. This alum is used to a limited extent in dyeing and calico printing. If caustic potash is added to a solution of iron alum, and the brown liquid allowed to evaporate, yellowish-brown crystals separate of the composition $5K_2SO_4,2Fe(SO_4)_2(OH)_2,16H_2O$. These crystals have the peculiar optical properties of tourmaline (*see* Lachaud and Lepierre, Compt. rend. 1892, 114, 915).

The corresponding ammonium alum is more permanent, and has been proposed as a standard in titrations (de Coninck, Bull. Soc. chim. 1909, 23, 222).

Ferric nitrate $Fe_2(NO_3)_6$ may be obtained in several states of hydration by crystallising the solution obtained by the action of concentrated nitric acid on scrap iron or iron oxide. The hydrate $Fe(NO_3)_3,6H_2O$ crystallises in cubes and the hydrate $Fe(NO_3)_3,9H_2O$ in colourless monoclinic crystals. It is usually prepared by the first method for use as a mordant for producing buffs and blacks in dyeing. An alkaline mordant is prepared for dyeing and calico printing by treating a ferric salt with caustic soda, with addition preferably of glycerol, or sometimes of glucose, to prevent precipitation of the oxide.

Nitroso-compounds of Iron. Anhydrous ferric chloride absorbs nitric oxide, forming the compounds $2FeCl_3{\cdot}NO$ and $4FeCl_3{\cdot}NO$ as reddish-brown, hygroscopic powders. The action of nitric oxide on an ethereal solution of ferric chloride gives nitrosyl chloride and a solution which, when evaporated over sulphuric acid, deposits black needles of the composition $FeCl_2{\cdot}NO,2H_2O$; or at 60° gives the anhydrous salt $FeCl_3{\cdot}NO$, crystallising in yellow needles (Thomas, Compt. rend. 1895, 120, 447).

The stable nitroso compounds were discovered by Roussin (Compt. rend. 1858, 46, 224), and are formed by the action of ferrous sulphate on alkali nitrites and sulphides. They are salts of complex acids, containing iron and the monovalent group NO′ in the acid radicle (Cambi, Atti. R. Accad. Lincei. 1908, [v.] 17, i. 202), and fall into two classes:

(1) *Ferrodinitroso* derivatives.
(2) *Ferroheptanitroso* derivatives.

Potassium ferrodinitroso sulphide

$$K[Fe(NO)_2S],2H_2O$$

is formed by the action of caustic potash on the heptanitrososulphide (*v. infra*). It forms dark red crystals, insoluble in water, and decomposes violently when heated, yielding potassium and ammonium sulphates and other products.

The free acid $H[Fe(NO)_2S]$ is obtained by the action of sulphuric acid on the potassium salt and slowly decomposes into hydrogen sulphide, nitrogen, nitrous oxide, and the heptanitroso acid. The ethyl and phenyl derivatives have been prepared: $C_2H_5[Fe(NO)_2S]$, and

$$C_6H_5[Fe(NO)_2S].$$

Potassium ferrodinitroso thiosulphate

$$K[Fe(NO)_2S_2O_3],H_2O$$

is prepared by passing nitric oxide into a solution of ferrous sulphate and potassium thiosulphate for 10 hours. It forms reddish-brown crystals with a bronze lustre which are but slightly soluble in water. The ammonium and sodium salts are similar, but the latter is the more soluble.

Potassium ferroheptanitroso sulphide

$$K[Fe_4(NO)_7S_3],H_2O$$

is the most stable of these salts and is formed by the action of ferrous sulphate on potassium nitrite and sulphide in solution, or by boiling a solution of the ferrodinitroso thiosulphate. It forms dark-coloured monoclinic crystals having an adamantine lustre and is only sparingly soluble in water.

The free acid is obtained as an amorphous brown mass by the action of sulphuric acid on the potassium salt.

The ammonium salt may be prepared by the action of nitric oxide on freshly precipitated ferrous sulphide suspended in water.

(For details as to these compounds *see:* Proczinsky, Annalen, 1863, 125, 302; Rosenberg, Ber. 1879, 3, 312; Pavel, *ibid.* 1882, 15, 2600; Marchlewski and Sachs, Zeitsch. anorg. Chem. 1892, 2, 175; Marié and Marquis, Compt. rend. 1896, 122, 137; Hofmann and Wiede, Zeitsch. anorg. Chem. 1895, 8, 318; 1895, 9 295; 1895, 11, 281; *see* also Atti. R. Accad. Lincei, 1906, [v.] 15, ii. 467; 1907, [v.] 16, i. 654.)

Ferric phosphates occur native as *beraunite* $Fe_2(PO_4)_2{\cdot}4Fe_2PO_4(HO)_3,8H_2O$, formed by the oxidation of *vivianite*, and as *dufrenite* $Fe_2(HO)_3PO_4$.

The normal phosphate, $FePO_4$, is produced as a yellowish-white precipitate by adding sodium hydrogen phosphate to ferric chloride solution; it is soluble in dilute acids (except acetic acid) and is slowly decomposed by water.

When ferric hydroxide is dissolved in orthophosphoric acid and the solution rapidly evaporated, the di-acid salt $Fe(H_2PO_4)_3$ is obtained as a pink crystalline powder, decomposed by moist air, with formation of the monacid salt $2FeH_3(PO_4)_2,5H_2O$.

Ferric metaphosphate is deposited in pink plates when the hydroxide is digested with glacial phosphoric acid at 100° (Hautefeuille and Margotte, Compt. rend. 1888, 106, 138; Johnson, Ber. 1889, 22, 976).

Pascal has described (Compt. rend. 1908, 146, 231, 279) certain complex salts of iron with phosphoric acid in which the iron exists in the acid radicle.

Sodium ferripyrophosphate $Na_6Fe_2(P_2O_7)_3$ is precipitated as a pale violet, micro-crystalline powder from a saturated solution of ferric pyrophosphate in 15 p.c. sodium pyrophosphate solution maintained at 30°. The silver and copper salts and the free acid have been prepared.

Ferric arsenite $Fe_2(AsO_3)_2$ is of interest as being the salt produced when freshly precipitated hydrated oxide of iron is taken as an antidote in cases of arsenical poisoning. It may be obtained as a brown precipitate by addition of arsenious acid or an arsenite to a solution of ferric acetate.

Ferric acetate *v.* ACETATES.

Ferric ferrocyanide *v.* CYANIDES.

Ferric tannate or *gallo-tannate* forms the basis of black inks (*v.* INK). The sponges, sand, pumice-stone, &c., of Gerson's filters are impregnated with the tannate, which is said to completely remove all organic matter from water (*v.* Steiger, J. Soc. Chem. Ind. 1886, 416).

Ferric citrate $Fe(C_6H_5O_7)$ is prepared by dissolving the hydrated oxide in citric acid, and evaporating the solution in thin layers. It forms permanent, transparent, garnet-coloured scales, which dissolve slowly in water, but are insoluble in alcohol.

Ferric ammonium citrate is prepared as above, with addition of ammonia. It forms thin, transparent, deep-red scales, which dissolve readily in water, but not in absolute alcohol.

It is used in medicine as is also the double citrate of iron and quinine.

IRON CARBONYLS. Three carbonyls of iron are known; viz.: Iron pentacarbonyl $Fe(CO)_5$, iron tetracarbonyl $Fe(CO)_4$, and diferrononacarbonyl $Fe_2(CO)_9$.

Iron pentacarbonyl. This compound was discovered by Mond, Langer, and Quincke, who prepared it by treating finely divided iron, obtained by reducing ferrous oxalate by hydrogen, with carbon monoxide. On heating to 120°, the carbonyl distilled over and was collected in a cooled tube. The yield is about 1 gram per 100 grams of iron (Chem. Soc. Trans. 1891, 604 and 1090).

Iron pentacarbonyl is a viscid yellow liquid of sp.gr. 1·466 at 18°; b.p. 102·8° at 749 mm.

At −21° yellow crystals are formed, which become white at the temperature of liquid air.

It is not acted upon by dilute acids, but concentrated acids form the corresponding salt with evolution of carbon monoxide and hydrogen. Upon exposure to air, it is converted into ferrous hydroxide and eventually into the red ferric hydroxide. The pentacarbonyl is soluble in most organic solvents and in nickel tetracarbonyl, forming $FeNi(CO)_9$ (?), insoluble in water.

Light decomposes the pentacarbonyl, giving the diferrononacarbonyl and carbon monoxide: $2Fe(CO)_5=Fe_2(CO)_9+CO$ (Dewar and Jones, Proc. Roy. Soc. 1905, A. 76, 588; 1907, A. 79, 66).

The decomposition of the pentacarbonyl is most rapid in blue light and least of all in red, green and yellow being intermediate in their effects; in fact, a solution exposed to blue light will deposit about ten times as much solid as a similar solution exposed for the same period to red light.

The action of light on the pentacarbonyl is reversible, as the substance in sealed tubes, after exposure to light, when left in the dark, gradually become colourless.

Diferrononacarbonyl crystallises in lustrous hexagonal golden or orange coloured crystals of sp.gr. 2·085 at 18°, which are perfectly stable in dry air. They are decomposed at 100° yielding the pentacarbonyl, carbon monoxide, and iron: $Fe_2(CO)_9=Fe(CO)_5+4CO+Fe$. It is insoluble in water and nearly so in benzene, but is slightly soluble in alcohol or acetone and very soluble in pyridine. The nonacarbonyl in solution heated to 95° becomes green and then contains the *tetracarbonyl* $Fe(CO)_4$. At a higher temperature it forms the pentacarbonyl together with iron and carbon monoxide, the reaction taking place in two stages:

$$2Fe_2(CO)_9=2Fe(CO)_5+2Fe(CO)_4$$
$$2Fe(CO)_4=Fe(CO)_5+Fe+3CO.$$

When strongly heated the action is:

$$2Fe_2(CO)_9=3Fe(CO)_5+Fe+3CO.$$

Iron tetracarbonyl. The method of preparation of the tetracarbonyl is as follows: a solution of the diferrononacarbonyl in toluene (1 gram to 20 c.c.) is gradually heated to 95° in an atmosphere of carbon dioxide until the reddish yellow solid has disappeared. On cooling, green crystals of the tetracarbonyl are formed:

$$Fe_2(CO)_9=Fe(CO)_4+Fe(CO)_5.$$

The yield is 20 p.c.

The tetracarbonyl forms dark green lustrous crystals of sp.gr. 1·996 at 18°, stable at ordinary temperatures: on heating at 140°–150°, iron and carbon monoxide are formed. The empirical formula is $Fe(CO)_4$, but the molecular formula in benzene appears to be $[Fe(CO)_4]_{20}$.

The substance is insoluble in water but soluble in most organic solvents giving green solutions. In pyridine, the solutions are first green, but soon become red, especially on warming. The change in colour is probably due to molecular dissociation. The green solutions lose their colour upon exposure to light, iron being deposited, but the red ones are unaffected by light.

IRON CEMENT *v.* Lutes.

IRONE *v.* Ketones.

IRON LIQUOR. *Ferrous acetate* (*v.* Acetic acid).

IRON PYRITES. *Ferric sulphide* (*v.* Pyrites; Iron).

IRVINGIA BUTTER *v.* Waxes.

ISATIN *v.* Bone-oil; Indigo, Natural; Indigo, Artificial.

ISATIN BLUE *v.* Bone-oil.

ISINGLASS (Fr. *Colle de poisson*; Ger. *Hausenblase*) consists of the dried swimming-bladders of various fishes. These bladders differ in shape and size, according to their origin, and are prepared either by simply drying them whilst slightly distended, which process forms ‘pipe isinglass,’ or by splitting them open, pressing, and drying them in the form of ‘leaf isinglass.’ That form, again, which is known as ‘purse isinglass,’ consists of such bladders as contain a natural opening.

The chief supply of isinglass is derived from Russia and Hudson’s Bay; some portion also being obtained from Brazil, West Indies, Penang, Bombay. and Manilla; the finest kind, the ‘Beluga leaf,’ coming from the first-named of these countries, and being the produce of a species of sturgeon. Other Russian or Siberian varieties are ‘Astrakhan leaf,’ ‘Saliansky leaf,’ and ‘Samovy leaf.’

The following are the principal species of fish from which Russian isinglass is obtained: *Acipenser huso*, or the Hausen; *A. Güldenstædtii*, or the Osseter; *A. ruthenus*, or the Sterlet; *A. stellatus*, or the Sewruga; *Silurus glanis* and *Cyprinus carpio*. The isinglass of New York is derived from *Labrus squeteague*; that of New England—the ‘ribbon isinglass’—from the common Cod, *Gadus Morrhua*. In Brazil, it is taken from a species of *Silurus*; and in Iceland, from *Gadus* and *Molva vulgaris*, or the Ling.

The chief emporium for Russian isinglass is the great fair of Nijni-Novgorod, whence the largest part of the merchandise finds its way to London, through the agency of St. Petersburg traders. It arrives here about the end of June. Those supplies which reach us from Brazil and other countries are received at all seasons.

The fish being taken, the bladders are immediately removed, sufficient care in the cleansing of them from mucus and blood-stains being often purposely neglected, since a loss of weight results in the process when properly performed. In consequence of this neglect, the value of the material is diminished in proportion to the impurities which it contains.

On its arrival here isinglass is a hard, tough substance, and for many purposes it is necessary to ‘cut’ it. The operations of ‘cutting’ consist, first, in soaking the flakes until somewhat pliable, trimming the edges, and scraping off the dark spots; next, in putting them through two sets of rollers, under great pressure, by which they are flattened to the thickness of writing-paper; and, finally, in cutting them into fibres of extreme fineness, a process now almost always effected by a machine constructed for that purpose.

The uses for which isinglass is employed are the ‘fining’ or clarifying of fermented beverages, as ale and wine, and various culinary preparations. For the former purpose, the properties of isinglass are remarkable; for, whilst possessing the exact chemical composition of gelatin, it has the power, which is wanting in gelatin, of entangling in the film or web which it forms as it dissolves, all the suspended impurities contained in the liquids which it is sought to clarify. The lower grades of isinglass are used either in the natural or the manufactured condition by brewers and the manufacturers of cider, and the better classes of the Russian material by wine merchants. For the purpose of the brewer it is usual to dissolve the isinglass in sulphurous acid which has a tendency to preserve the ale.

The choicest descriptions are used by the cook and the confectioner for the thickening of soups, jellies, &c., but as for these purposes the fining properties of isinglass are not of any account, gelatin serves equally well, and has, under the name of patent isinglass, been so employed (*v.* GLUE).

ISOCETIC ACID $C_{14}H_{29}COOH$, m.p. 55°, is obtained from the oil extracted from the seeds of *Jatropha Curcas* (Linn.) (Bouis, J. 1854, 462).

ISOFORM *v.* SYNTHETIC DRUGS.

ISOPRAL *v.* SYNTHETIC DRUGS.

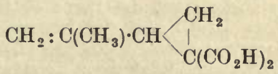
ISOPRENE. *β-Methyldivinyl*

$$CH_2:C(CH_3)CH:CH_2.$$

Discovered by Greville Williams among the products obtained by the destructive distillation of rubber (Phil. Trans. 1860, 241). Tilden obtained it among the more volatile compounds obtained by the action of heat on oil of turpentine and other terpenes (Chem. Soc. Trans. 1879, 417; 1884, 415), and Gladstone rom refraction and dispersion measurements came to the same conclusion as Tilden, viz. that the so-called *pentine* obtained from turpentine was identical with isoprene from rubber (Chem. Soc. Trans. 1896, 619). Mokiewski (J. Russ. Phys. Chem. Soc. 1898, 30, 885) found that isoprene obtained from turpentine contains some trimethylethylene, for on treatment with one molecule of bromine in a cooled ethereal solution, isoprene dibromide and an amylene derivative were obtained. Ipatiew and Wittorf (J. pr. Chem. 1897, [ii.] 55, 1) proved the presence of trimethylethylene in isoprene obtained from rubber. By treating isoprene dibromide with zinc-dust, pure isoprene is obtained. Staudinger and Klevor (Ber. 1911, 44, 2212), using Tilden's method, have shown that a better yield of isoprene can be obtained by working under reduced pressure. A 60 p.c. yield of isoprene can be obtained by passing the vapours of dipentene or limonene under very greatly reduced pressure over an electrically heated platinum spiral; the isoprene so obtained is almost pure, containing very little trimethylethylene. Terpineol, terpinene and camphene do not yield isoprene under these conditions.

Constitution.—Ipatiew (J. pr. Chem. 1897, [ii.] 55, 1, 4) found that isoprene unites with hydrogen bromide in acetic acid to form a dihydrobromide identical with β-methyl-βδ-dibromobutane $(CH_3)_2CBr{\cdot}CH_2{\cdot}CH_2Br$, b.p. 74°–75° (16 mm.). Alcoholic potash converts the latter into a hydrocarbon, which is not a monosubstituted acetylene, since it has no action on ammoniacal cuprous chloride or silver nitrate, is not a disubstituted acetylene, since the boiling-point is too low, and finally is not dimethylallene, since its boiling-point is not 40°–41° but 34°–35°. Hence it must be β-methyldivinyl. Euler (J. pr. Chem. [iii. iv.] 57, 131; Ber. 1897, 1989) synthesised β-methyldivinyl by treating β-methylpyrollidine twice with methyliodide followed by caustic potash, and found it to be identical with isoprene, and both substances yielded the same addition product with hypochlorous acid. Mokiewski (J. Russ. Phys. Chem. Soc. 1900, 32, 207) obtained a compound C_5H_9Br, b.p. 66°–67°, by the action of hydrogen bromide on isoprene, and treatment with alcoholic potash converted this into an alcohol $C_5H_{10}O$. The esterification constant was determined and it was found that both the alcohol and bromide were tertiary, and since dimethylallene gives the same bromide, this confirms isoprene as being β-methyldivinyl.

Isoprene is a colourless liquid, b.p. 33·5° (Mokiewski; Ipatiew, *l.c.*); sp.gr. 0°/0° 0·6989 (M. *l.c.*); magnetic rotation, 7·529; sp.gr., 15°/15°, (from turpentine) 0·6768, (from rubber) 0·6748 (Perkin, Chem. Soc. Trans. 1895, 258); thermal expansion (Thorpe and Jones, *ibid.* 1893, 277). By heating isoprene to 300°, only a little dipentene is formed, but a quantity of another hydrocarbon (b.p. 64°–66° (12 mm.)), possibly diisoprene, and also di- and polymyrcene (*v.* RUBBER) (Harries, Ber. 1902, 3265; Tilden, Chem. News, 46, 120; Bouchardt, Compt. rend. 87, 654; 89, 361). According to Bouchardt (*l.c.*) and Tilden (Chem. News, 1892, 65, 265), strong acids, such as hydrochloric acid, convert isoprene into a tough elastic substance resembling rubber. Bourchardt (Gummi-Zeit, 1901, 16, [viii.] 133) finds that when isoprene (1 part) and hydrochloric acid (12–15 parts) saturated at 0° are sealed in a tube and placed in a freezing mixture, much heat is evolved on shaking. After leaving for 2 or 3 weeks, the contents were diluted and distilled until oily drops ceased coming over. The residue was purified by boiling with water, had all the properties of rubber and gave similar distillation products. Analysis gave the following figures: C=87·1; H=11·7; Cl=1·7. Tilden found that on standing for some months, isoprene is slowly polymerised into a rubber-like substance. Harries (Chem. Zeit. 1910, 34, 315) converted isoprene into rubber by means of acetic acid, but could not effect the change with hydrochloric acid. Chromic acid oxidises isoprene into carbon dioxide, formic and acetic acids; nitric acid yields oxalic acid. Isoprene dibromide $CH_2:C(CH_3)CHBr{\cdot}CH_2Br$ is formed when isoprene is treated with bromine in carbon disulphide solution at 0° (Blaise and Courtot, Bull. Soc. chim. [iii.] 35, 989); b.p. 101° (19 mm.). On treatment with sodium ethoxide and ethyl malonate, it yields an ethyl ester $C_{12}H_{18}O_4$, which on hydrolysis yields isoprenic acid (*iso*propyltrimethylenedicarboxylic acid)



$$CH_2:C(CH_3){\cdot}CH\left\langle\begin{array}{l}CH_2\\ |\\ C(CO_2H)_2\end{array}\right.$$

m.p. 115° (Ipatiew, J. Russ. Phys. Chem. Soc. 1901, 33, 540).

ITROL *v.* SYNTHETIC DRUGS.

IVORY is essentially *dentine*, the main constituent of all teeth, but usage restricts the term to the dentine of those teeth which are available for industrial purposes; chiefly those of the elephant, hippopotamus, walrus, narwhal, and sperm-whale.

Ivory contains 57–60 p.c. of calcium salts, chiefly the phosphate, with 40–43 p.c. of an organic matrix and 0·24–0·34 p.c. of fat. It differs from other dentines chiefly in the large amount of organic matter it contains (*cp.* human dentine containing 25 p.c. of organic matter), and in its structure (*v. infra*) and from bone in its greater elasticity and the absence of the larger canals conveying blood vessels.

The substance of ivory is permeated by an immense number of fine canals, about $\frac{1}{1500}$ inch in diameter and strongly curved, to which are due its fineness of grain and probably much of its elasticity. That obtained from the tusks of *Proboscidea* exhibits, on a transverse section, a characteristic pattern of curved decussating lines. The cross-section shows a central spot, the residue of the pulp-centre (*v. infra*), surrounded by concentric circular 'contour lines,' due to a number of minute, irregular 'interglobular spaces.' These spaces and the canals are probably filled with protoplasmic matter in the living tooth. The exterior of the tooth is covered with cementum, usually of a brown colour.

Most of the ivory now used is obtained from the upper incisor teeth of the elephant. The tusks of the African elephant are 9–10 feet long and weigh up to 160 lbs., and are possessed by both males and females. Of Indian elephants, none of the females and not all the males have tusks, and those of the latter are usually less than 8 feet in length and 90 lbs. weight. Captive elephants have their tusks shortened and the ends bound with metal. The tusks grow continuously, and if cut at intervals of ten years yield a useful amount of ivory, although that from wild elephants, especially African elephants, is more highly valued.

The tusks are implanted to the extent of about half their length in curved bony sockets which run nearly vertically upwards to the level of the eyes. The part within the socket has a conical centre of pulp by the conversion of which into dentine growth takes place, fresh pulp being continually formed at the base of the tooth. The pulp is not easily injured and sometimes foreign bodies, such as bullets and spear-heads, have been found embedded in solid ivory, their presence in the pulp having failed to inhibit its conversion into dentine.

In Russia the tusks of mammoths from North Siberia are much used: they have been preserved unchanged from prehistoric times by the low temperatures of that region.

The canine teeth of the hippopotamus yield an ivory harder and whiter than that of the elephant, and less prone to turn yellow.

Among Northern nations, the upper canine teeth of the walrus are used as a source of ivory. They consist of dentine covered with cementum and have an axis of secondary dentine which is nodular in appearance but usually dense and uniform. The spiral tusk of the narwhal is similarly employed.

Ivory is largely used for making billiard balls, graduated scales, knife-handles, piano-keys, combs, fans, &c., and a considerable quantity is imported into China for the manufacture of ornamented articles. Dieppe is the principal centre for ivory-working in Europe.

As ivory shrinks when dried it is usually cut roughly to shape first, then dried spontaneously or by heat, and finally finished. Because of its high price, great care is taken to cut it up economically and all chips, cuttings, &c., are used for making *ivory-black* or for the preparation of a very pure gelatin.

Ivory can be made flexible by treatment with phosphoric acid and re-hardened by washing and drying, but not without injury to its quality. It takes dyes well and it may be bleached by exposure to sunlight and moisture, by the action of hydrogen peroxide, or by washing alternately with solutions of potassium permanganate and of oxalic acid (Textile Colourist, 1901. 23, 285; *v.* also Livache, J. Soc. Chem. Ind. 1903, 307).

J

JABORANDI. *Pilocarpus.* The natives of the eastern parts of South America employ the word 'jaborandi' to designate a group of plants having similar diaphoretic and sialagogue properties. The most important of these, the official jaborandi, was introduced into European medicine by Coutinho and Gubler in 1874 (Rép. de Pharm. 2, 171). The leaves of the plants are used. The jaborandi leaves at present in the market are those of *Pilocarpus pennatifolius* (Lem.) and the Maranham jaborandi, *Pilocarpus microphyllus* (Stapf.).

Three alkaloids have been separated from jaborandi. Rabuteau (Pharm. J. [iii.] 4, 911) and Byasson (*ibid.* [iii.] 5, 826) investigated the leaves chemically, but the first definite compound, *pilocarpine* $C_{11}H_{16}N_2O_2$, was discovered by Hardy (Compt. rend. Soc. Biol. 1875, 109; Bull. Soc. chim. 24, 497; J. Pharm. Chim. [iv.] 23, 95; Pharm. J. [iii.] 6, 887; 7, 496) and independently just afterwards by Gerrard (*ibid.* [iii.] 5, 865, 965; 6, 227; 7. 255; 10, 214; 11, 608). To obtain it, Hardy prepares an aqueous extract which is treated with alcohol, the alcoholic solution evaporated to a thick syrup, and this dissolved in a little water and precipitated with ammoniacal lead acetate. The mixture is filtered and the lead removed from the filtrate by sulphuretted hydrogen which then contains the alkaloid as acetate. Mercuric chloride is added, which forms an insoluble double chloride. This is separated, washed with water and decomposed by sulphuretted hydrogen. The solution contains pilocarpine hydrochloride, and treated with ammonia and chloroform it yields to the latter the free alkaloid. Gerrard suggests the following process. The leaves are exhausted with 84 p.c. alcohol, containing 1 p.c. of strong solution of ammonia. The solution is neutralised with tartaric acid, the alcohol removed by distillation, and the residue treated with excess of ammonia and alcohol and the alcohol again distilled off. From the residue chloroform extracts crude pilocarpine which is best purified by conversion into the nitrate; this admits of easy recrystallisation from alcohol, and from it the free alkaloid may be readily obtained. Poehl (Bull. Soc. chim. [ii.] 24, 340) uses phosphomolybdic acid as a precipitant for pilocarpine, both in valuing the drug and in the preparation of the alkaloid; and Christensen (Pharm. J. [iii.] 12, 400) for the former purpose weighs the alkaloid in the form of a gold salt. Another process is proposed by Petit (*ibid.* [iii.] 8, 46).

Pilocarpine forms long colourless crystals, melting at 34°, but is usually obtained as a thick syrup. It is freely soluble in alcohol, water, or chloroform, but is almost insoluble in ether or light petroleum. It is poisonous, and like nicotine, which it resembles in physiological action, it contracts the pupil of the eye. Pilocarpine yields well defined salts and when dissolved in sodium hydroxide forms the sodium salt of *pilocarpic acid*, of which pilocarpine is the anhydride (Petit and Polonowsky, J. Pharm. Chim. [vi.] 5, 370, 430, 475; Jowett, Chem. Soc. Trans. 77, 473; Pinner and Schwartz, Ber. 1902, 35, 192).

Pilocarpidine $C_{10}H_{14}N_2O_2$ was isolated from jaborandi leaves by Merck (Pharm. J. [iii.] 16, 106) and by Harnack (Annalen, 238, 230). It is a syrupy liquid, moderately soluble in water, easily in alcohol and chloroform, but insoluble in light petroleum. The researches of Jowett show that this base is found only in the leaves of the true jaborandi, *P. jaborandi* (Baill.), and is not contained in the leaves at present available.

isoPilocarpine is isomeric with pilocarpine and is formed by the action of heat or alkalis on this base. It was discovered by Petit and Polonowsky, but was considered by them to be the same as the pilocarpidine described above. *iso*Pilocarpine occurs in small quantity in the leaves of the drug but the greater portion is formed during the process of manufacture. It forms colourless deliquescent prisms (Petit and Polonowsky) or a viscid oil (Jowett). It can be distilled in a vacuum without decomposition. A solution of *isopilocarpic acid*, the analogue of pilocarpic acid, may be obtained by passing carbon dioxide into a solution of its salts in absolute alcohol and removing the alkali carbonate by filtration. *iso*Pilocarpine nitrate is present as an impurity in the commercial pilocarpine nitrate.

(For the constitution and reactions of the above compounds, *v.* ALKALOIDS.)

The alkaloid described as jaborine by Harnack and Meyer (Annalen, 204, 67), appears to be a mixture of *iso*pilocarpine, pilocarpidine, and possibly pilocarpine.

The physiological action of the jaborandi alkaloids has been studied by Marshall (J. Physiol. 31, 123). Pilocarpine is the most active physiologically, *iso*pilocarpine produces a similar but much weaker effect than pilocarpine, while pilocarpidine is so very slightly active, it may be said to be almost inactive.

The microchemical detection of the alkaloids in the leaves of *Pilocarpus pennatifolius* (Lem.) has been investigated by Tunmann (Chem. Zentr. 1909, i. 1510).

Of the constituents of jaborandi which have been examined, there only remains to be mentioned the volatile oil, which exists to the extent of about ½ p.c. in the leaves. This consists of a dextrorotatory terpene which boils at 178°, *pilocarpene* $C_{10}H_{16}$, and some higher boiling liquid and solid compounds. Pilocarpene has the sp.gr. 0·852, and forms a crystalline hydrochloride $C_{10}H_{16},2HCl$ which melts at 49·5°.

An examination of a species of jaborandi, *Pilocarpus spicatus* (St. Hilaire) [*Aracati jaborandi* (Holmes)], by Petit and Polonowsky (J. Pharm. Chim. [vi.] 5, 369), has led to the isolation of two alkaloids. The leaves were extracted in the usual way and the mixture of the bases converted into nitrates. The mixed nitrates were then treated with sodium hydroxide and extracted with chloroform. From the chloroform solution, *pseudo-jaborine* was obtained as a colourless oil with strongly alkaline properties. The second alkaloid *pseudo-pilocarpine* has very much the same properties as pilocarpine except that it is optically inactive. A. S.

JADE. Under this term are included two distinct minerals differing widely in chemical composition, but strikingly similar to one another in external characters. These are nephrite and jadeite. They rank as precious stones, being especially valued in the East as the material for elaborately carved ornaments. Stone implements worked in these materials have been found in the ancient Swiss lake-dwellings and amongst prehistoric remains in many other countries. These minerals have, in common, a white to green (rarely a pale violet) colour, with a certain degree of translucency and a greasy appearance on highly polished surfaces. They are remarkable for their extreme toughness (as distinct from hardness), it being very difficult to fracture pebbles by blows from a hammer. This toughness is a result of the peculiar texture of the material: thin sections examined under the microscope show a close, felted aggregate of short, minute fibres.

The name nephrite from the older name *lapis nephriticus*, meaning kidney-stone, refers to the ancient belief that when worn as a charm this stone was a remedy for kidney disease. The name jade has the same meaning, through the Spanish 'piedra de yjada.' A well-known Chinese name is 'yu,' and the ancient Mexican is 'chalchihuitl.' Jadeite was first distinguished chemically and so named by A. Damour in 1863.

Nephrite is a metasilicate of magnesium and calcium $CaMg_3(SiO_3)_4$, with usually a small and variable amount of ferrous oxide (to which is due the range in colour). It is a member of the amphibole group, differing from tremolite, actinolite, and amphibole-asbestos only by reason of the peculiar texture of the material. Under the microscope, the fibres show prismatic cleavages inclined at 124° and the optical characters of amphibole; sp.gr. 2·91–3·1.

Jadeite is a metasilicate of sodium and aluminium $NaAl(SiO_3)_2$; small amounts of ferrous and ferric oxides are often present, and in the dark green variety known as chloromelanite there is 6–10 p.c. Fe_2O_3 isomorphously replacing alumina. Jadeite is a member of the pyroxene group, having an angle of 93° between the prismatic cleavages and the optical properties characteristic of this group; sp.gr. 3·30–3·35 (3·4 in chloromelanite). The hardness (H. 6½–7) is rather greater in jadeite than in nephrite (H. 6–6½).

These two minerals are of course readily distinguished by chemical tests; and also by the easier fusibility of jadeite, which at the same time imparts a yellow colour to the flame. In thin sections under the microscope, the optical characters and cleavage angles afford distinguishing features. In many cases, however, it is the material of a carved ornament that requires determination, and then the only available test is that given by the difference in sp.gr. Some other minerals, *e.g.* the hard compact variety of serpentine known as bowenite (sp.gr. 2·6), which are often confused with jade, may also be readily distinguished by their sp.gr.

Nephrite and jadeite each occur as constituents of metamorphic silicate rocks, and they are frequently so intimately intermixed with other minerals that the material itself is at times of the nature of a rock. Much of the material used for carving is collected as pebbles and boulders from the beds of streams. Quarries in the solid rock are, however, worked in Eastern Turkestan (nephrite) and at Tawmaw in Upper Burma (jadeite). The well-known New Zealand 'greenstone' is a dark green nephrite. (On New Zealand nephrite, *see* A. M. Finlayson, Quart. J. Geol. Soc. 1909, 65, 366.)

Jade presents many points of interest to the ethnologist and collector as well as to the mineralogist, and it is the subject of a considerable literature. A monumental work in two huge, beautifully illustrated volumes is the 'Investigations and Studies in Jade,' based on the Heber R. Bishop collection (New York, 1906; a privately printed edition limited to 100 copies was prepared at enormous expense for free distribution to the principal royal and public libraries of the world). The subject is here dealt with by numerous contributors from all possible points of view; in the chemical portion 58 new analyses are given. A briefer and more accessible general account of jade is given in M. Bauer's Edelsteinkunde, 2nd edit. 1909; English translation, Precious Stones, by L. J. Spencer, 1904. L. J. S.

JAK-WOOD, or Jack-wood, is derived from the *Artocarpus integrifolia* (Linn.) which belongs to the *Urticaceæ*, and is cultivated throughout India, Burmah, and Ceylon, except in the north. It is largely used for carpentery, furniture, &c., and is stated to be imported to Europe for this purpose. The rasped wood is used by the natives of India and Java as a yellow dye in conjunction with alum, for the robes of the Burmese priests, also for dyeing silk and for general purposes.

An aqueous solution of the wood possesses the characteristic property that when it is treated with alkali and gently warmed, the yellow solution at first obtained assumes a beautiful blue tint.

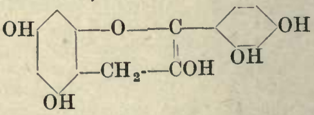
Jackwood (Perkin and Cope, Chem. Soc. Trans. 1895, 67, 937) is very similar to old fustic, and its dyeing properties are due to *morin* (*see* OLD FUSTIC). Unlike old fustic, however, it contains no maclurin, but there is present a second substance, cyanomaclurin, which is devoid of tinctorial property. These compounds can be isolated from jackwood by methods which are almost identical with those which have been applied to fustic itself, and their separation may be effected by means of lead acetate as this precipitates only the morin.

Cyanomaclurin $C_{15}H_{12}O_6$ crystallises in colourless prisms, somewhat readily soluble in water, and gives with basic lead acetate a colourless precipitate, and with ferric chloride a violet coloured liquid. Its solution in dilute alkalis is colourless, but if this be gently warmed a beautiful deep indigo colouration is produced, which on longer digestion passes into green and finally becomes brown-yellow. When fused with alkali, it gives *β-resorcylic acid* and *phloroglucinol.*

Acetylcyanomaclurin $C_{15}H_7O_6(C_2H_3O)_5$, colourless needles, melts at 136°–138°, and *benzoylcyanomaclurin* $C_{15}H_7O_6(C_7H_5O)_5$, colourless prisms, melts at 171°–172°. *Disazobenzenecyanomaclurin* $C_{15}H_{10}O_6(C_6H_5N_2)_2$, scarlet needles, m.p. 245°–247° (decomp.), gives an *acetyl* derivative probably

$$C_{15}H_7O_6(C_6H_5N_2)_2(C_2H_3O)_3$$

orange red needles, m.p. 209°–210° (decomp.) (Perkin, Chem. Soc. Trans. 1905, 87, 715). In certain respects, cyanomaclurin resembles the catechins of gambier and acacia catechus, and more especially so in that by boiling with dilute acids it gives reddish-brown amorphous substances, which are very similar to the so-called catechin anhydrides. The product obtained by the action of hydrochloric acid on a boiling acetic acid solution of cyanomaclurin is insoluble in alkalis and all solvents, and has a percentage composition almost identical with the catechin anhydride similarly produced. According to Perkin, cyanomaclurin is possibly a reduction product of morin, thus:



Jackwood dyes shades very similar to those given by old fustic; that is, olive yellow with chromium, dull yellow with aluminium, and a brighter yellow with tin mordant. On the other hand, the sample examined by Perkin and Cope possessed only about one-third of the dyeing power of old fustic. A. G. P.

JALAP *v.* RESINS.

JALAPIN *v.* GLUCOSIDES.

JAMBA OIL is obtained from a plant belonging to a variety of the genus *Brassica.* The oil behaves, in most respects, very similarly to ordinary rape oil, but differs from it most distinctly in that it does not lend itself so readily to the manufacture of 'blown' oil, as the other oils belonging to the rape oil group. Hence jamba oil is distinctly inferior to rape oil prepared from genuine rape seed oil, a difference which finds its ready expression in the lower commercial value of jamba oil, as compared with that of colza oil.

Jamba oil is most readily recognised by its peculiar taste and smell. It is chiefly used as a burning oil, although it does not burn so well as colza oil. It is also used for lubricating purposes, and takes its place, as regards quality, between Indian rape oil and ravison oil.

J. L.

JAMESONITE. A sulphantimonite of lead, invariably containing 2–3 p.c. of iron, the formula being $4PbS\cdot FeS\cdot 3Sb_2S_3$ (W. T. Schaller, Zeitsch. Kryst. Min. 1911, 48, 562; L. J. Spencer, Min. Mag. 1907, 14, 207, 310). It is orthorhombic with a distinct basal cleavage, but only acicular crystals (*v.* Feather-ore), columnar masses, or more usually finely fibrous masses have been found. Coarse columnar masses associated with stibnite have been mined at Endellion in Cornwall. The mineral is of frequent occurrence in Bolivia, and, as it sometimes contains small amounts of silver, it has been worked as a silver-lead ore as well as for antimony. L. J. S.

JANTHONE. A synthetic perfume obtained by condensing citral or lippial and mesityl oxide. *Lippial* $C_{10}H_{16}O$ is present in the oil of *Lippia citriodora* (H. B. & K.). Janthone is a tetrahydrobenzene derivative containing two ethylene bonds in the ketone side chain: b.p. 162° under 10 mm.; sp.gr. 0·9452. When diluted it has a characteristic odour of violets and orris root. (D. R. P. 118288, 1898; Farbw. Durand, Hugenin & Co., Zeitsch. angew. Chem. 1901, 14, 346.)

JAPACONITINE *v.* Vegeto-alkaloids.

JAPAN BLACK *v.* Brunswick black.

JAPAN EARTH. *Terra japonica v.* Catechu.

JAPANESE SARDINE OIL is obtained from *Clupanodon melanosticta* (T. and S.), a fish belonging to the *Clupeidæ*. Japanese sardine oil differs distinctly from the ordinary sardine oil (*see* Sardine oil) by its higher iodine value, which in pure specimens reaches as high a figure as 187. The commercial oil has, until recently, been prepared in a very crude manner, the fish refuse having been boiled with water to separate the oil. Japanese sardine oil is characterised by a considerable proportion of *clupanodonic acid*, of which as much as 14·2 p.c. is yielded by genuine specimens.

The commercial Japanese sardine oil has hitherto been more or less mixed with other fish oils, so that the commercial specimens of oil exhibit much lower iodine values than the genuine oils. Japanese fish oil (which must not be confounded with Japanese cod liver oil) is largely exported to Europe and to Australia, where it is used in soap making and in the leather industries. J. L.

JAPANNING. A term synonymous with 'lacquering' (*v.* Lacquer).

In Europe, japanning is also taken to mean the art of coating surfaces with varnishes which are then hardened by subjecting them to a high temperature, an art which holds an intermediate position between painting and enamelling. The varnishes are transparent and durable bodies, in black or other colours, black being the hue which is most extensively used. Black varnish is composed of pure natural asphaltum mixed into a preparation of gum anime dissolved in linseed oil and turpentine. This in thin coatings appears brown, and requires several courses to acquire the requisite blackness; the article treated being placed in a stove at about 150° after each coating. For colours, the necessary mineral pigments or metallic powders are mixed with a transparent copal varnish of less body than ordinary painters' varnish.

European japanning, although very far behind the work produced by the process described as in use among the Japanese, produces a very brilliant and durable coating to small articles of metal work and papier mâché. It is also applied as a facing for stone to imitate marble.

JAPAN SAGO. Starch obtained from the stem of *Cycas revoluta* (Thunb.).

JAPAN WAX (Japan tallow) is obtained from the berries of several species of the sumach tree, viz.: *Rhus succedanea* (L.), known in Japan as 'hazé'; *R. acuminata* (DC.); *R. vernicifera* (DC.), known in Japan as 'urushinoki'; *R. sylvestris* (Sieb. et Zucc). The first-named species is grown chiefly in China, whereas the last-named one flourishes especially in the western provinces of Japan; the species *R. succedanea* grows also in Indo-China and in India. In China, Japan, and Tonkin, the trees are cultivated chiefly for the sake of the lacquer which they exude. Japan wax must therefore be considered as a by-product of the lacquer industry.

The seeds of the several species of *Rhus* consist of a small kernel surrounded by a greenish, striated, shrivelled mass. In China the wax is prepared by crushing the seeds, together with their coating, and steaming them in perforated cylinders so that the fat melts and runs off. In Japan the manufacture is still carried out in a somewhat crude fashion, by storing the berries in straw until they are fully matured, then crushing them by hand in a wooden funnel-shaped trough, and winnowing the mass so as to separate the kernels. The powdered mass thus obtained is put into hempen sacks and subjected to pressure in wooden wedge presses. The yield from the berries ranges from 15 to 20 p.c. The fat is a coarse greenish tallow-like mass. It is refined by remelting, pressing through cotton sacks, and allowing the fat to drop into cold water. The thin flakes of the wax are then bleached by exposure to the sun in shallow baskets (in a similar manner as is done in the process of bleaching bees' wax), the material being continually turned over and sprinkled with water. The bleached wax is finally melted and cast into slabs, in which form it is exported to Europe.

The production of Japan wax cannot be largely extended, as it takes 7 to 8 years for a wax tree to reach maturity, and if the tree promises to become a fruitful source of lacquer, this leads to its sacrifice as a source of wax.

Japan wax is a pale yellow, somewhat hard substance of conchoidal, somewhat lustrous fracture. On keeping, Japan wax turns deep yellow and becomes coated with a white powder consisting of microscopical prismatic needles. The term 'wax' is a misnomer, as Japan wax is a glyceride, consisting chiefly of palmitin and free palmitic acid. Hence, it is more appropriately termed Japan tallow.

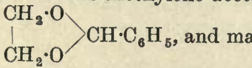
Japan wax is insoluble in cold alcohol, but dissolves readily in boiling alcohol, separating almost completely on cooling as a granular, crystalline mass. In addition to palmitic acid, it also contains small quantities of dibasic acids, as also of a soluble acid, the proportion of which has been found to amount to almost 6 p.c. The proportion of dibasic acids amounts to nearly 1 p.c.; amongst these, the largest in amount is *japanic acid* $C_{19}H_{38}(COOH)_2$ (nonadecamethylenedicarboxylic acid), which is accompanied by its lower homologues, heptadecamethylenedicarboxylic acid $C_{17}H_{34}(COOH)_2$, and octodecamethylenedicarboxylic acid

$$C_{18}H_{36}(COOH)_2.$$

These dibasic acids probably occur as mixed glycerides of palmitic and dibasic acids. The constitution of Japan wax being that of a glyceride, it is most readily differentiated from the true waxes by yielding glycerol on saponification. The iodine value of genuine Japan wax is about 4. The commercial wax has a higher iodine value—from 10 to 15—as in consequence of the increased demand for Japan wax it has become the practice in Japan to extract the press residues with the (hazé) kernel oil. In the Chinese mode of manufacture, the kernel oil passes automatically into the 'wax.' At a temperature of 16°–18°, Japan wax has the density of water of the same temperature.

Japan wax is largely used for waxing floors, and as a constituent of polishes. As it forms an emulsion with water, it can be used for currying leather. Notwithstanding its high proportion of palmitic acid, it does not constitute a suitable candle material. The proposal to use it as an admixture with edible fats, or with margarine, is to be strongly deprecated. J. L.

JARGON or **JARGOON** *v.* ZIRCON.

JASMAL. The active odoriferous principle of the jasmine flower. Is the methylene acetal of phenyl glycol,  $\begin{matrix} CH_2{\cdot}O \\ | \\ CH_2{\cdot}O \end{matrix}\!\!>CH{\cdot}C_6H_5$, and may be synthetically formed by condensation of phenyl glycol and formaldehyde in presence of sulphuric acid: b.p. 218°; sp.gr. 1·1334 (Verley, Compt. rend. 1899, 128, 314).

JASPER. A compact and opaque variety of quartz, intimately intermixed with iron oxide and hydroxide, clay, &c.; these impurities being present sometimes to the extent of 20 p.c. The material has a dull, even fracture, but it takes a good polish; the colours are various—red, yellow, brown, green, &c. It is cut and polished as an ornamental stone, and was much prized by the ancients, but their *jaspis* included other minerals than those now designated as jasper. The well-known *Egyptian jasper* is found as nodules and pebbles in the Nile Valley, and resembles a brown flint, with dark zones and cloudings. *Banded jasper* is a striped variety, well illustrated by the beautiful red and green 'riband jaspers' of the Ural Mountains. Some banded jaspers appear to be metamorphic sedimentary rocks, whilst others are striated felsitic tuffs. The so-called *porcelain-jasper* is merely a shale highly indurated by exposure to a high temperature. F. W. R.

JAUNE ACIDE. *Acid yellow* (*v.* AZO-COLOURING MATTERS).

JAUNE ANGLAIS. *Victoria yellow* (*v.* CRESOL).

JAUNE BRILLIANT. *Cadmium sulphide* (*v.* CADMIUM).

JAUNE DE FER, JAUNE DE MARS. *Mars yellow* (*v.* PIGMENTS).

JAUNE D'OR. *Martius's yellow* (*v.* NAPHTHALENE).

JAUNE N. *Curcumeïn; Orange N.* (*v.* AZO-COLOURING MATTERS).

JAUNE SOLIDE. *Fast yellow* (*v.* AZO-COLOURING MATTERS).

JAVA WAX, FIG WAX *v.* WAXES.

JESTERIN *v.* GLUCOSIDES.

JET. (Fr. *Jais, Jaïet*; Ger. *Gagat, Agstein.*) A variety of fossil coal or lignite, similar in appearance to cannel-coal. Being hard and capable of taking a lustrous surface by polishing, it is used for making small ornamental articles; sp.gr. 1·35. It is found on the Yorkshire coast near Whitby, in Spain, France, and Würtemberg, occurring in the shale and limestone formations. The name is supposed to be a corruption of the *Gagates* of Pliny and Dioscorides, who described the mineral as found near the mouth of the river Gagas in Lycia, Asia Minor.

The jet of Whitby is evidently a fossilised coniferous wood, as shown by its structure in thin sections under the microscope. On its surface impressions of fossils, especially ammonites, frequently appear.

Whitby jet is divided into 'hard' and 'soft,' of which the former is the more esteemed; it is found near the base of the Upper Lias and, sparingly, in other parts of that formation. Soft jet occurs in the sandstones and oolitic shales. The hard variety is obtained in compressed layers varying from an inch or two in length and $\frac{1}{8}$th in thickness, to 6 feet long, 30 inches wide, and 4 inches thick. The largest piece ever found was 6 feet 4 inches long, $4\frac{1}{2}$ to $5\frac{1}{2}$ inches wide, and 1 and $1\frac{1}{2}$ inches thick; it weighed 11 lbs. 8 oz.

The collection of jet was formerly effected by cutting down the cliffs until the jet-veins showed themselves; to-day the cliffs are almost abandoned and the works are carried on inland to a distance of 20 miles. The operation is described by J. A. Bower (Jour. Soc. of Arts, 22) in these words: 'The process of obtaining jet here is simple; the faces of the hills are turned down bodily, and by then tunnelling for some distance, and after carrying several passages parallel from the face of the hill, transverse shafts are cut. When the rock becomes too hard the miners retire, pulling down the roofs on their return; in these falls the bulk of the jet is found.' The rough jet obtained from the inland mines is encased in a brown skin; that from the cliffs is covered with a blue skin. This is chipped off, the pieces of jet are sawn into suitable sizes and handed over to the carver or turner. (*See* Whitby Jet and its Manufacture, Jour. Soc. of Arts, 22, 80; Illustrations of the Geology of Yorkshire, Part I. The Yorkshire Coast, by John Phillips; A. C. Seward, The Structure and Origin of Jet, Rep. Brit. Assoc. 1901, 856; P. E. Spielmann, The Origin of Jet, Chem. News, 1906, 94, 281; 1908, 97, 181). L. J. S.

JUAR-ROOT. A powerful narcotic used in India to enhance the intoxicating power of bhang.

JUDSON POWDER *v.* EXPLOSIVES.

JUGLONE *v.* NAPHTHALENE.

JUNIPER. (*Genièvre*, Fr.; *Wachholder*, Ger.) The fruit, or so-called berries, of juniper have been employed in medicine from very early times. It is a reputed diuretic. Sometimes it has been used as an article of food, and the large proportion of sugar which it contains has rendered it available for fermentation and the distillation of spirit. Such a product was in France called *Genièvre* and hence the contracted form *gin* employed in this country for a spirit which now is merely flavoured with juniper. The juniper of modern medicine is the *Juniperus communis* (Linn.) (Bentl. a. Trim. 255) a well-known evergreen shrub which inhabits the northern regions of both hemispheres. The fruits are gathered chiefly in Hungary, Austria, and the south of France (Flück. a. Hanb. 624; Morel, Pharm. J. [iii.] 8, 886).

The most important constituent of juniper is the *volatile oil*, which although it occurs in all parts of the plant, is found chiefly in, and is always distilled from, the fruit. Both the quantity and quality of the oil varies with the age of the fruit. That obtained from the green fruit is larger in proportion, and is a lighter oil, than that distilled from the ripe fruit. The former is the more highly esteemed. The yield varies from 0·4 to 1·2 or perhaps 2·0 p.c. It is a colourless liquid, having a strong odour of juniper and a hot aromatic taste. It boils at 155° to 200° or 205° and its sp.gr. varies from 0·86 to 0·88 (Morel). It consists of a *terpene* boiling at 155°, sp.gr. 0·839 at 25° (Blanchet, Annalen, 7, 165), together with *polymeric terpenes*, chiefly $(C_{10}H_{16})_2$(?), which boil above 180°, mostly about 200°. Wallach (Annalen, 227, 228) has examined the terpene (*pinene*). The oil is lævorotatory. According to Blanchet, it forms a crystalline *hydrate*, and Soubeiran and Capitaine (J. Pharm. Chim. 26, 78) describe a liquid *hydrochloride*. Tilden (Pharm. J. [iii.] 8, 189) prepared from it a *nitrosyl chloride compound* $C_{10}H_{16}NOCl$. On long standing it deposits a *camphor* (Gm. 14, 295). Generally, its reactions are similar to those of turpentine oil (Gm. 14, 292; Dragendorff, Pharm. J. [iii.] 6, 581; Barth, Zeitsch. Chem. 1867, 509; Morel). The analytical constants of oil of juniper are given in Haensel's Half-yearly Report, Oct. 1908.

The other constituents of juniper fruits may be seen from the analyses of Donath (Dingl. poly. J. 208, 300) and Ritthausen (Landw. Versuchs-Stat. 20, 423). The chief of these is *glucose*, of which Donath finds 29·65 and Ritthausen 14·36 p.c. The bitter substance *juniperin*, which occurs only to the extent of 0·37 p.c., was first studied by Steer (Sitz. Ber. 21, 383). *Resins*, *cf.* Trommsdorff (Gm. 17, 449). A. S.

JUNIPER, OIL OF, *v.* OILS, ESSENTIAL.

JUTE is the bast fibre almost exclusively of two plants of the natural order *Tiliaceæ*, viz. *Corchorus capsularis* (Linn.) and *Corchorus olitorius* (Linn.), cultivated for the most part in Bengal, where they are indigenous. Although differing in size and in the form of their seed-pods, the plants are not greatly dissimilar in appearance and are not commercially distinguished from each other. The seed is sown annually, in April or May, and the plants after flowering, which takes place from August to September, and having now attained a height of 5 or 6 feet in the case of *C. olitorius*, and of 5 to 10 feet in that of *C. capsularis*, are cut down and thrown into pits of water to soak, after the manner of steeping flax. From a few days to a month is required to bring the stalks into a condition for stripping the bast from the wood and freeing it from cortex, these operations being purely manual. After being washed and dried the jute is made up into bales for sale.

Jute is very largely used for the manufacture of sacking and wrapping cloths (Hessians), as a paper-making fibre, and as a substitute for hair in making theatrical wigs. It is also employed for carpet-making and inferior cordage and, in India, for making small domestic articles such as nets and muzzles for oxen. In these islands the principal seat of the jute industry is Dundee.

The fibre occurs in strands of considerable length, 6–12 feet; the spinning unit or filament is of various lengths, according to the degree of subdivision practised. The filament is a complex of the ultimate fibres, of which from 5 to 12 are usually seen in the section at any point. They are polygonal in section and much thickened (lignified); their length does not exceed 2–3 mm., whereas those of flax and hemp—also bast fibres—are from 25–40 mm. long. This structural inferiority, together with the fact that the fibre substance yields somewhat readily to the action of oxidants (air and light) in presence of water, characterises jute as a 'weak fibre.'

Treated by the 'line spinning' process it may be spun into yarns of considerable fineness, but, owing to the large proportion of waste ('tow'), at relatively large cost. These yarns when bleached—preferably by 'soda bleach' (sodium hypochlorite)—have considerable lustre; they are soft and of a cream shade, and take up the majority of colouring matters—wood and aniline dyes—directly from the dye-bath. Jute fabrics are also successfully printed in steam styles, the presence of sodium sulphite being necessary to preserve the fibre substance from the action of the steaming process (Développement de l'Industrie de Jute, Cross and Witt, Bull. Mulhouse, 1881).

According to the investigations of Cross and Bevan, jute does not contain cellulose as such, but in the form of bastose or lignocellulose, which is a link between the carbohydrates and the aromatic compounds. Treated with chlorine it gives a yellow chlorinated derivative which when hydrolysed yields substances belonging to the tannic acid group. Hence it may be said that jute possesses a mordant which makes it receptive of aniline colours in a degree possessed by none of those fibrous materials which require the intervention of a mordant. When quantities of the fibre are kept in a damp situation, more especially when exposed to sea-water, it is decomposed into substances analogous to tannin and to acids of the pectic acid group. Under treatment by acids, jute is disintegrated, yielding xylose and furfural (*v.* also Tollens, Annalen, 254, 325). It is easily bleached by potassium permanganate after cleansing with soap or alkali, with a loss in weight of 3 to 4 p.c. In practice this is generally too expensive a process, and the substances usually employed are hypochlorites, in which great care is necessary, as chlorinated compounds may be formed and the fibre destroyed (*supra*) (*v.* CELLULOSE).

K

KAINITE. A hydrated double salt

$$MgSO_4 \cdot KCl, 3H_2O,$$

occasionally found in the potash-salt deposits as sharply developed, water-clear, monoclinic crystals; sp.gr. 2·1. As granular masses of a white, grey, or reddish colour it forms large beds near Stassfurt in Prussia, and at Kalusz in Galicia (*v.* POTASSIUM). On the artificial production of kainite, *see* van 't Hoff, Sitz.-Ber. Akad. Wiss. Berlin, 1901, 420; 1903, 678.

L. J. S.

KAIRINE, KAIROCOLL, KAIROLINE, *v.* QUINOLINE.

KAISERGELB *v.* AURANTIA.

KAISERROTH. The sodium salt of dinitrodibromfluoresceïn. Called also Eosin Scarlet, Safrosine, and Lutétienne.

KALIBORITE. A mineral resembling *pinnoite*, found by Feit in the salt deposits at Schmidtsmannshall, near Ascherleben, Prussia. Is a hydrated borate of potassium and magnesium

$$2K_2B_6O_{10} \cdot 9MgB_4O_7, 39H_2O.$$

Water disintegrates the mineral, but is otherwise without action on it. Easily soluble in warm mineral acids. Sp.gr. 2·05 (Chem. Zeit. 13, 1188).

KAMALA. Kamala is the orange red powder which exists as a glandular pubescence on the exterior of the fruits of the *Mallotus phillipinensis* (Muell.) (*Rottlera tinctoria* [Roxb.]), a small evergreen tree, met with throughout tropical India, Burma, and Ceylon, also in Java, China, the Malay Islands, and Australia. The ripe capsules are gathered in February or March, and shaken in bags until the powder separates.

Kamala is extensively employed by the Hindoos as an antithelmic drug and for dyeing silk and wool a bright orange colour. The fabric is dyed in a boiling bath containing 4 parts kamala, 1 part alum and 2 parts sodium carbonate (native barilla), previously well rubbed together in the powdered state with a small quantity of oil of sesamum. The alum is sometimes omitted, but the addition of alkali is absolutely necessary in order to dissolve the colouring matter, which is of a resinous character and quite insoluble in water. Kamala is also apparently used for the adulteration of Annatto. According to Perkin (private communication), samples of calico obtained from India and presumably dyed with kamala have proved on examination to owe their colour partially if not entirely to annatto. Kamala was formerly employed in this country as a remedy for taenia, but appears now to be very little used for this purpose.

Anderson was the first chemist to investigate kamala (Edin. New. Phil. J. 1, 300), and he isolated from it by means of ether a crystalline compound *rottlerin* $C_{11}H_{10}O_3$, a wax $C_{20}H_{34}O_4$, and a resin melting below 100°, to which he gave the formula $C_{30}H_{30}O_7$. Leube (J. 1860, 562) was unable to obtain any crystalline product from this drug, but he describes two resins, $C_{15}H_{18}O_4$, m.p. 80°, and $C_8H_{12}O_5$, m.p. 191°. Oettingen (Dissert. St. Petersburg, 1862) also could not obtain any crystalline substance from kamala. A. and W. Perkin (Ber. 1886, 19, 3109), however, isolated the crystalline rottlerin ('mallotoxin') of Anderson, and its existence was subsequently confirmed by Jawein (Ber. 20, 182).

As the result of a more extended examination of kamala and employing carbon disulphide for the extraction, A. G. Perkin (Chem. Soc. Trans. 1893, 63, 975) isolated not only Anderson's compounds, but small quantities of two crystalline substances, homorottlerin, which is yellow, and *iso*rottlerin, a salmon coloured powder, together with a high melting resin.

Rottlerin $C_{33}H_{30}O_9$ (Perkin, *ibid.* 1895, 67. 230), salmon coloured plates, melts at 191°–191·5° (P.), 200° (Jawein), 202°–204° (Telle, Arch. Pharm. 1906, 244, 441), readily soluble in ether. Solutions of the alkali carbonates and hydroxides dissolve rottlerin, the former only on gently warming. On boiling these orange-coloured liquids, decomposition gradually takes place, an odour of benzaldehyde is evolved and a resinous product separates. An alcoholic solution of rottlerin is coloured brown on the addition of ferric chloride.

Acetylrottlerin $(C_{11}H_8O_3(C_2H_3O)_2)_3$, yellow crystalline powder, m.p. 130°–135° (P.), and *benzoylrottlerin* $C_{33}H_{24}O_9(C_7H_5O)_6$, yellow powder (Bartolotti, Gazz. chim. ital. 24, [ii.] 480), have been prepared.

Rottlerin forms the following salts:

$$C_{33}H_{29}O_9Na, H_2O$$

orange brown glistening leaflets; $C_{33}H_{29}O_9K, H_2O$ leaflets; $(C_{33}H_{29}O_9)_2Ba$ minute reddish brown prisms; $(C_{33}H_{29}O_9)_2Sr$, $(C_{33}H_{29}O_9)_2Ca$, and $C_{33}H_{29}O_9Ag$, fine yellow needles.

Fused with alkali, rottlerin gives *benzoic acid, acetic acid*, and *phloroglucinol* (P.), and when oxidised with hydrogen peroxide in alkaline solution, *benzaldehyde* and *benzoic acid* are produced. With potassium permanaganate (Bartolotti), benzoic acid is also formed. Nitric acid (sp.gr. 1·5) gives *p-nitrocinnamic acid, o-nitrocinnamic acid, p-nitrobenzaldehyde,* and *p-nitrobenzoic acid* (P.). When heated with 2 p.c. sodium carbonate solution, a compound termed *rottlerone* separates (P.), which crystallises in garnet-red prisms, and to which the formula $C_{29}H_{26}O_6$ has been provisionally assigned.

According to Telle, if rottlerin is heated for 10 minutes with barium hydroxide solution, *phloroglucinolmethylether,* a resinous substance and *ψ-rottlerin,* m.p. 235°, are produced. When heated for 10 minutes with zinc powder and sodium hydroxide, rottlerin gives 60 p.c. of resin and about 30 p.c. of phenols, also *β-phenylpropionic acid,* acetic acid, and a small quantity of a crystalline acid, m.p. 185°–185·5. From the mixture of phenols, *phloroglucinolmonomethylether* and *phloroglucinoldimethylether,* were isolated. *Phloroglucinoltrimethylether* and a camphor-like substance, m.p. 170°–172°, were produced, when, with the zinc powder, only 2 p.c. sodium hydroxide solution was employed.

The molecular weight of rottlerin, determined cryoscopically in naphthalene, was 486, and agrees with that assigned to this substance by Perkin (*l.c.*).

Homorottlerin $C_{33}H_{36}O_9$(?), pale yellow needles, m.p. 192°–193°, is present in exceedingly small amount in kamala. It differs from rottlerin in being much less soluble in toluene, chloroform, or acetic acid, but otherwise the properties of these two compounds are similar (P.).

iso-Rottlerin $C_{12}H_{12}O_5$ (?), has been obtained in the form of plates, m.p. 198°–199°, insoluble in hot benzene, carbon disulphide, or chloroform. Cold solutions of the alkali carbonates dissolve it readily, and these solutions when boiled do not deposit resinous matter or emit an odour of benzaldehyde, as is the case with the alkali salts of rottlerin itself. It is probable that this compound, very little of which has been yet obtained, may prove to consist of hydroxyrottlerin (P.).

The low melting resin of Anderson, $C_{30}H_{30}O_7$(?), $C_{12}H_{12}O_3$(?) (Perkin), consists of a brittle transparent dark red mass, melting below 100°, and is readily soluble in carbon disulphide, ether, or chloroform. With hot alkaline solutions, it behaves similarly to rottlerin and evolves an odour of benzaldehyde, and with nitric acid (sp.gr. 1·5) gives *p*-nitrobenzoic acid. Perkin's *high melting resin* is a pale straw coloured mass, m.p. about 150°, and in general properties resembles the low melting variety.

According to Hummel and Perkin (J. Soc. Chem. Ind. 1895, 14), for silk dyeing it is best to add 1 part of kamala, and 0·5–1 part sodium carbonate to boiling water, then to enter the silk and to dye at the boiling temperature for 2–5 minutes only. Other experiments indicated that the amount of sodium carbonate to employ should be regulated by the quantity of water used rather than by that of the kamala, namely at the rate of 13–14 grams (Na_2CO_3,10aq) per litre. After dyeing for a short time with the addition of alkali only, to the extent of one-fifth of the weight of the kamala used, the addition of alum or stannous chloride to the dyebath makes the colour fuller and more orange. A similar but by no means identical effect is obtained by making a slight addition of sulphuric acid.

As pointed out by Perkin (*l.c.*), rottlerin is decomposed by boiling sodium carbonate solution, and the colour ultimately fixed on the fibre most probably consists of rottlerone. Although rottlerin itself does not dye mordanted fabrics, the potassium and sodium salts of this colouring matter give on calico mordanted with aluminium and iron, pale orange red and brownish-black shades.

Pure Java kamala contains, according to Flückiger (Arch. Pharm. 1892), 1·363 to 1·488 p.c. of ash, whereas in the kamala examined by Anderson (*l.c.*), 3·49 p.c. was present. The best commercial varieties usually contain about 5 p.c. of mineral matter (Seidler and Waage, Ber. Deut. pharm. Ges. 1891, 80); but the inferior qualities are highly adulterated (50 to 87 p.c.) with sand, earthy impurities, red brick dust, &c. (Perkin (*l.c.*) and J. Soc. Chem. Ind. 1900). A. G. P.

KAMALA RESINS *v.* RESINS.

KAMPHERITRIN *v.* GLUCOSIDES.

KAOLIN *v.* KAOLINITE.

KAOLINITE. A mineral species consisting of hydrated aluminium silicate $H_4Al_2Si_2O_9$, crystallising in the monoclinic system. Analyses of the pure crystallised material agree closely with the theoretical quantities: SiO_2, 46·5; Al_2O_3, 39·5; H_2O, 14·0 p.c. The water is expelled only at a high temperature (above 330°). As a white, glistening, crystalline powder, the mineral is occasionally met with in small amount in cavities and fissures in sedimentary rocks and in mineral-veins. The best crystals have been found near Amlwch in the island of Anglesey, and in the National Bell mine near Silverton in Colorado. These crystals have the form of six-sided plates or pyramids with a perfect micaceous cleavage parallel to the base; and do not exceed 0·1 to 0·2 mm. across. Their mean index of refraction is 1·563, and their birefringence (0·004) is much lower than that of mica (with small scales of which the mineral might be confused); sp.gr. 2·62; H. 2½. On the optical characters of crystals of kaolinite, *see* A. B. Dick, Min. Mag. 1888, 8, 15; 1908, 15, 124. The 'nacrite' of the Einigkeit mine, Freiberg, Saxony, and 'pholerite,' also from Saxony, form fan-shaped aggregates of rather larger pearly scales of kaolinite.

The mineralogical name *kaolinite* was proposed by S. W. Johnson and J. M. Blake in 1867 for this crystallised mineral, which is usually assumed to form a large part of kaolin or china-clay. The name *kaolin* is a French corruption of the Chinese name *kau-ling* for the white, earthy material long used in the manufacture of porcelain at King-te-chin (prov. Kiangsi), and first brought to Europe in the year 1712. This material is obtained in the neighbouring Kau-ling Hills (= 'high ridge') from a compact, green stone, occurring in clay-slates and somewhat resembling jade in appearance, from which when crushed the finer particles are separated by washing (F. von Richthofen, Amer. J. Sci. 1871, 1, 180). This material, although a hydrated aluminium silicate, differs essentially from our kaolin, containing as much as 73 p.c. of silica and only a few p.c. of water. It is perhaps the same as the Japanese 'rōseki,' which has been referred to the agalmatolite (*q.v.*) variety of pyrophyllite.

It is thus seen that the name kaolin has been loosely applied to any white clays suitable for the manufacture of porcelain (*v.* CLAY), such as those found near Limoges in France, St. Austell in Cornwall, &c. These white clays have been formed by the decomposition of granite under somewhat special conditions; and when separated from grains of quartz, scales of mica, &c., by a process of washing, they yield the china-clay of commerce. In composition this varies between wide limits; but in many instances it approximates to the kaolinite formula given above. Microscopical examination very rarely reveals the presence of any six-sided scales that can be definitely referred to the species kaolinite. L. J. S.

KAURI-COPAL (-Bush Copal, -Gum or -Resin) is the solidified turpentine of the Kauri tree (*Dammara australis* [Steud.]) and occurs in great abundance in a fossil condition in various parts of New Zealand. It is dug up on the driest fern-hills as well as in the deepest swamps, but that from the latter is of inferior quality as is also the gum obtained from the forks of living trees (J. Soc. Chem. Ind. 1893, 71; *ibid.* 1895, 528; *ibid.* 1898, 621; Bull. Imp. Inst. 1904, 2, 91). To obtain kauri-copal, it is first searched out a little below the surface by feeling for it with a steel-pointed piece of iron, after which it is dug out with an ordinary spade. It is then prepared for the market by scraping off the outer crust by hand, or better, by machinery (Eng. Pat. 17009, 1890).

Four types of kauri-copal are known in commerce: (1) Pale kauri or fossil copal found in large masses varying from yellowish white to clear yellow in colour, has an aromatic smell, brilliant fracture and can be pulverised to a white powder. It has sp.gr. 1·036, m.p. 165°, acid value 70·9, saponification value 73. (2) Brown kauri fossil copal is of a yellow brown or deep yellow colour. It is difficult to powder, has a conchoidal fracture and an aromatic camphor-like odour. It has sp.gr. 1·053; m.p. 185°, acid value 78·8, saponification value 89·7. (3) Bush kauri is obtained at the foot of trees in irregular amber-like masses. It can readily be reduced to a yellow powder with an aromatic odour and has sp.gr. 1·03, m.p. 150°, acid value 83·1, saponification value 78·5. (4) Bush kauri gathered from the tree itself has a vitreous fracture; sp.gr. 1·038, m.p. 125°, acid value 81·8, saponification value 87 (Coffignier, Bull. Soc. chim. 1909, 5, 289; *see* also Tschirsch and Niederstadt, Arch. Pharm. 1901, 239, 145; Worstall, J. Amer. Chem. Soc. 1903, 25, 860). The various kinds of kauri differ in their solubilities in organic solvents but all of them are only very slightly soluble in turpentine and more readily so in alcohol (Coffignier, *l.c.*). They are all almost completely soluble in amyl alcohol, amyl acetate, benzaldehyde, or aniline.

Kauri-copal is readily attacked by chlorine, bromine, or concentrated nitric acid (Muir, J. 1874, 923). On dry distillation it yields pinene and dipentene (Wallach, Annalen, 271, 309; Rennie, Chem. Soc. Trans. 1881, 240).

A recent fossil specimen of kauri copal was found by Tschirsch and Niederstadt (*l.c.*) to consist of the following substances: 50 p.c. α and β-*kaurolic acids* $C_{12}H_{20}O_2$, m.p. 81°–83° and 85°–87° respectively (the α-acid yields a lead salt insoluble in alcohol, whereas the β-acid gives a soluble lead salt); 20 p.c. *kaurinolic* $C_{17}H_{34}O_2$, m.p. 128°–130°, and *kauronolic acids* $C_{12}H_{24}O_2$, m.p. 86°–89° (all these acids are monobasic and give a monoiodide); 12·0 p.c. *kauroresene* a light yellow indifferent substance, m.p. 63°–65° and not volatile in steam; 12·5 p.c. of an ethereal essential oil, b.p. 150°–160°, sp.gr. 0·835 at 15°; 1·5 p.c. *kauric acid* $C_{10}H_{16}O_2$, m.p. 192°, forming microscopic crystals $[\alpha]_D$ $+51{\cdot}66°$. It is a monobasic acid, yielding an iodine number corresponding to a monoiodide and a potassium and lead salt. Only about 2 p.c. of carbon was left on distillation of the kauri-copal (*see* also Thomson, Annalen, 1843, 47, 351). Kauri gum is used in the manufacture of oil varnishes, as an ingredient of the cement for linoleum manufacture, and also for dressing glazed calico. The transparent and semitransparent varieties are employed as substitutes for amber in the manufacture of mouthpieces for cigar-holders, pipes, &c.

The commercial product often contains as an admixture dammar resin, which is a much cheaper substance. Whether the kauri contains the latter can be determined rapidly in the following way: 0·5 gram of the finely ground sample is stirred up with chloroform in a porcelain crucible. It is then filtered through a small filter into a test tube, washed once and absolute alcohol added to the filtrate, when if the sample is pure kauri, the solution will remain clear, whereas if dammar is present a cloudiness or a precipitate will appear, according to the amount (Stewart, J. Soc. Chem. Ind. 1909, 349).

KEENE'S CEMENT *v.* CALCIUM.

KELP *v.* IODINE.

KEPHIR *v.* MILK.

KERAMYL. An aqueous solution of commercial hydrofluosilicic acid used as a disinfectant.

KERATIN is the principal constituent of the epidermis, hair, nails, hoofs, horns, wool, feathers, the skin of egg shells, &c. (Hedin, Zeitsch. physiol. Chem. 1894, 20, 186; Mohr, *ibid.* 1895, 20, 403; Abderhalden, *ibid.* 1905, 46, 31, 40; *ibid.* 48, 530, 535; *ibid.* 1907, 52, 348; *ibid.* 1908, 57, 339; Breinl and Baudisch, *ibid.* 1907, 52, 159; Friedmann, Chem. Zentr. 1903, i. 15).

It can be prepared from any of these substances by treating them successively with ether, alcohol, water, and dilute acids, or successively with artificial gastric juice, artificial pancreatic juice, boiling alcohol and boiling ether, pure keratin then remaining as a residue. Keratin is an albuminoid or sclero-protein, rich in sulphur (Bibra, Annalen, 96, 292; Raikow, Chem. Zeit. 1905, 29, 900; Baudisch, *ibid.* 1908, 32, 620), and like the other members of this class of substances, it is insoluble in all neutral solvents. When treated with concentrated alkalis it swells and dissolves on warming, but it is more sparingly soluble in dilute acids.

When boiled with acids and generally on hydrolysis, it yields a variety of decomposition products amongst which may be mentioned leucine, cystine, glycine, tyrosine, aspartic, and glutamic acids, alanine, arginine, &c., the relative quantities of the products as well as their nature depending on the source of the keratin (*see* above references; also Bleunard, Ann. Chim. Phys. 1882, [v.] 26, 40). Keratin resists the action of pepsin and trypsin. When treated with hydrogen peroxide it gives sulphur, ammonia, sulphuretted hydrogen, carbon dioxide, acetaldehyde, and nitric, sulphuric, acetic, oxalic, succinic, and a small quantity of aromatic amino acids (Breinl and Baudisch, *l.c.*). According to Lissizin (Zeitsch. physiol. Chem. 1909, 62, 226), azelaic acid is also an oxidation product of keratin. Keratin gives Millon's protein reaction and a yellow colour with nitric acid, this being the origin of the yellow colour when nitric acid comes in contact with the skin. Keratin has been converted into useful products which can be used instead of casein for many purposes, by treating horn scraps, hair, &c., with 15 p.c. hydrochloric acid at ordinary temperature. After 10 days the liquid is decanted, the residue washed with water, digested with 6 p.c. sodium hydroxide solution for 24 hours; potassium permanganate is then added and after standing for 12 hours the residue is washed and subjected to a pressure of 400 atmospheres

(Eng. Pat. 360895; J. Soc. Chem. Ind. 1906, 548).

Keratin or keratin substances can be converted into digestible albumoses and peptones containing sulphur by treatment with dilute mineral acids at moderate temperatures. The reaction is complete and the albumoses and peptones are isolated when a diluted sample, after treatment with phosphotungstic acid or other reagent for albumoses, gives a filtrate containing but little amino acid (U. S. Pat. 926999, 1909).

Thermoplastic keratin compounds have been obtained by mixing intimately keratin with β-naphthol and subjecting the mixture to heat and pressure (U. S. Pat. 922692; J. Soc. Chem. Ind. 1909, 721).

Atmidkeratin and *atmidkeratose* are the products obtained when keratin is acted on by superheated steam; the gaseous products of this reaction being sulphuretted hydrogen and methyl mercaptan (Bauer, Zeitsch. physiol. Chem. 1902, 35, 343; *see* also Krukenberg, Jahrb. Thierchem. 1886, 27).

KERMES. Kermes is the most ancient dyestuff on record, for it was known in the time of Moses, and is mentioned in Scripture by its Hebrew name, 'tola' or 'tolaschani.' According to Tychsen (Bancroft's Philosophy of Permanent Colours, 1, 394) 'the scarlet or kermes dye was known in the East in the earliest ages before Moses, and was a discovery of Phœnicians in Palestine, but certainly not of the small wandering Hebrew tribes.' Under the name 'coccus' it is frequently referred to by the Greek and Latin writers.

Kermes is an insect found on the oak kermes (*Quercus coccifera* [Linn.]), and when living the female insects, which are fixed to the twigs of the tree, resemble bluish berries, and are covered with a whitish powder. As soon as their eggs are on the point of hatching these insects should be collected, killed by exposure to the steam of vinegar, and dried, and the product has then the appearance of pale reddish-brown grains. According to Bancroft it would require 10 or 12 lbs. of kermes to produce the effect of a single lb. of cochineal.

Kermesic acid $C_{18}H_{12}O_9$. The colouring matter of kermes was first isolated, in the crystalline condition, by Heise (Arbeit. ausd. Kaiserl. Gesundheitsamt, 1895, 513), and has been examined subsequently by Dimroth (Ber. 1910, 43, 1387). To isolate the kermesic acid, the kermes is first extracted with ether to remove wax, and the residue is then allowed to stand overnight with an ethereal solution of hydrochloric acid. By this means the kermesic acid which exists in the kermes in the form of a salt is liberated, and can now be removed by repeated extraction with ether. For purification the substance is converted into its sparingly soluble sodium salt; this is collected and dissolved in sodium hydroxide solution. The boiling liquid, when treated with excess of hydrochloric acid, yields a crystalline precipitate of kermesic acid.

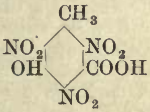
Thus obtained it consists of brick-red needles, which decompose without melting at about 250°. It is distinguished from carminic acid by the fact that it is soluble in ether, and is much more sparingly soluble in cold water. On the other hand, the colour of the alkaline solutions of both colouring matters is practically identical.

Disodium kermesate $C_{18}H_{10}O_9Na_2$, prepared by means of sodium acetate, consists of a red-brown crystalline powder, soluble in water, with a violet-red colour.

Barium kermesate $(C_{18}H_{11}O_9)_2Ba$ is brown, and contains water of crystallisation.

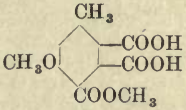
Tetra-acetylkermesic acid $C_{18}H_8O_9(C_2H_3O)_4$, yellow needles, melts at 245°, and *kermesic acid trimethyl ether* $C_{21}H_{18}O_9$ orange-red needles, m.p. 310°, dissolves in sulphuric acid with a violet colour, and is prepared from the potassium salt by means of methyl sulphate in the presence of boiling toluene.

Kermesic acid is decomposed by warm concentrated nitric acid, and thus yields *nitrococcusic acid* (trinitro-cresotic acid)



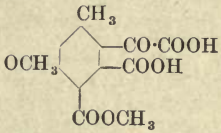
identical with the acid obtained in a similar way from carminic acid.

When oxidised with potassium permanganate kermesic acid methyl ether gives *methyl cochenillate monomethyl ether*, which melts at 178°–180°



with formation of the anhydride, m.p. 149°. Digestion with boiling potassium hydroxide solution gives cochenillic acid methyl ether $C_{11}H_{10}O_7$, m.p. 200°.

A second product of the oxidation consists of the *dimethyl ether* of *cresotinglyoxyldicarboxylic acid*



m.p. 108°–110°, and this by oxidation with permanganate is converted into the above-described *methyl cochenillate methyl ether.* There can be little doubt, therefore, that a very close relationship exists between kermesic and carminic acids.

Dyeing properties.—According to Hellot (Bancroft, Philosophy of Permanent Colours, 1, 404) 'the red draperies of the figures exhibited in the ancient Brussels and other Flemish tapestries were all dyed from kermes.' 'The fine red or crimson colour of these tapestries, which was originally called simply scarlet, took the name of *Venetian scarlet*, after the cochineal scarlet upon a tin base was discovered, . . .' For the production of this scarlet, the wool, previous to dyeing, was mordanted with alum and tartar; and, according to Bancroft, there is no evidence even in more recent years of the employment of a tin mordant in respect of this colouring matter, although the experiments he carried out indicated that by this latter method a scarlet colour could be produced 'in every respect as beautiful and estimable as any which can be dyed with cochineal.' A. G. P.

KERMESITE. *Red antimony. Antimony blende. Pyrantimonite. Pyrostibite.* An oxysulphide of antimony formed by the oxidation of antimony sulphide, and occurring associated with grey and white antimony in Hungary, Saxony, Dauphiné, &c. Found in monoclinic crystals or in capillary tufts of six-sided prisms, of a cherry-red colour and adamantine lustre. Composition $Sb_2O_3 \cdot 2Sb_2S_3$ (*v.* ANTIMONY).

KEROSENE or **KEROSINE** *v.* PETROLEUM.

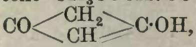
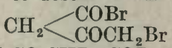
KETENES. A series of compounds containing the group $>C:CO$. They were discovered in 1905 by Staudinger, the first member to be isolated being diphenylketene $(C_6H_5)_2C:CO$. Ketenes may be prepared: (i) by the action of zinc on the chloride or bromide of an α-halogen substituted fatty acid; or (ii) by the action of heat on the anhydride of a dibasic acid. The ketenes are very reactive substances, and may be divided into two groups:—

I. *Aldo-ketenes.* These consist of ketene itself, monoalkyl derivatives and carbon suboxide. They are colourless and do not undergo auto-oxidation. They are polymerised by pyridine and quinoline, and do not form additive compounds with substances containing the $>C:O$ and $>C:N—$ groups.

II. *Keto-ketenes.* The dialkyl derivatives of ketene belong to this group. They are coloured substances, and readily undergo auto-oxidation. They yield ketene bases with pyridine and quinoline, and form additive compounds with substances containing the $>C:O$ and $>C:N—$ groups, such as quinone and benzylidineaniline.

Both groups combine readily with water, alcohols, and amines, and also with chlorine and bromine (Staudinger and Klever, Ber. 1908, 41, 906).

Ketene $H_2C:CO$. Discovered by Wilsmore and Stewart, who obtained it by the action of a heated platinum wire on the vapour of acetic anhydride. The gaseous products were liquefied, and then submitted to fractional distillation (Nature, 1907, 75, 510; Chem. Soc. Trans. 1907, 1938). Schmidlin and Bergman (Ber. 1910, 43, 2821) obtained a 14 p.c. yield of ketene by passing the vapour of acetone through a hard glass tube filled with porous earthenware, heated at 500°–600°. It may also be prepared by the action of zinc on bromacetyl bromide in ethyl acetate. The products of the reaction are rapidly distilled, the ketene being removed from the warm solvent in a current of hydrogen, condensed in liquid air, and freed from traces of ethyl acetate by repeated fractionation at −60° (Staudinger and Klever, Ber. 1908, 41, 594). By the last method the yield of ketene from bromacetyl bromide is 7–13 p.c.; from bromacetyl chloride 3–4 p.c.; from chloracetyl chloride or chloracetyl bromide *nil* (Staudinger and Kubinsky, Ber. 1909, 42, 4213).

Ketene is a colourless liquid, b.p. −56°, and can be solidified to a mass of colourless crystals, m.p. −151°. It has a very penetrating odour, and its vapour attacks the mucous membrane. It combines with water, alcohol, aniline, &c., to form acetic acid, ethyl acetate, and acetanilide respectively, and with bromine in ethereal solution to form bromacetyl bromide. Liquid hydrogen chloride and sulphuretted hydrogen at the ordinary temperature yield acetyl chloride and thioacetic anhydride. When it reacts with water no trace of glycollic aldehyde is produced, and for this and other reasons, ketene is represented as $H_2C:CO$ and not as $CH:C \cdot OH$ (Staudinger and Klever, *l.c.*; Chick and Wilsmore, Chem. Soc. Proc. 1908, 77). It does not give an additive compound with quinone, nor ketene bases with pyridine and quinoline. Metallic chlorides and tertiary bases induce polymerisation to a dark-coloured liquid, this change also taking place when ketene is kept for some time. The chief constituent of this polymeride is a colourless liquid of pungent odour, b.p. 126°–127°, and when frozen, m.p. −6° to −7°. It has the formula $C_4H_4O_2$, and hence is formed by the condensation of two molecules of ketene. It combines with water and aniline to form acetoacetic acid and acetoacetanilide respectively, but only combines with alcohol to produce ethyl acetoacetate on addition of a trace of acid. On standing in sealed tubes, or by the addition of pyridine, dehydracetic acid is formed. Hence this substance may be acetylketene $CH_3COCH:CO$ or Δ′-*cyclo*butene-1-ol-3-one  $CO{<}\begin{smallmatrix}CH_2\\CH\end{smallmatrix}{>}C \cdot OH$, the semi-enol of *cyclo*butane-1:3-dione. The action of bromine was found to result in the formation of a γ- derivative  $CH_2{<}\begin{smallmatrix}COBr\\COCH_2Br\end{smallmatrix}$ and not an α- derivative, $CH_3CO \cdot CHBr \cdot COBr$, thus proving it to have the latter configuration (Chick and Wilsmore, Chem. Soc. Trans. 1908, 946; 1909, 1978; *cf.* Staudinger and Bereza, Ber. 1909, 42, 4908).

Methyl ketene $CH_3 \cdot CH:CO$. Obtained in dilute ethereal solution by the action of zinc on an ethereal solution of α-bromopropionyl bromide.

Ethyl ketene $C_2H_5 \cdot CH:CO$. Similarly from α-bromobutyl bromide.

Carbon suboxide $O:C:C:C:O$. Obtained by action of zinc on dibromomalonyl bromide *v.* CARBON SUBOXIDE.

Dimethyl ketene $(CH_3)_2C:CO$. Prepared by the action of zinc on a solution of α-bromo*iso*butylbromide in ethyl acetate, and distilling the resulting product under 15–16 mm. at −20° (Staudinger and Klever, Ber. 1906, 39, 968). Also by heating dimethylmalonic anhydride under 12 mm. pressure at 160°–180° (Staudinger and Ott, Ber. 1908, 41, 2208). It is a mobile yellow liquid, b.p. 48·5° (12 mm.); m.p. −97·5°; stable at −20° under atmospheric pressure, but at ordinary temperature polymerises to a colourless substance, m.p. 112°, apparently the diketone $(C \cdot (CH_3)_2CO)_2$. Water converts dimethylketene into *iso*butyric acid, and it undergoes the other reactions common to the keto-ketenes. Dimethylketene bases *v.* Staudinger, Klever, and Kober, Annalen, 1910, 374, 1. In the preparation of this ketene a liquid polymeride $(C_4H_6O)_2$, b.p. 170°–171°, having an odour of peppermint, is also formed (Staudinger and Klever, Ber. 1907, 40, 1149).

Diethylketene $(C_2H_5)_2C:CO$. Prepared by heating diethylmalonic anhydride under 12 mm. pressure at 160°–180°. It forms a yellow liquid, b.p. 91°–92° (749 mm.), solidifying to a mass of yellow crystals in liquid air (Staudinger and Ott, *l.c.*)

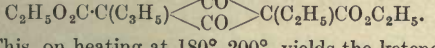
Diphenylketene $(C_6H_5)_2C:CO$. Prepared by the action of zinc on diphenylchloracetyl chloride in ethereal solution (Staudinger, Ber. 1905, 38, 1735); by the action of tertiary bases on diphenylacetyl chloride (Ber. 1907, 40, 1145); or by the interaction of benzil and hydrazine, oxidation of the hydrazibenzil, and warming the azibenzil to 60° (Curtius, Ber. 1889, 2161; J. pr. Chem. [ii.] 4, 182; Schroeter, Ber. 1909, 2346). It is a liquid having the colour of a concentrated solution of potassium dichromate, and solidifies in a freezing mixture to a mass of yellow crystals; b.p. 146° (12 mm.). Water converts it into diphenylacetic acid, and it undergoes similar reactions to the other keto-ketenes. On exposure to air it becomes viscid, addition of light petroleum throwing out a white oxidation product. Dry hydrogen chloride passed into a benzene solution of the ketene yields diphenylacetylchloride, whilst a dilute solution of hydrochloric acid yields diphenyl acetic anhydride. It shows no tendency to polymerise and treated with magnesium phenylbromide, yields triphenylvinyl alcohol. With quinone the β-lactone $O:C_6H_4<\begin{matrix}C(C_6H_5)_2\\ O\end{matrix}>CO$ is formed, and with benzylidine aniline the β-lactam $C(C_6H_5)_2<\begin{matrix}CO\\ CH(C_6H_5)\end{matrix}>N{\cdot}C_6H_5$. The former, on heating yield compounds of the type of diphenylquinomethane and tetraphenylquinodimethane, and the latter acylic fulvenes (Staudinger, Ber. 1908, 41, 1355, 1493).

Diphenylene ketene $\begin{matrix}C_6H_4\\ |\\ C_6H_4\end{matrix}>C:CO$. Prepared by the action of zinc on chlorodiphenylene acetyl chloride (from phosphorus pentachloride and diphenyleneglycollic acid) in ether in absence of air and moisture. It forms red crystals, m.p. 90° to a red liquid, decomposing at 150°; gives an indigo blue colour with sulphuric acid. With excess of water diphenylene acetic acid is formed, and with the requisite quantity diphenylene acetic anhydride. It undergoes the usual reactions (Staudinger, Ber. 1906, 39, 3062).

Ethylketene carboxylate

$$CO:C(C_2H_5){\cdot}CO_2{\cdot}C_2H_5.$$

An ethereal solution of ethylbromomethylmalonate chloride $C_2H_5{\cdot}CBr<\begin{matrix}CO_2C_2H_5\\ COCl\end{matrix}$ reacts with zinc, producing ethylketenecarboxylate, which rapidly polymerises into 1 : 3-diethyl-*cyclo*-butane-2 : 4-dione-1 : 3-dicarboxylate

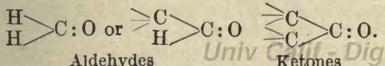


$$C_2H_5O_2C{\cdot}C(C_3H_5)<\begin{matrix}CO\\ CO\end{matrix}>C(C_2H_5)CO_2C_2H_5.$$

This, on heating at 180°–200°, yields the ketene as a colourless liquid, b.p. 48° (15 mm.), m.p. 57·8° (Staudinger and Bereza, Ber. 1909, 42, 4908).

KETOHYDRINDENE *v.* Indene.

KETONES. The ketones are a class of organic compounds characterised by the presence of the carbonyl group $>C:O$, united by each of its valencies to carbon. They are differentiated in this way from the aldehydes which contain the carbonyl group united on the one hand to hydrogen, and on the other to hydrogen or carbon. The characteristic groupings of aldehydes and ketones are shown as follows:—



Aldehydes Ketones

Ketones proper have hydrocarbon radicles or simple derivatives thereof (substituted by halogens, &c.) united with the carbonyl group, but a large number of other compounds of ketonic character are known, such as the keto-alcohols (*e.g.* $CH_3{\cdot}CO{\cdot}CH_2OH$), and the ketonic acids (*e.g.* $CH_3{\cdot}CO{\cdot}CO_2H$). Such compounds, besides showing specific properties due to the presence of the carbinol or carboxyl groups, also exhibit ketonic reactions due to the presence of the carbonyl group.

Ketones may be classified according to the number of carbonyl groups into *simple ketones, diketones*, &c., whilst, according to the radicles united with the carbonyl, they may be separated into *aliphatic*, *aromatic*, and *mixed ketones.*

Another type of ketone is furnished by those compounds in which the carbon atom of the carbonyl group is a member of a closed ring; such *cyclic ketones*, in which the carbon chain is saturated, closely resemble the aliphatic ketones in their properties. Unsaturated cyclic ketones also exist; one class, the quinones, will be treated separately, as they possess many distinctive properties not shared by the other ketones.

Respecting the nomenclature of the ketones, a few are known by trivial names, *e.g.* acetone, benzophenone, acetophenone, &c., but usually a more systematic nomenclature is adopted. This may refer either to the radicles attached to the carbonyl group, or to the position of the carbonyl groups in the chain. Acetone $CH_3{\cdot}CO{\cdot}CH_3$ may be more systematically termed dimethylketone or propanone; benzophenone $C_6H_5{\cdot}CO{\cdot}C_6H_5$ diphenylketone or diphenylmethanone; and acetophenone $C_6H_5{\cdot}CO{\cdot}CH_3$ phenyl methyl ketone or ethylonephene.

Whilst for simple ketones the second systematic nomenclature, that recommended by the Geneva Congress, has no striking advantages; in the case of polyketones it is very useful, as it enables the trivial names given to various substances to be replaced and rational names to be given to new compounds as they are discovered. Thus diacetyl becomes butane-dione, acetylacetone is pentane-2 : 4-dione, and is thus completely differentiated from acetylpropional which is pentane-2 : 3-dione.

Open Chain Monoketones.

Preparation.—(1) By addition of water to hydrocarbons of the type $R{\cdot}C{\vdots}C{\cdot}H$; thus allylene, if led into an aqueous solution of mercuric chloride at 90°–95°, yields acetone (Kutscherow, Ber. 1884, 17, 15)

$$CH_3{\cdot}C{\vdots}CH+H_2O=CH_3{\cdot}CO{\cdot}CH_3.$$

Béhal and Desgrez find that hydrocarbons of the formula C_nH_{2n-2} add the elements of acetic acid at 280°, the addition products being decomposed by water with formation of ketones.

(2) Secondary alcohols are directly oxidised to ketones. The use of manganic salts for this purpose has been patented by W. Lang (D. R. P. 166357). Ketones may also be obtained from secondary alcohols by passing their vapours over heated, finely divided copper (P. Sabatier and J. B. Senderens, Ann. Chim. Phys. 1905 [viii.] 4, 433).

(3) Primary alcohols of the type

$$CHRR'{\cdot}CH_2OH$$

give formic acid and a ketone on oxidation

(Kannonikow and Saytzew, Annalen, 1875, 175, 377)

$$CH(CH_3)(C_2H_5)CH_2OH+3O = CH_3\cdot CO\cdot C_2H_5+H\cdot CO_2H+H_2O.$$

(4) Hydrolysis of some halogen compounds which might be expected to yield unsaturated tertiary alcohols furnishes ketones in their place

$$CH_3\cdot CCl:CH_2 \rightarrow (CH_3\cdot C(OH):CH_2) \rightarrow CH_3\cdot CO\cdot CH_3$$

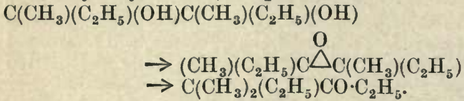
(Oppenheim, Annalen, 1868, Spl. 6, 365).

It has also been found that certain chlorhydrins when heated with water under pressure, yield ketones instead of glycols:

$$C(CH_3)_2(OH)CH(CH_3)Cl = CH(CH_3)_2CO\cdot CH_3+HCl$$

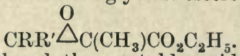
(K. Krassusky, J. Russ. Phys. Chem. Soc. 1901, 33, 791; 1902, 34, 287).

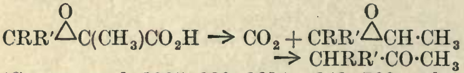
(5) On warming pinacones (ditertiary glycols) with dilute acids pinacolines (ketones containing a tertiary alkyl radicle) are produced:



$$C(CH_3)(C_2H_5)(OH)C(CH_3)(C_2H_5)(OH) \rightarrow (CH_3)(C_2H_5)C\overset{O}{\triangle}C(CH_3)(C_2H_5) \rightarrow C(CH_3)_2(C_2H_5)CO\cdot C_2H_5.$$

The mechanism of the reaction discovered by G. Darzens is probably similar. Ethyl α-chloropropionate condenses with ketones $R\cdot CO\cdot R'$ to form αβ-trisubstituted glycidic esters of the general type $CRR'\overset{O}{\triangle}C(CH_3)CO_2C_2H_5$. When these are hydrolysed the unstable acid loses carbon dioxide, and the oxide isomerises to a ketone





$$CRR'\overset{O}{\triangle}C(CH_3)CO_2H \rightarrow CO_2+CRR'\overset{O}{\triangle}CH\cdot CH_3 \rightarrow CHRR'\cdot CO\cdot CH_3$$

(Compt. rend. 1905, 139, 1214; 141, 766; also R. Stoermer, Ber. 1906, 39, 2288; 1907, 40, 488; M. Tiffeneau and Dorlencourt, Compt. rend. 1906, 143, 126; Ann. Chim. Phys. 1907, [viii.] 10, 322).

(6) By the dry distillation of the calcium or barium salts of acids

$$(R\cdot CO\cdot O)_2Ca = CaCO_3+R\cdot CO\cdot R.$$

The products obtained in this way are never pure; calcium acetate, for example, yields not only acetone, but also homologous ketones (R. Fittig, Annalen, 1859, 110, 17). When a mixture of the calcium salts of two acids is distilled together the separate ketones corresponding to each salt and their usual impurities are obtained, together with a greater or less yield of the mixed ketone.

The aliphatic acids are directly converted into ketones by heating with iron-filings or passing their vapours over heated aluminium or thorium oxides:

$$2R\cdot COOH = R\cdot CO\cdot R+CO_2+H_2O$$

(W. Ipatiew, J. Russ. Phys. Chem. Soc. 1908, 40, 514; Ber. 1910, 43, 3383; J. B. Senderens, Compt. rend. 1909, 148, 297; 149, 995; 1910, 150, 111; 1911, 152, 384; Easterfield and Taylor, Chem. Soc. Trans., 1911, 2298).

(7) Ketones are obtained from tertiary α-hydroxy acids either by oxidation (chromic acid) or by heating with mineral acids:

$$CRR'(OH)CO_2H+O = R\cdot CO\cdot R'+CO_2+H_2O.$$

$$CRR'(OH)CO_2H = R\cdot CO\cdot R'+H\cdot CO_2H \text{ (or } H_2O+CO).$$

Since acids of the type $CRR'H\cdot CO_2H$ may be oxidised by alkaline permanganate to acids with the structure $CRR'(OH)CO_2H$, they might serve as a source of ketones; in fact, electrolytic oxidation of *iso*butyric acid leads directly to acetone (M. Moest, D. R. P. 138442).

An analogous reaction is that by which the amides of α-bromo acids lose hydrogen bromide and cyanide on heating with aqueous or alcoholic sodium hydroxide, an aldehyde or a ketone being produced (G. Mossler, Monatsh. 1908, 29, 69):

$$CRR'Br\cdot CO\cdot NH_2+2NaOH = R\cdot CO\cdot R'+NaCN+NaBr+2H_2O.$$

Aldehydes and ketones are respectively obtained from amino acids $R\cdot CH(NH_2)CO_2H$ and $RR'C(NH_2)CO_2H$ by the action of hypochlorites:

$$RR'C(NH_2)CO_2H+HOCl = RR'C{:}O+CO_2+NH_4Cl$$

(K. Langheld, D. R. PP. 226226 and 226227).

(8) The β-ketocarboxylic acids, or their esters, undergo 'ketonic fission' on heating with dilute acids or alkalis (heating with concentrated alkaline solutions effects acid fission):

$$R\cdot CO\cdot CHR'\cdot CO_2C_2H_5+H_2O = R\cdot CO\cdot CH_2R'+CO_2+C_2H_5OH.$$

A simple method of effecting the ketonic fission of higher members of this series of esters by heating for a few minutes with sulphuric acid, pouring into water and distilling in a current of steam has been described by L. Bouveault and R. Locquin (Bull. Soc. chim. 1904, [iii.] 31, 1153; *cp.* Michael and Wolgast, Ber. 1909, 42, 3176).

(9) Ketones are produced by the interaction of acid chlorides and organo-metallic compounds (Freund, Annalen, 1861, 118, 1):

$$2C_nH_{2n+1}\cdot COCl+Zn(C_mH_{2m+1})_2 = ZnCl_2+2C_nH_{2n+1}\cdot CO\cdot C_mH_{2m+1}.$$

(10) Latterly magnesium alkyl halides (Grignard's reagents) have been largely applied to the synthesis of ketones. Nitriles yield imino derivatives, which are hydrolysed by dilute acids to ammonia and ketones (E. E. Blaise, Compt. rend. 1901, 132, 38; 133, 1217):

$$R\cdot C{⋮}N+MgBrR' = RR'C:N\cdot MgBr.$$

$$2RR'C:N\cdot MgBr+2H_2SO_4+2H_2O = MgBr_2+MgSO_4+(NH_4)_2SO_4+2RR'C:O.$$

A similar reaction using the esters of α-bromo acids and zinc leads to the synthesis of β-ketonic esters

$$R\cdot C{⋮}N+Zn+CR'HBr\cdot CO_2C_2H_5 = BrZn\cdot N:CR\cdot CHR'\cdot CO_2C_2H_5.$$

Ketones may also be obtained from cyanogen by the action of magnesium alkyl halides:

$$CN\cdot CN+Mg(C_2H_5)I = CN\cdot C(C_2H_5):N\cdot MgI$$

$$CN\cdot C(C_2H_5):NMgI+Mg(C_2H_5)I = MgI(CN)+C(C_2H_5)_2:N\cdot MgI$$

(11) Acid amides may be employed in place of nitriles (C. Béis, Compt. rend. 1903, 137, 575):

$$R\cdot CO\cdot NH_2+2MgR'X = CRR'(NHMgX)OMgX+R'H.$$

$$CRR'(NHMgX)OMgX+2H_2O = NH_2\cdot CRR'\cdot OH+MgX_2+Mg(OH)_2.$$

$$NH_2\cdot CRR'\cdot OH = R\cdot CO\cdot R'+NH_3.$$

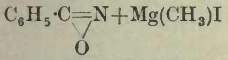
The yields obtained by this method vary from 20 to 50 p.c., increasing as the complexity of the radicle R increases.

Imino esters (*e.g.* $C_6H_5\cdot C(:N\cdot C_6H_5)\cdot OCH_3$)

and imino chlorides may also be employed (R. Marquis, Compt. rend. 1906, 142, 711), whilst H. Fournier finds ketones amongst the products of the reactions between Grignard's reagents and acid anhydrides (Bull. Soc. chim., 1910, [iv.] 7, 836).

In certain cases ketones may be obtained by the action of organo-magnesium compounds on dried sodium salts, *e.g.* methyl *iso*butyl ketone from magnesium *iso*butyl bromide and sodium acetate (Salkind and Beburischwili, Ber. 1909, 42, 4500). For other syntheses involving organo-metallic compounds *v.* Blaise and Maire (Ann. Chim. Phys. 1908, [viii.] 15, 556; Barbier and Locquin, Bull. Soc. Chim., 1911, 9, 717, 722; Reynolds, Amer. Chem. J., 1911, 46, 198; Darzens a. Rost, Compt. rend. 1911, 153, 772).

(12) The nitrile oxside yield ketones on reaction with magnesium alkyl halides. Thus benzonitrile-oxide and magnesium methyl iodide yield benzonitrile (by reduction), acetophenone, and its oxime:

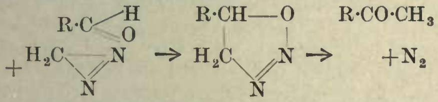


$C_6H_5{\cdot}C{=}N + Mg(CH_3)I$

$\rightarrow C_6H_5{\cdot}C(:NO{\cdot}MgI)CH_3 \rightarrow C_6H_5{\cdot}C(:NOH){\cdot}CH_3$

(H. Wieland, Ber. 1907, 40, 1667).

(13) Ketones containing one methyl group can be obtained by the reaction of diazomethane with aldehydes. In this case it is probable that an unstable furodiazole is first produced, which breaks down into nitrogen and a ketone:



The method is of general applicability; ketones may be obtained from *iso*valeraldehyde, benzaldehyde, &c., whilst trichloroacetone has been obtained in a pure condition by using chloral (Schlotterbeck, Ber. 1907, 40, 479, 1826, 3000; 1909, 42, 2559, 2565).

(14) In certain cases ketones may be converted into higher homologues by the action of sodamide and an alkyl halide. In this way diethyl ketone yields ethyl *iso*propyl ketone, di*iso*propyl ketone, and a compound $C_{15}H_{26}O$:

$$CH_3{\cdot}CH_2{\cdot}CO{\cdot}CH_2{\cdot}CH_3 \rightarrow (CH_3)_2CH{\cdot}CO{\cdot}CH_2{\cdot}CH_3$$
$$\rightarrow (CH_3)_2CH{\cdot}CO{\cdot}CH(CH_3)_2$$

(A. Haller and Bauer, Compt. rend. 1910, 150, 661; 1911, 153, 21, 1415; 1912, 154, 555).

(15) Formaldehyde acts on ketones in presence of alkaline condensing agents, giving keto alcohols, which may be dehydrated to unsaturated ketones (Farbenfab. vorm. Fr. Bayer & Co. D. R. PP. 222551 and 223207):

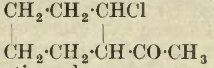
$$CH_3{\cdot}CO{\cdot}CH_3 + CH_2O = CH_3{\cdot}CO{\cdot}CH_2{\cdot}CH_2OH$$
$$= CH_3{\cdot}CO{\cdot}CH : CH_2 + H_2O.$$

(16) Aromatic ketones (also mixed ketones) can be obtained by the action of acid chlorides on aromatic hydrocarbons in presence of aluminium chloride, &c. (Friedel and Crafts, Ann. Chim. Phys. 1884, [vi.] 1, 507):

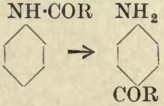
$$C_6H_6 + CH_3{\cdot}CO{\cdot}Cl = CH_3{\cdot}CO{\cdot}C_6H_5 + HCl.$$

Ketones in which both radicles attached to the carbonyl group are the same may be obtained by the action of carbonyl chloride on aromatic hydrocarbons in presence of aluminium chloride:

$$2C_6H_6 + COCl_2 = C_6H_5{\cdot}CO{\cdot}C_6H_5 + 2HCl.$$

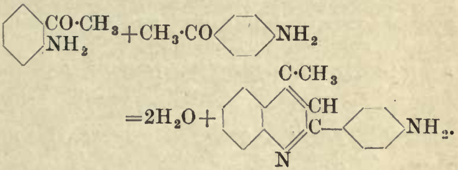
When acetyl chloride acts on a solution of *cyclo*hexene in carbon disulphide solution under the influence of aluminium chloride, an addition product  $\begin{array}{l} CH_2{\cdot}CH_2{\cdot}CHCl \\ | \qquad\qquad\quad | \\ CH_2{\cdot}CH_2{\cdot}CH{\cdot}CO{\cdot}CH_3 \end{array}$ is formed, from which tertiary bases remove the elements of hydrogen chloride with production of tetrahydroacetophenone (Darzens, Compt. rend. 1910, 150, 707).

(17) The introduction of amino or hydroxyl groups renders aromatic nucleï still more liable to attack. Dimethylaminobenzoyl chloride and tetramethyldiaminobenzophenone (Michler's ketone) are successively produced by the reaction of phosgene with dimethylaniline, no condensing agent being necessary (Ber. 1876, 9, 715, 1900). *p*-Aminoacetophenone is formed by boiling 2 parts of aniline with 5 parts of acetic anhydride and 3 parts of zinc chloride for 4–5 hours (Klingel, Ber. 1885, 18, 2688); whilst 2:4-dihydroxyacetophenone (resacetophenone) is obtained when 2 parts of resorcinol and 3 parts each of acetic acid and zinc chloride are heated to 150° (Nencki and Sieber, J. pr. Chem. 1881, [ii.] 23, 147). Probably acyl derivatives are first formed which subsequently undergo isomerisation, *e.g.*:



For the mechanism of isomerisation of acyl anilides, *see* F. D. Chattaway (Chem. Soc. Trans. 1904, 85, 340, 386, 589, 1663).

The conversion of acetanilide into aminoacetophenone is of interest in connection with the formation of flavaniline, which may be obtained by several hours' heating at 250°–270° of 2 parts of acetanilide with 1 part of zinc chloride (O. Fischer and Rudolph, Ber. 1882, 15, 1500); or a mixture of *o*- and *p*-aminoacetophenones with zinc chloride at 90° (O. Fischer Ber. 1886, 19, 1038):



(18) Aromatic ketones may be obtained by the oxidation of diaryl methanes with chromic acid (Zincke, Annalen, 1871, 159, 377):

$$C_6H_5{\cdot}CH_2{\cdot}C_6H_5 + 2O = C_6H_5{\cdot}CO{\cdot}C_6H_5 + H_2O.$$

General properties and reactions.—(1) The aliphatic ketones are generally liquid, the aromatic ketones solid at ordinary temperatures; usually they possess an ethereal or aromatic odour; most of them are insoluble in water, but dissolve easily in alcohol, ether, &c. They usually boil without decomposition; on passing the vapour of acetone over baked clay at 500°–600°, methane and ketene $CH_2:CO$ are produced (J. Schmidlin and M. Bergman, Ber. 1910, 43, 2821).

(2) Reduction of ketones by sodium amalgam gives secondary alcohols, ditertiary glycols (pinacones) are formed at the same time:

$$CH_3{\cdot}CO{\cdot}CH_3 + 2H = CH_3{\cdot}CH(OH)CH_3.$$
$$2CH_3{\cdot}CO{\cdot}CH_3 + 2H = (CH_3)_2C(OH)C(OH)(CH_3)_2$$

(3) Ketones resist the action of oxidising agents to a far greater extent than aldehydes. They do not readily reduce ammoniacal silver solutions; the resistency to alkaline oxidation is instanced by the fact that substances may be dissolved in acetone for treatment with permanganate. Ketones are, however, attacked by chromic acid, the carboxyl group usually remaining attached to the smaller hydrocarbon radicle; thus methyl propyl ketone yields a mixture of acetic and propionic acids, but a good deal depends on the nature of the radicle (Popow, Annalen, 1872, 161, 285). Wagner has found that propyl *iso*butyl ketone gives propionic and *iso*valeric acids, whilst, when ethyl *iso*propyl ketone is oxidised, for every molecule of acetic and *iso*butyric acids produced, 4 molecules of acetone and propionic acid are formed (Ber. 1882, 15, 1194; 1885, 18, 2266; J. Russ. Phys. Chem. Soc. 1884, 16, 645).

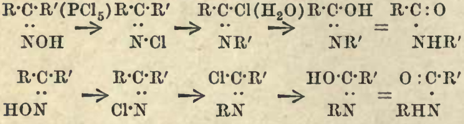
Oxygen may also be added to ketones without rupturing the molecule; thus by the use of Caro's acid, acetone gives a peroxide $C_3H_6O_2$ (A. V. Baeyer and V. Villiger, Ber. 1899, 32, 3627; 1900, 33, 124, 859; *see* also J. Pastureau, Bull. Soc. chim. 1909, [iv.] 5, 227).

(4) Ketones react less readily than aldehydes with ammonia, but resemble aldehydes in giving oximes, although not always as easily as aldehydes

$$(CH_3)_2C:O+H_2NOH=H_2O+(CH_3)_2C:NOH$$

(V. Meyer and Janny, Ber. 1882, 15, 1324; Janny, *ibid.* 1778; *cf.* Lapworth and Steele, Chem. Soc. Trans. 1911, 1884; Clarke, Lapworth and Wechsler, *ibid.* 1908, 30).

When the radicles connected with the carbonyl group are different, two oximes may be produced from a monoketone. The isomerisim in such cases is generally referred to different spatial arrangement (Hantzsch and Werner, Ber. 1890, 23, 11). In determining the configuration of stereoisomeric oximes considerable use has been made of the Beckmann rearrangement (Ber. 1886, 19, 992), whereby they map be converted into one of two structurally isomeric substituted acid amides:

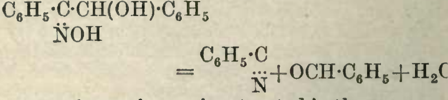


$$\underset{\ddot{N}OH}{R\cdot C\cdot R'}(PCl_5)\rightarrow\underset{\ddot{N}\cdot Cl}{R\cdot C\cdot R'}\rightarrow\underset{\ddot{N}R'}{R\cdot C\cdot Cl}(H_2O)\rightarrow\underset{\ddot{N}R'}{R\cdot C\cdot OH}=\underset{\dot{N}HR'}{R\cdot C:O}$$

$$\underset{HO\ddot{N}}{R\cdot C\cdot R'}\rightarrow\underset{Cl\cdot\ddot{N}}{R\cdot C\cdot R'}\rightarrow\underset{R\ddot{N}}{Cl\cdot C\cdot R'}\rightarrow\underset{R\ddot{N}}{HO\cdot C\cdot R'}=\underset{RH\dot{N}}{O:C\cdot R'}$$

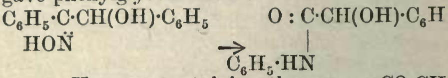
In effecting the transformation, a very dilute and strongly cooled ethereal solution of the oxime is treated with a considerable excess of phosphorus pentachloride, which is added in small portions at a time. The ethereal solution is decanted from the excess of the pentachloride and shaken with ice-cold water, separated and dried by potassium carbonate. The substituted amide is left on evaporation.

The rearrangement may sometimes be effected by warming for 1 hour with 10 parts of sulphuric acid on the water bath, whilst benzene-sulphonyl chloride has been used by Tiemann and Pinnow (Ber. 1891, 24, 4162) and A. Werner and A. Pignet (Ber. 1904, 37, 4295). The latter chemists determined the configuration of the oximes of benzoïn in the following manner: 5 grams of α-benzoïn oxime were dissolved in 20 c.c. of pyridine, 4 grams of benzene-sulphonyl chloride added drop by drop, and the mixture allowed to stand 3 hours at th ordinary temperature. After adding dilut sulphuric acid, the benzaldehyde and benzo nitrile were extracted with ether:



$$\underset{\ddot{N}OH}{C_6H_5\cdot C}\cdot CH(OH)\cdot C_6H_5=\underset{\dddot{N}}{C_6H_5\cdot C}+OCH\cdot C_6H_5+H_2$$

The isomeric β-oxime treated in the same wa gave phenylglycollanilide:



$$\underset{HO\ddot{N}}{C_6H_5\cdot C}\cdot CH(OH)\cdot C_6H_5\rightarrow\underset{C_6H_5\cdot HN}{\overset{|}{O:C}}\cdot CH(OH)\cdot C_6H$$

(5) Ketones containing the group ·CO·CH react with nitrous acid, giving the monoxim of diketones:

$$CH_3\cdot CO\cdot CH_2\cdot CH_3+HNO_2$$
$$=CH_3\cdot CO\cdot C(:NOH)\cdot CH_3+H_2$$

(L. Claissen and Manasse, Ber. 1889, 22, 526 O. Diels, Ber. 1902, 35, 3290; 1907, 40, 4336).

(6) Ketones react with hydrazine to giv ketazines (Curtius and Thun, J. pr. Chem. 189 [ii.] 44, 161):

$$2R\cdot CO\cdot R'+N_2H_4=2H_2O+RR'C:N\cdot N:CRR$$

or hydrazones (E. Fischer, Annalen, 1878, 19 136; Ber. 1883, 16, 661, 2241; 1884, 17, 572 1889, 22, 90; 1897, 30, 1240):

$$R\cdot CO\cdot R'+H_2N\cdot NHR''=H_2O+RR'C:N\cdot NH\cdot$$

In using phenylhydrazine, a dilute acet acid solution is generally employed; whe hydrazone formation only takes place wit difficulty the ketone may be dissolved in glaci acetic acid, treated with a slight excess phenylhydrazine and allowed to stand in t cold. In certain cases (*e.g.* carvole, v. Baeye Ber. 1894, 27, 813) the ketone and phenylhydr zine may be mixed in equimolecular proportio without solvent and allowed to stand.

In many cases the use of phenylhydrazine f the isolation and identification of aldehydes a ketones may be advantageously replaced by o of the following hydrazino compounds:

p-Bromophenylhydrazine (E. Fischer, Be 1891, 24, 4221; L. Michaelis, *ibid.* 1893, 2 2190).

p-Nitrophenylhydrazine (A. Purgotti, Atti. Accad. Linc. 1902, 7, ii. 266; E. Bamberger a H. Sterintzki, Ber. 1893, 26, 1306; E. Hyd *ibid.* 1899, 32, 1810; H. D. Dakin, J. Biol. Che 1908, 4, 235).

as-Methylphenylhydrazine $C_6H_5(CH_3)N\cdot N$ (C. Neuberg, Ber. 1902, 35, 959, 2626).

Semicarbazide $NH_2\cdot CO\cdot NH\cdot NH_2$ (Baey Ber. 1894, 27, 1918).

Aminoguanidine $NH_2\cdot C(:NH)NH\cdot NH_2$. T condensation products with ketones may isolated as well crystallised picrates (Baey Ber. 1894, 27, 1919).

Thiosemicarbazide $NH_2\cdot CS\cdot NH\cdot NH_2$. T resulting thiosemicarbazones

$$NH_2\cdot CS\cdot NH\cdot N:CRR'$$

give insoluble or sparingly soluble salts of t heavy metals (C. Neuberg and W. Neiman Ber. 1902, 35, 2049).

Benzhydrazide $C_6H_5\cdot CO\cdot NH\cdot NH_2$ and its *m*-, and *p*-nitro- derivatives

$$C_6H_4(NO_2)CO\cdot NH\cdot NH_2.$$

With aromatic ketones it is advisable to war in alcoholic solution; aldehydes react mo readily (Curtius and co-workers, J. pr. Che 1894, [ii.] 50, 275, 295; 1895, 51, 165, 353).

(7) Ketones react with phosphorus pentachloride as follows:—

$$R{\cdot}CO{\cdot}R'+PCl_5=POCl_3+R{\cdot}CCl_2{\cdot}R'.$$

(8) Some ketones, usually those containing the group $CH_3{\cdot}CO{\cdot}$, unite with acid sodium sulphite; acetone, for example, gives

$$(CH_3)_2C(OH)(SO_3Na),H_2O.$$

The ketone is regenerated by sodium carbonate solution.

(9) Hydrogen cyanide yields nitriles

$$RR'C(OH)CN$$

which react with ammonia to give the nitriles of α-amino acids $RR'C(NH_2)CN$.

(10) Hydrogen sulphide converts the ketones into thioketones, *e.g.* acetone yields thioacetone (W. Spring, Bull. Acad. Roy. Belg. 1883, [iii.] 5, 236).

(11) The ketones do not so readily form addition products as the aldehydes, *e.g.* with water and alcohol, but when a mixture of a ketone and a mercaptan is treated with gaseous hydrogen chloride a mercaptol is formed (Baumann, Ber. 1885, 18, 887):

$$(CH_3)_2CO+2C_2H_5SH=H_2O+(CH_3)_2C(SC_2H_5)_2$$

(12) Polyhalogenated ketones and polyketones are exceptional, thus trichloracetone gives a hydrate $CCl_3{\cdot}C(OH)_2{\cdot}CH_3$.

(13) The acetals of the ketones (as well as of the aldehydes) may be obtained by the action of orthoformic esters (Claisen, Ber. 1907, 40, 3903):

$$RR'C:O+HC(OC_2H_5)_3 \\ =RR'C(OC_2H_5)_2+H{\cdot}CO{\cdot}OC_2H_5$$

The ketone and calculated amount of ethyl formate are dissolved in alcohol (3 or more molecular proportions) and a small amount of mineral acid, ferric chloride, &c., as catalysing agent added. The mixture is either warmed for a short time or allowed to stand for a longer period at the ordinary temperature.

Nascent ethyl orthoformate from alcohol and ethyl iminoformate hydrochloride may also be used (*cp.* E. Hess, D. R. P. 197804):

$$H{\cdot}C(:NH,HCl)(OC_2H_5)+2C_2H_5OH \\ =NH_4Cl+H{\cdot}C(OC_2H_5)_3$$

(*see* Pinner, Ber. 1883, 16, 356).

(14) Many ketones, notably cyclic ketones, behave towards acylating agents as if they possessed the tautomeric enolic structure, thus *cyclo*hexanone gives esters of *cyclo*hexenol (C. Mannich, Ber. 1906, 39, 1594; 1908, 41, 564; *cp.* F. W. Semmler, *ibid.* 1909, 42, 584, 1161, 2014). A striking example is the conversion of diethyl and dipropyl ketones into acetyl derivatives of their enolic forms by heating with 1½ parts of acetic anhydride, and ⅛ part of fused sodium acetate for 70 hours at 205°–215° (V. Hâncu, Ber. 1909, 42, 1052).

(15) Magnesium alkyl halides react with ketones, giving tertiary alcohols:

$$C_6H_5{\cdot}CO{\cdot}CH_3+CH_3{\cdot}MgI=C_6H_5{\cdot}C(OMgI)(CH_3)_2$$

$$C_6H_5{\cdot}C(OMgI)(CH_3)_2+H_2O \\ =Mg(OH)I+C_6H_5{\cdot}C(CH_3)_2(OH).$$

(V. Grignard, Compt. rend. 1900, 130, 1322; Bull. Soc. chim. 1901, [iii.] 25, 497; Ann. Univ. Lyon. 1901, No. 6, 1–116).

(16) A mixture of alkyl halide and sodium frequently behaves like the Grignard reagents. P. Schorigin has obtained diphenyl ethyl carbinol $C(C_6H_5)_2(C_2H_5)OH$ by the action of 21·5 grams of sodium wire on 30 grams each of ethyl iodide and benzophenone dissolved in 150 c.c. of dry benzene (Ber. 1908, 41, 2711).

(17) Ketones containing at least one aliphatic radicle react with esters and sodium ethoxide to give β-diketones. In this way benzoylacetone may be obtained from ethyl benzoate and acetone (Claisen, Ber. 1887, 20, 655), or from ethyl acetate and acetophenone (Beyer and Claisen, *ibid.* 2180; *see* also R. W. L. Clarke, A. Lapworth, and E. Wechsler, Chem. Soc. Trans. 1908, 93, 30).

(18) Ketones of suitable structure react with 1 or 2 molecules of an aldehyde giving unsaturated ketones. Methyl cinnamyl ketone (monobenzalacetone) may be prepared by adding 10 parts of 10 p.c. caustic soda solution to a mixture of 10 parts of benzaldehyde, 900 parts of water, and 20 parts of acetone, allowing to stand 2 or 3 days in the cold, extracting with ether and distilling under reduced pressure:

$$C_6H_5{\cdot}CHO+CH_3{\cdot}CO{\cdot}CH_3 \\ =H_2O+C_6H_5{\cdot}CH:CH{\cdot}CO{\cdot}CH_3.$$

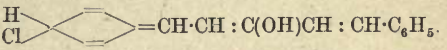
Benzalacetone forms shining tabular crystals, m.p. 41°–42°, b.p. 260°–262°, b.p. (at 25 mm.) 151°–153° (Claisen and Ponder, Annalen, 1884, 223, 139).

If, however, to 20 parts of benzaldehyde, 6 parts of acetone and 40 parts of acetic acid, 30 parts of sulphuric acid are added drop by drop whilst the mixture is cooled very thoroughly, dibenzalacetone is formed. The mixture, after standing 6–8 hours at 0°, is poured into water, the precipitate washed with caustic soda and crystallised from ether. Monoclinic crystals, m.p. 112°–112·5°.

$$2C_6H_5{\cdot}CHO+CH_3{\cdot}CO{\cdot}CH_3 \\ =2H_2O+C_6H_5{\cdot}CH:CH{\cdot}CO{\cdot}CH:CH{\cdot}C_6H_5$$

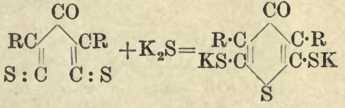
(Claisen and Claparède, Ber. 1881, 14, 2460).

The colouration produced by strong acids with dibenzalacetone is attributed by Baeyer and Villiger to the formation of quinonoïd carbonium salts (Ber. 1902, 35, 1189, 3013), *e.g.*:



(19) Ketones react with carbon disulphide in presence of caustic alkalis, giving 4-keto-3 : 5-dialphylpenthiophen-2 : 6-dithiols:

$$R{\cdot}CH_2{\cdot}CO{\cdot}CH_2{\cdot}R+2CS_2+4KOH \\ =SC:CR{\cdot}CO{\cdot}CR:C:S+4H_2O+2K_2S.$$



(H. Apitzsch, Ber. 1904, 37, 1599; 1905, 38, 2888; 1908, 41, 4028, 4039, 4047; 1909, 42, 2940; 1910, 43, 1259).

(20) At 180°–200° hydrogen (with nickelised asbestos as catalytic agent) reduces unsaturated to saturated ketones (G. Darzens, Fr. Pat. 350390).

Differentiation of Ketones from Aldehydes.

Aldehydes and ketones possess many reactions in common, but, on oxidation, the ketones do not give acids containing the same number of carbon atoms as the ketone (General Reaction 3).

A. Einhorn finds that aldehydes react with catechol monocarbazinic ester

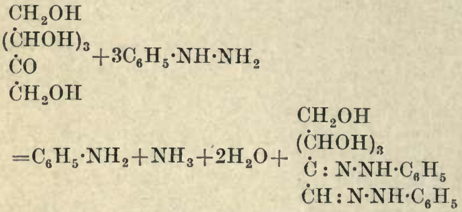
$$C_6H_4(OH)O{\cdot}CO{\cdot}NH{\cdot}NH_2$$

in dilute alcoholic solution, whilst ketones do not, although condensation may be effected in a few cases when glacial acetic acid or zinc chloride is employed as condensing agent (Annalen, 1898, 300, 135; 1901, 317, 190). Resorcinol and quinol monocarbazinates behave similarly.

A. Angeli finds that nitrohydroxylamine and other 'nitroxyl' (NOH) yielding substances convert aldehydes directly into the corresponding hydroxamic acids (Gazz. chim. ital. 1904, 34, i. 50).

Hydroxyl and Amino Substituted Ketones.

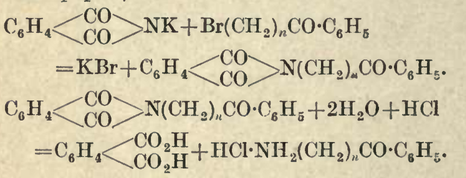
The substituted ketones usually exhibit the specific ketonic characters as well as properties due to the substituent groups. Thus keto alcohols form esters, and amino ketones are basic. The different groupings may, however, affect one another, keto alcohols of the type $R{\cdot}CO{\cdot}CH_2OH$ usually give osazones, as lævulose when warmed with phenylhydrazine solutions gives phenylglucosazone:



$$\begin{array}{l}CH_2OH\\ \dot{C}HOH)_3\\ \dot{C}O\\ \dot{C}H_2OH\end{array} + 3C_6H_5{\cdot}NH{\cdot}NH_2 = C_6H_5{\cdot}NH_2 + NH_3 + 2H_2O + \begin{array}{l}CH_2OH\\ (\dot{C}HOH)_3\\ \dot{C}:N{\cdot}NH{\cdot}C_6H_5\\ \dot{C}H:N{\cdot}NH{\cdot}C_6H_5\end{array}$$

(E. Fischer, Ber. 1884, 17, 579; 1887, 20, 821).

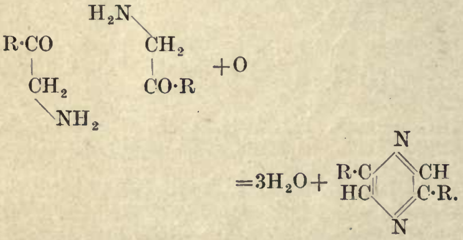
The salts of aminoketones may be prepared from the halogenised ketones by condensation with potassium phthalimide and subsequent hydrolysis (Gabriel, Ber. 1907, 40, 2649, and other papers).



$$C_6H_4{<}^{CO}_{CO}{>}NK + Br(CH_2)_nCO{\cdot}C_6H_5 = KBr + C_6H_4{<}^{CO}_{CO}{>}N(CH_2)_nCO{\cdot}C_6H_5.$$

$$C_6H_4{<}^{CO}_{CO}{>}N(CH_2)_nCO{\cdot}C_6H_5 + 2H_2O + HCl = C_6H_4{<}^{CO_2H}_{CO_2H} + HCl{\cdot}NH_2(CH_2)_nCO{\cdot}C_6H_5.$$

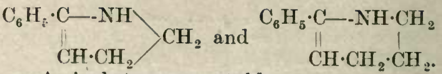
α-Aminoketones, when isolated from their salts, condense in the following manner:



β-Aminoketones are capable of existence as free bases, *e.g.* diacetoneamine

$$CH_3{\cdot}CO{\cdot}CH_2{\cdot}C(CH_3)_2NH_2.$$

γ- and δ-aminoketones condense internally, giving substituted pyrrolines and tetrahydropyridines respectively, *e.g.*:



ε-Aminoketones are stable.

INDIVIDUAL OPEN-CHAIN MONOKETONES.

1. *Aliphatic Ketones.*

Acetone is treated in a separate article (*q.v.*). It forms basic products with ammonia, diacetoneamine $CH_3{\cdot}CO{\cdot}CH_2{\cdot}C(CH_3)_2NH_2$ (Heintz, Annalen, 1877, 189, 214) and triacetoneamine $NH{<}^{C(CH_3)_2CH_2}_{C(CH_3)_2CH_2}{>}CO + H_2O$ (Heintz, *ibid.* 1875, 178, 305), the former of which has found application in the preparation of pharmaceutical products (Schering, D. R. PP. 95620, 95621, 95622, 95623; *cp.* Harries, D. R. PP. 99004, 99005).

The hypnotic, 'sulphonal,'

$$(CH_3)_2C(SO_2C_2H_5)_2$$

is obtained either by the oxidation of the mercaptol $(CH_3)_2C(SC_2H_5)_2$ with potassium permanganate (Baumann, Ber. 1886, 19, 2808), or by the methylation of ethylidene diethylsulphone $CH_3{\cdot}CH(SO_2C_2H_5)_2$, or diethylsulphonemethane $CH_2(SO_2C_2H_5)_2$ with alcoholic potash and methyl iodide (Fromm, Annalen, 1889, 253, 147) (*v.* SULPHONAL).

Methyl ethyl ketone (*Butanone*), b.p. 78·6°, occurs in the distillate from crude calcium acetate, and may be obtained from the water used in washing wool; this is evaporated with lime, and the resultant calcium salts distilled. About 45–50 p.c. of 'acetone oil' is obtained, 80 p.c. is soluble in water, and when fractionated 60 p.c. of methyl ethyl ketone is obtained. This compound is employed for the denaturation of alcohol, the similarity of boiling-points making separation by fractionation nearly impossible (A. and P. Buisine, Compt. rend. 1897, 125, 777; 1898 126, 351; 1899, 128, 561) (*v.* ACETONE OIL).

Methyl ethyl ketone, like acetone, may be employed instead of formaldehyde for preparing sulphoxylates (M. L. B., D. R.-PP. 162875, 207846, 210467).

Methyl hydroxyethyl ketone

$$CH_3{\cdot}CO{\cdot}CH_2{\cdot}CH_2{\cdot}OH$$

results from the condensation of acetone and formaldehyde; dehydrated by means of 2 p.c. of zinc chloride *methyl vinyl ketone*

$$CH_3{\cdot}CO{\cdot}CH:CH_2,$$

b.p. 80°, is formed (Farbenfab. vorm. Fr. Bayer & Co., D. R. P. 222551).

Methyl propyl ketone (2-pentanone) is found in the crude acetone obtained by distilling the calcium salts from pyroligneous acid, b.p. 101·7°.

Methyl-*n*-amyl ketone (2-heptanone) occurs in oil of cloves (Schimmel & Co., Ber. April, 1897, 50) and boils at 151°–152°. It possesses a penetrating fruity odour.

Methyl nonyl ketone (2-undecanone) forms the chief constituent of oil of rue (*Ruta graveolens* [Linn.]), being accompanied by a small amount of a ketone $C_{12}H_{24}O$ (Williams, Annalen, 1858, 107, 374). It also forms 75 p.c. of the ketonic portion of the 'essence' of cocoa-nut butter, in which it is accompanied by methyl heptyl and methyl undecyl ketones (A. Haller and A. Lassieur, Compt. rend. 1910, 151, 697).

2-Methyl-Δ²-heptene-6-one

$(CH_3)_2C : CH{\cdot}CH_2{\cdot}CH_2{\cdot}CO{\cdot}CH_3$

occurs in oil of linaloes (Barbier and Bouveault, Compt. rend. 1895, 121, 168), and is a constituent of lemon-grass oil (Bertram and Tiemann, Ber. 1899, 32, 834); b.p. 173°–174°, sp.gr. 0·8602, at 20° n^{20}_D 1·4445. This ketone has been artificially prepared by the slow distillation of cineolic anhydride $C_{10}H_{14}O_4 = C_8H_{14}O + CO + CO_2$ (Wallach, Annalen, 1890, 258, 324), and together with other substances by the oxidation of geraniol, gerianial, and methylheptenol by chromic acid (Tiemann and Semmler, Ber. 1893, 26, 2722). The same authors also obtained it by boiling geranonitrile with alcoholic potash and by the oxidation of citral (Ber. 1895, 28, 2126).

Verley (Bull. Soc. chim. 1897 [iii.] 17, 175) obtains it by boiling 500 grams of citral with a solution of 500 grams of potassium carbonate in 5 litres of water for 12 hours, the ketone is then distilled in steam and fractionated under reduced pressure. Verley records the constants, b.p. 168° (84° at 26 mm.), sp.gr. 0·910 at 14°, $n^{31°}_D$ 1·437.

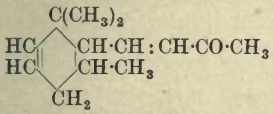
Methylheptenone gives an *oxime* and *phenylhydrazone*; it is converted into dihydro-*m*-xylene by the action of zinc chloride (Wallach) or concentrated sulphuric acid (Verley).

II. *Hydroaromatic Ketones.*

Of the non-cyclic ketones containing hydroaromatic nuclei, irone, and its isomers are of especial importance.

Irone $C_{13}H_{20}O$ was recognised by Tiemann and Kruger (Ber. 1893, 26, 2675; 1895, 28, 1754; Tiemann, *ibid.* 1898, 31, 808; Haarmann and Reimer, D. R. P. 72840) as the odoriferous principle of iris root (*Iris florentina* [Linn.], *I. germanica* [Linn.], *I. pallida* [Linn.]). Violet or iris oil is obtained chiefly from *I. florentina*; at ordinary temperatures it forms a fairly firm yellowish mass, possessing an intense odour of violets. It consists of about 80 p.c. of myristic acid associated with irone, methyl myristate, oleïc aldehyde, acid, and esters. Irone and volatile esters distil in a current of steam, the esters are saponified, the irone again steam distilled, and the product rectified under reduced pressure. Pure irone is dextrorotatory, b.p. (16 mm.) 144°, sp.gr. at 20° 0·939; *oxime* $C_{13}H_{20} : NOH$ m.p. 121·5°; *p*-bromo-phenylhydrazone $C_{13}H_{20} : N{\cdot}NH{\cdot}C_6H_4Br$, m.p. 140°–145°.

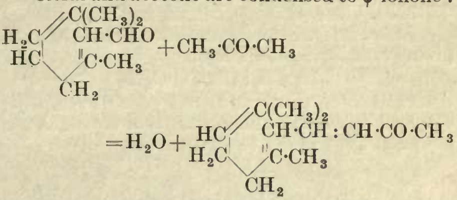
Tiemann and Krüger (*l.c.*) determined the constitution of irone as



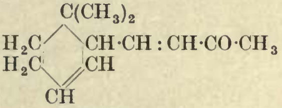
and attempted to synthesise it from citral (lemon-grass oil).

Ionones (α- and β-). These ketones, isomeric with irone, and differing from it and from one another by the position of the double linkage in the ring, were actually obtained from citral; as they also have an odour of violets they have attained very considerable technical importance (Haarmann and Reimer, D. R. PP. 73089, 75128).

Citral and acetone are condensed to ψ-ionone :

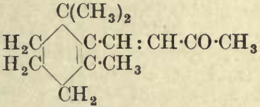


which, on boiling with sulphuric acid, gives a mixture of



α-Ionone

and



β-Ionone

The formation of the former is favoured by a dilute acid, the latter when more concentrated sulphuric acid is employed. The separation of the two isomerides is effected by the more sparing solubility of the bisulphite compound of α-ionone (Tiemann, Ber. 1898, 31, 870), the process may be aided by salting out with sodium chloride (P. Chuit, Rev. gén. Chim. pure appl. 1903, 6, 422).

According to patent D. R. P. 129027 α-ionone is formed preferentially with concentrated phosphoric acid at 30°, β-ionone almost exclusively when 70–100 p.c. sulphuric acid is employed in the cold (Haarmann and Reimer).

Citral may be isomerised to α- and β-*cyclo*-citrals, which condense with acetone, yielding ionones (Haarmann and Reimer, D. R. P. 123747; Tiemann, Ber. 1900, 33, 3721). Other information about the preparation of ionones and higher homologues using methyl ethyl and methyl *iso*propyl ketones in place of acetone is given in Haarmann and Reimer's patents (D. R. PP. 126959, 126960, 127424, 127831, 129027, 132222, 133758, 150827, 183855).

α-Ionone is an oil with strong, sweet smell of fresh violets, b.p. (12 mm.) 127·6°, sp.gr. at 20° 0·9301; *oxime* $C_{13}H_{20} : NOH$, m.p. 89°–90°; *semicarbazone* $C_{13}H_{20} : N{\cdot}NH{\cdot}CO{\cdot}NH_2$, m.p. 107°–108°.

β-Ionone is also an oil smelling pleasantly like violets, b.p. (10 mm.) 127°–128·5°; sp.gr. at 20° 0·9442; *oxime*, oily; *semicarbazone*, m.p. 148°–149°.

III. *Mixed Ketones.*

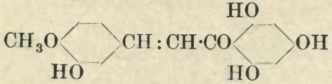
Acetophenone $C_6H_5{\cdot}CO{\cdot}CH_3$, used medicinally as *hypnone*, is formed by distilling a mixture of calcium acetate and benzoate, and is conveniently prepared by the action of acetyl chloride on benzene in the presence of aluminium chloride (Friedel and Crafts, Ann. Chim. Phys. 1884, [vi.] 1, 507), m.p. 20·5°, b.p. 202°, sp.gr. 1·032 at 15°.

Acetophenone does not combine with sodium bisulphite; phosphorus pentachloride gives $C_6H_5{\cdot}CCl_2{\cdot}CH_3$; halogens substitute in the methyl group (Gautier, Bull. Soc. chim. 1886, 45, 875). The *phenylhydrazone* has m.p. 105°.

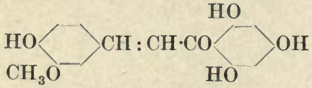
Acetophenone condenses with benzaldehyde, giving *cinnamyl phenyl ketone*

$C_6H_5{\cdot}CH : CH{\cdot}CO{\cdot}C_6H_5$

derivatives of this compound occur naturally; *e.g.* hesperitin and homœriodictyol to which are assigned the respective structures:



and



(Power and Tutin, Trans. Chem. Coc. 1907, 91, 887; *cp.* Tiemann and Will, Ber. 1881, 14, 970; Perkin, Chem. Soc. Trans. 1898, 73, 1037; and Tutin and Caton, *ibid.* 1910, 97, 2062).

ω-Chloroacetophenone (phenacyl chloride) $C_6H_5{\cdot}CO{\cdot}CH_2Cl$ is obtained by leading the theoretical amount of chlorine into boiling acetophenone. The product is distilled, the portion passing over below 200° is chlorinated again, whilst the fraction between 240° and 250° is collected separately, and the monochloro-derivative crystallised by cooling; m.p. 58°–59°; b.p. 244°–245° (Staedel, Ber. 1887, 10, 1830).

ω-Bromoacetophenone $C_6H_5{\cdot}CO{\cdot}CH_2Br$ is prepared by adding gradually one molecular proportion of bromine to acetophenone dissolved in carbon disulphide (Hunnius, Ber. 1877, 10, 2007), a current of dry carbon dioxide being led through (Staedel, Kleinschmidt, *ibid.* 1880, 13, 837; 1883, 16, 22); m.p. 50°.

Both phenacyl chloride and bromide are of use as synthetic agents; thus with ammonia 2 : 5-diphenylpyrazine is produced (Gabriel, Ber. 1908, 41, 1127; Tutin, Chem. Soc. Trans. 1910, 97, 2495) a compound previously described by Staedel and Rügheimer as *iso*indol (Ber. 1876, 9, 563; 1880, 13, 836).

***p*-Aminoacetophenone** $NH_2{\cdot}C_6H_4{\cdot}CO{\cdot}CH_3$; m.p. 106°; b.p. 293°–295°. One method of preparing this compound has been given previously (general methods of preparation, 17). F. Kunckell (Ber. 1900, 33, 2641) obtains *p*-acetylaminoacetophenone by the action of 70 grams of aluminium chloride on a mixture of 20 grams of acetanilide, and 50 grams each of carbon disulphide and acetyl chloride, a yield of 15·5 grams (m.p. 166°–167°) being obtained. The free aminoketone is readily obtained by boiling for half an hour with three times its weight of 15 p.c. hydrochloric acid, and precipitating with sodium carbonate.

***p*-Hydroxyacetophenone** $HO{\cdot}C_6H_4{\cdot}CO{\cdot}CH_3$ may be obtained from the amino compound by diazotisation; m.p. 107° (Klingel, Ber. 1885, 18, 2691).

Resacetophenone

$CH_3{\cdot}CO{\cdot}C_6H_3(OH)_2,(OH : OH = 2 : 4,$

a compound of synthetical importance, is obtained as described in General Method 17; m.p. 142°.

Gallacetophenone 2 : 3 : 4-$(OH)_3C_6H_2{\cdot}CO{\cdot}CH_3$ similarly obtained from acetic acid and pyrogallol is used as a mordant dyestuff. The analogous purely aromatic hydroxy ketones, which are similarly employed, are described later.

IV. *Aromatic Ketones.*

Diphenylketone (Benzophenone)

$C_6H_5{\cdot}CO{\cdot}C_6H_5$.

This ketone is obtained by several of the general methods (2, 4, 6, 7, 10, 11, 16).

Preparation.—(i.) Dry calcium benzoate mixed with one-tenth of its weight of lime is distilled from an iron retort. The distillate is fractionated, the portion distilling at 290°–310° being collected separately. This for the most part solidifies on cooling, liquid impurities are removed by pressure, and the ketone crystallised from alcohol. The yield amounts to about one-fourth of the weight of the calcium benzoate used, the other products of distillation consisting of benzene, diphenyl, and anthraquinone.

(ii.) A mixture of equivalent amounts of benzene and benzoyl chloride dissolved in carbon disulphide is treated with aluminium chloride, equal in weight to the benzoyl chloride used. The reaction is completed under reflux on the water-bath, water is carefully added, and carbon disulphide, unattacked benzene, and benzoic acid removed in a current of steam. The residual oil is washed successively with dilute hydrochloric acid, dilute caustic soda and water, dried and fractionated. Yield 70–75 p.c.

(iii.) Well-cooled benzene is saturated with carbonyl chloride, and aluminium chloride added in small quantities at a time. The operation is conducted under reflux, and the product worked up as in the last case. From 100 grams of benzene, 55 grams of phosgene and 36 grams of aluminium chloride, 33 grams of benzophenone may be obtained.

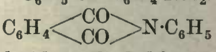
Properties.—Rhombic prisms; m.p. 48°–49°. An unstable allotropic form (? monoclinic), melts at 26°–27° (Zincke, Annalen, 1871, 159, 377; Oechsner de Coninck, Compt. rend. 1900, 130, 40); b.p. 306° (170° at 15 mm.). For variation of boiling-point with pressure, *see* Crafts (Bull. Soc. chim. 1883, [ii.] 282). *Oxime* $(C_6H_5)_2C : NOH$; m.p. 139·5°–140°; *phenylhydrazone* $(C_6H_5)_2C : N{\cdot}NH{\cdot}C_6H_5$; m.p. 137°.

The ketone gives benzhydrol $(C_6H_5)_2CH(OH)$ when reduced with sodium amalgam, but it is preferable to add zinc dust to an alcoholic solution to which a small amount of aqueous potash has been added (Elbs, J. pr. Chem. 1886, [ii.] 33, 184).

Substitution (halogen, nitro, amino, &c.) derivatives are known; of these the amino and especially the dialkylamino derivatives are of considerable technical importance.

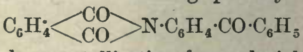
***p*-Aminobenzophenone** $C_6H_5{\cdot}CO{\cdot}C_6H_4{\cdot}NH_2$.

(i.) 75 grams of phthalanil



$C_6H_4\left<\begin{matrix}CO\\CO\end{matrix}\right>N{\cdot}C_6H_5$

and 50 grams of benzoyl chloride are boiled for 10 or 12 hours, zinc chloride (1 gram) being added from time to time. The resulting phthalylbenzoanilide



$C_6H_4\left<\begin{matrix}CO\\CO\end{matrix}\right>N{\cdot}C_6H_4{\cdot}CO{\cdot}C_6H_5$

may be purified by crystallisation from glacial acetic acid; when hydrolysed by alcoholic potash it gives *p*-aminobenzophenone (benzoaniline) and phthalic acid (Doebner, Annalen, 1881, 210, 268).

(ii.) Aniline and 2 molecular proportions of benzoyl chloride are heated gradually at 220°–230°, and the temperature maintained for 20 hours. The dibenzanilide first produced is thus isomerised to a mixture of *o*- and *p*-benzoylaminobenzophenones; the change may be aided by the addition of 10 p.c. of zinc chloride. After hydrolysis of the product the two aminobenzophenones may be separated by steam distillation, the ortho- compound being volatile. Calculated on the weight of aniline used, 15 p.c. of the ortho- and 45 p.c. of the para- derivatives are obtained (Chattaway, Chem. Soc. Trans. 1904, 85, 394).

Shining leaflets; m.p. 124°.

Aminobenzophenone and dimethyl- and diethylaminobenzophenones, as well as dimethylaminobenzophenone sulphonic acid condense with pyrogallol in acid solution to form triphenylmethane mordant dyestuffs (Ges. f. Chem. Ind. Basel, D. R. P. 58689).

***p*-Dimethylaminobenzophenone**

$$C_6H_5{\cdot}CO{\cdot}C_6H_4{\cdot}N(CH_3)_2$$

is obtained from malachite green and concentrated hydrochloric acid at 250° (Ber. 1880, 13, 2225), and by methylation of *p*-aminobenzophenone (Doebner, Annalen, 1881, 210, 270). Technically, it is more easily prepared by interaction of benzanilide, dimethylaniline, and phosphoryl chloride, and hydrolysis of the resulting product:

$$C_6H_5{\cdot}CO{\cdot}NH{\cdot}C_6H_5 \rightarrow C_6H_5{\cdot}CCl:N{\cdot}C_6H_5$$
$$\rightarrow C_6H_5{\cdot}C(C_6H_4{\cdot}N[CH_3]_2):N{\cdot}C_6H_5$$
$$\rightarrow C_6H_5{\cdot}CO{\cdot}C_6H_4{\cdot}N(CH_3)_2.$$

20 kilos. benzanilide, 40 kilos. dimethylaniline, and 20 kilos. phosphoryl chloride are stirred and warmed until spontaneous heating takes place, the temperature is then kept below 120°, and the reaction subsequently finished by one or two hours' heating on the water bath.

Hydrolysis may be effected in one of two ways:

(*a*) The mass is poured into 100 litres of water and 5 kilos. of hydrochloric acid warmed to 50°, the liquid allowed to stand, whereby a portion of the ketone separates, the remainder being precipitated by the addition of 500 litres of water and careful neutralisation with caustic soda. The ketone is collected, extracted with hydrochloric acid, washed, and dried.

(*b*) The mass is made alkaline, excess of dimethylaniline removed in a current of steam, and the granular residue hydrolysed at 50°–70° with 100 litres of water and 10 kilos. of hydrochloric acid. A portion of the ketone is precipitated, the remainder is obtained by addition of aqueous caustic soda, care being taken not to throw the aniline out of solution. Other dialkylaminobenzophenones may be similarly obtained (Farb. vorm. Meister, Lucius, and Brüning, D. R. PP. 41751, 42853).

p-Dimethylaminobenzophenone forms colourless leaflets; m.p. 90°–91°. It is a weak base, insoluble in water, sparingly soluble in cold alcohol. Phosphorus trichloride yields a yellow compound, probably

$$C_6H_5{\cdot}CCl_2{\cdot}C_6H_4{\cdot}N(CH_3)_2 \text{ or }$$
$$C_6H_5{\cdot}CCl:C_6H_4:N(CH_3)_2Cl,$$

which can be purified by solution in chloroform and reprecipitation by petroleum spirit. It is easily converted into the original ketone by heating with water, and condenses directly with dimethylaniline, forming malachite green (B. A. S. F., D. R. P. 27789).

The hydrol $C_6H_5{\cdot}CH(OH){\cdot}C_6H_4{\cdot}N(CH_3)_2$ (m.p. 69°–70°), obtained by reduction of dimethylaminobenzophenone, condenses with dimethylaniline to leuco malachite green.

4 : 4′-Diaminobenzophenone

$$NH_2{\cdot}C_6H_4{\cdot}CO{\cdot}C_6H_4{\cdot}NH_2$$

(m.p. 172°), and its trimethyl derivative $(CH_3)_2N{\cdot}C_6H_4{\cdot}CO{\cdot}C_6H_4{\cdot}NH(CH_3)$ (m.p. 156°) are obtained from pararosaniline (or rosaniline) and pentamethyl violet, respectively by prolonged heating with hydrochloric acid (Wichelhaus, Ber. 1886, 19, 109).

Diaminobenzophenone and its derivatives can be condensed with pyrogallol to green or blue mordant dyestuffs (Ges. f. chem. Ind. Basel, D. R. P. 61326).

Tetramethyldiaminobenzophenone (Michler's ketone) $CO[C_6H_4{\cdot}N(CH_3)_2]_2$ is a valuable intermediate product in the preparation of many dyestuffs, and was first obtained by Michler (Ber. 1876, 9, 716, 1900). Dimethylaniline is saturated at ordinary temperature with the theoretical quantity of phosgene, and the reaction completed by warming in a closed vessel to 100°. Water is added, excess of dimethylaniline removed by steam distillation, and the ketone purified from adherent blue colouring matter by repeated solution in hydrochloric acid and reprecipitation with soda.

Michler's ketone may also be prepared by carefully heating on the water-bath 10 kilos. of dimethylaminobenzanilide

$$(CH_3)_2N{\cdot}C_6H_4{\cdot}CO{\cdot}NH{\cdot}C_6H_5$$

18 kilos. of dimethylaniline, and 8·5 grams of phosphoryl chloride, the product being worked up in a similar manner to that adopted in the case of dimethylaminobenzophenone.

Disubstituted dialkylaminobenzamides (Meister, Lucius, Brüning, D. R. P. 44238) may also be employed. Thus 10 kilos. of dimethylaminobenzodiphenylamine $(CH_3)_2N{\cdot}C_6H_4{\cdot}CO{\cdot}N(C_6H_5)_2$, 12 kilos. of dimethylaniline, and 5 kilos. of phosphoryl chloride are heated on the water-bath for 2 hours; the product being subsequently worked up by hydrolysis with hydrochloric acid, precipitation of the ketone and diphenylamine and separation of the latter by washing with alcohol (D. R. P. 44077).

The ketone forms silvery leaflets, m.p. 174° (corr.), boils with some decomposition above 360°; it is easily soluble in alcohol and ether. The basic properties are weak. *Picrate*

$$C_{17}H_{20}ON_2,C_6H_2(OH)(NO_2)_3;$$

mp. 156°–157°.

Tetraethyldiaminobenzophenone obtained similarly melts at 95°–96° (Michler and Gradman, Ber. 1876, 9, 1914).

Replacement of oxygen in the above ketones by the imino group gives auramines (*q v.*).

In presence of condensing agents (*e.g.* $POCl_3$, $COCl_2$, &c.) the tetralkyldiaminobenzophenones condense with aromatic amines to give dyestuffs of the triphenyl (diphenylnaphthyl, &c.) series, but cleaner products are generally obtained by reducing the ketones to hydrols, and condensing these with amines, &c., to leuco-compounds, which are subsequently oxidised to the corresponding dyestuffs.

Reduction to hydrols may be effected by sodium amalgam in alcoholic solution; technically zinc dust and caustic soda in amyl alcoholic solution are employed (B. A. S. F., D. R.-P. 27032). Tetramethyldiaminobenzhydrol dissolves in acetic acid with an intense blue colour, which is discharged on rendering alkaline.

Amino (and acetamino) derivatives of tetra-alkyldiaminobenzophenones may be obtained from nitro derivatives by reduction. Michler's ketone, when nitrated, gives 3-nitro- and 3 : 3′-dinitro-4 : 4′-tetramethyldiaminobenzophenone (Kliegl, Ber. 1906, 39, 1266); the latter compound has also been obtained by the action of dimethylamine on 3 : 3′-dinitro-4 : 4′-dichlorobenzophenone (Consonno, Gazz. chim. ital. 1904, 34, i. 386). Introduction of the nitro group in position 2 may be effected by nitrating tetramethyldiaminodiphenylmethane, and subsequently oxidising the CH_2 group (Farbenf. vorm. Fr. Bayer & Co., D. R. P. 79250).

Hydroxyl derivatives of Benzophenone.

Numerous hydroxyl derivatives of benzophenone have been prepared, many by reactions involving the condensation of benzoic acid and its derivatives with phenols:

$$C_6H_{5-x}(OH)_xCOOH+C_6H_{6-y}(OH)_y$$
$$=C_6H_{5-x}(OH)_xCO{\cdot}C_6H_{5-y}(OH)_y+H_2O.$$

The trihydroxybenzophenones obtained from pyrogallol contain the grouping $\cdot CO{\cdot}C_6H_2(OH)_3(CO : OH : OH : OH=1 : 2 : 3 : 4)$, they are generally yellow in colour, and are used as mordant dyestuffs.

Alizarin yellow A, $C_6H_5{\cdot}CO{\cdot}C_6H_2(OH)_3$, is obtained by heating 1 part of pyrogallol and 1 part of benzoic acid to 145°, and adding 3 parts of zinc chloride with continuous stirring. The end of the reaction, which takes about 3 hours to complete, is recognised by the solution of the product in hot water giving slender bright yellow needles, and not benzoic acid on cooling. The mass is dissolved in 60 parts of boiling water, boiled 2 hours with animal charcoal, filtered, and allowed to crystallise. It forms yellow needles (with $1H_2O$); m.p. 137°–138°. *Acetyl* derivative, colourless; m.p. 119°. On cotton mordanted with alumina it dyes golden-yellow shades, which incline to orange in presence of calcium salts. A fine yellow is produced with aluminium acetate and tin salt; the chromium lake is brownish-yellow, and the iron lake dark olive. The colours produced are very fast.

Dyestuffs giving similar shades are produced by the condensation of pyrogallol with *m*- and *p*-hydroxybenzoic acid, and *β*-resorcylic acid; those from pyrogallol and salicylic or pyrogallolcarboxylic acids give redder lakes, whilst the lakes are of a greenish-yellow shade if dyestuffs obtained by condensing gallic acid with resorcinol or pyrogallol are employed. The chemistry of these hydroxyketone dyestuffs has been studied by C. Graebe and A. Eichengrün (Annalen, 1892, 269, 295).

New dyestuffs, greener in shade, are obtained by fusing alizarin yellow A or C with the ammonium salts of organic acids (Prud'homme, Rev. gén. Mat. col. 1906, 10, 225).

Two unsaturated aromatic ketones, the benzalacetones, have been described under general methods of preparation (No. 18).

Thioketones.

Thiobenzophenone $C_6H_5{\cdot}CS{\cdot}C_6H_5$ was first obtained by Bergreen (Ber. 1886, 21, 341) in an impure condition by the action of 2 parts of aluminium chloride on 1 part of thiophosgene ($CSCl_2$) dissolved in 5 parts of benzene, the reaction being completed on the water-bath. After treatment with ice, and extraction with ether, the ethereal solution was washed with soda and water, and the ether distilled off, the thioketone remaining as an oil.

L. Gattermann and H. Schulze (Ber. 1896, 29, 2944) found that it is impossible to obtain the thioketone in a pure condition by this method, but were successful in treating benzophenone chloride $C_6H_5{\cdot}CCl_2{\cdot}C_6H_5$ with very slightly over the theoretical quantity of alcoholic potassium sulphide. The mixture becomes hot, potassium chloride separates, and the solution assumes a blue colour. After cooling, water is added, the thioketone extracted with ether, the latter distilled off, and the product fractionated under reduced pressure. The thioketone passes over at 174° (14 mm.) as a deep-blue oil, which solidifies to long blue needles.

Thiobenzophenone is very unstable, and can only be preserved in sealed tubes filled with carbon dioxide. Its colour is discharged on warming with alcoholic potash, benzophenone being regenerated; it reacts with hydroxylamine giving benzophenone-oxime, and on heating with copper powder gives tetraphenylethylene.

Gattermann has also described corresponding alkyloxythioketones obtained by the action of thiophosgene on anisole, phenetole, *o*-cresyl ethyl ether, *o*-cresyl methyl ether, *o*-chloroanisole, *o*-chlorophenetole, and *o*-bromoanisole. The compounds obtained resemble thiobenzophenone in their reactions (Ber. 1895, 28, 2869).

On account of the greater reactivity of the : C : S group as compared with carbonyl, the sulphur analogue of Michler's ketone has been prepared by several methods.

Tetramethyldiaminothiobenzophenone

$$(CH_3)_2N{\cdot}C_6H_4{\cdot}CS{\cdot}C_6H_4{\cdot}N(CH_3)_2.$$

Preparation.—(i.) 5 parts of dimethylaniline are cooled to 0°–10°, and 1 part of thiophosgene in 3 parts of carbon disulphide added in the course of 3 or 4 hours with continual stirring, which is continued for 10–12 hours without further cooling. Alkali is added, carbon disulphide and dimethylaniline removed in a current of steam, and the thioketone crystallised (Kern, D. R. P. 37730).

(ii.) An intimate mixture of Michler's ketone and one-fifth of its weight of phosphorus pentasulphide is heated not above 160°. The mass is exhausted successively with water, very dilute sodium carbonate solution and water, and finally crystallised from amyl alcohol (B. A. S. F., D. R. P. 39074).

(iii.) 100 parts of Michler's ketone, 38 parts of phosphoryl chloride, and 400 parts of toluene are heated on a water bath and hydrogen sulphide led in until a test specimen no longer dissolves in water with a blue colour; or

37 parts of phosgene are passed into a solution of 100 parts of Michler's ketone in 400 parts of chloroform at 15°–20°, after the evolution of carbon dioxide has ceased, 90 parts of sodium sulphide in 800 parts of water are added. The solvent is removed by steam distillation, and the thioketone crystallised from alcohol (B. A. S. F., D. R. P. 40374).

(iv.) An alcoholic solution of auramine base is saturated with hydrogen sulphide, first in the cold, then on the water bath (Fehrmann, Ber. 1887, 20, 2857; Graebe *ibid.* 3267).

Properties.—M.p. 202°. Fairly soluble in chloroform, sparingly so in cold alcohol or ether. Yields Michler's ketone on warming with hydrochloric acid.

OPEN CHAIN DIKETONES.

The diketones are most conveniently classified according to the relative positions of the carbonyl groups in the carbon chain. Thus they may be divided in the following way:—

1 : 2- or α-diketones $R\cdot CO\cdot CO\cdot R'$.
1 : 3- or β-diketones $R\cdot CO\cdot CH_2\cdot CO\cdot R'$.
&c. &c.

1 : 2- *or α-Diketones.*

Preparation.—(1) The α-diketones may be obtained as monoximes by the action of nitrous acid on monoketones or β-ketonic esters:

$$R\cdot CO\cdot CH_2\cdot R' + HNO_2 = H_2O + R\cdot CO:(NOH)\cdot R'.$$

$$R\cdot CO\cdot CHR'\cdot CO_2C_2H_2 + HNO_2 = CO_2 + C_2H_5OH + R\cdot CO\cdot C(:NOH)\cdot R'.$$

The monoximes of the 1 : 2-diketones can often be prepared by the action of diazonium salts on alkaline solutions of *iso*nitrosoacetone (Borsche, Ber. 1907, 40, 707):

$$C_6H_5N_2Cl + NaON:CH\cdot CO\cdot CH_3 = C_6H_5\cdot C(:NOH)\cdot CO\cdot CH_3 + NaCl + N_2.$$

The results with *iso*nitrosoacetophenone are not so favourable.

The replacement of the *iso*nitroso- group by oxygen may be effected:

(i.) By boiling with dilute sulphuric acid (v. Pechmann, Ber. 1887, 20, 3213; 1888, 21, 1411).

$$CH_3\cdot CO\cdot C(:NOH)\cdot CH_3 + H_2O = CH_3\cdot CO\cdot CO\cdot CH_3 + H_2NOH.$$

(ii.) By conversion into salts of iminosulphonic acids by the action of alkaline bisulphites, and subsequently hydrolysing by boiling with 15 p.c. sulphuric acid:

$$CH_3\cdot CO\cdot C(:NOH)\cdot CH_3 + NaHSO_3 = CH_3\cdot CO\cdot C(:N\cdot SO_3Na)\cdot CH_3 + H_2O$$

$$CH_3\cdot CO\cdot C(:N\cdot SO_3H)\cdot CH_3 + 2H_2O = CH_3\cdot CO\cdot CO\cdot CH_3 + (NH_4)HSO_4$$

(v. Pechmann, Ber. 1887, 20, 3162; 1889, 22, 2115).

(iii.) By warming with *iso*amyl nitrite (Manasse, Ber. 1888, 21, 2177):

$$CH_3\cdot CO\cdot C(:NOH)\cdot CH_3 + C_5H_{11}\cdot ONO = CH_3\cdot CO\cdot CO\cdot CH_3 + C_5H_{11}OH + N_2O.$$

Similarly diethyl acetosuccinate gives *iso*nitrosolævulic acid, the latter compound yielding diacetyl on boiling with dilute sulphuric acid (Thal, Ber. 1892, 25, 1723).

The mixed aliphatic-aromatic diketones are obtained in a similar way from mixed *iso*nitrosoketones (v. Pechmann and Müller, Ber. 1888, 21, 2119; 1889, 22, 2128).

(2) Ketones of the structure $CH_3\cdot CO\cdot CH_2R$, when warmed with nitric acid (sp.gr. 1·38) give ketones $CH_3\cdot CO\cdot CO\cdot R$ (Fileti and Ponzio, Gazz. chim. ital. 1895, 25, i. 233).

(3) Aromatic (and some heterocylic) diketones are obtained from aldehydes $R\cdot CHO$ by condensation to the keto alcohols

$$R\cdot CO\cdot CH(OH)\cdot R$$

under the influence of potassium cyanide and subsequent oxidation with chlorine (Laurent. Annalen, 1836, 17, 91), or more frequently nitric acid (Zinin, *ibid.* 1840, 34, 188).

(4) By heating compounds of the type $R\cdot CBr:CBr\cdot R$ with water to 200° (*e.g.* tolane bromide) (Limpricht and Schwanert, Ber. 1871, 4, 380):

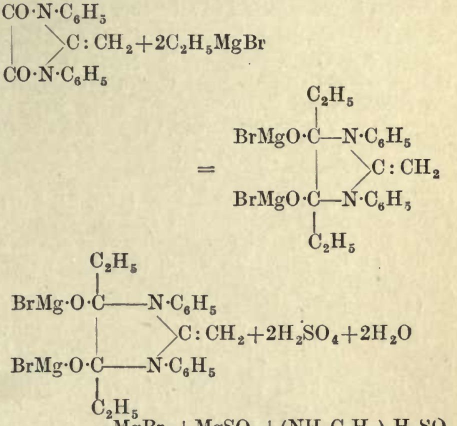
$$2C_6H_5\cdot CBr:CBr\cdot C_6H_5 + 2H_2O = C_6H_5\cdot CO\cdot CO\cdot C_6H_5 + C_6H_5\cdot C:C\cdot C_6H_5 + 4H_2O.$$

(5) By hydrolysis of compounds

$$R\cdot CX_2\cdot CX_2\cdot R$$

(X=halogen). Thus tolane tetrachloride, when heated with sulphuric acid to 165°, or with glacial acetic acid to 230°–250° (Liebermann and Homeyer, Ber. 1879, 12, 1975).

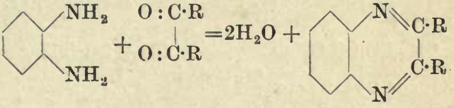
(6) The vinylidene-oxanilide prepared by v. Pechmann by 8 hours boiling of 1 part of oxanilide, 1 part of fused sodium acetate, and 10 parts of acetic anhydride (Ber. 1897, 30, 2791) reacts readily with the Grignard reagents, forming compounds which furnish diketones on decomposition with dilute sulphuric acid:



$$= MgBr_2 + MgSO_4 + (NH_2C_6H_5)_2H_2SO_4 + CH_3\cdot COOH + C_2H_5\cdot CO\cdot CO\cdot C_2H_5$$

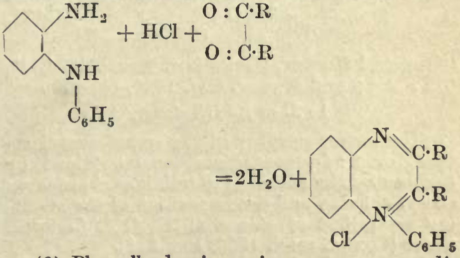
(L. Tschugaeff, Ber. 1907, 40, 186).

General properties and reactions.—(1) The most characteristic reaction of the α-diketones is their condensation with aromatic *o*-diamines to quinoxalines:



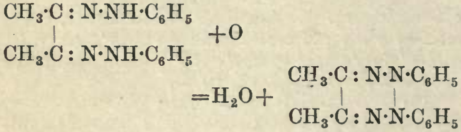
The resulting coloured compounds crystallise well, have definite melting-points, and are readily identified (Hinsberg, Ber. 1884, 17, 322; Annalen, 1887, 237, 327).

When monosubstituted *o*-diamines are employed, salts of ammonium type are produced:



(2) Phenylhydrazine gives *mono-* or *di*-hydrazones; for preparation of the former, *see*

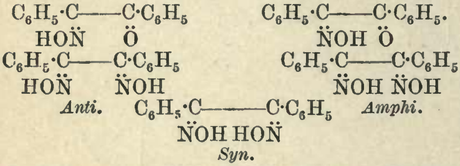
Petrenko-Kritschenko and Eltschaninoff (Ber. 1901, 34, 1699). The dihydrazones (usually called osazones) derived from aliphatic diketones or diketones containing only one aromatic radicle, are readily oxidised by ferric chloride to red or brown osotetrazones (v. Pechmann, Ber. 1888, 21, 2751):



$$\begin{array}{l} CH_3\cdot C:N\cdot NH\cdot C_6H_5 \\ \quad | \qquad\qquad\qquad\qquad +O \\ CH_3\cdot C:N\cdot NH\cdot C_6H_5 \end{array} = H_2O + \begin{array}{l} CH_3\cdot C:N\cdot N\cdot C_6H_5 \\ \qquad | \qquad\quad | \\ CH_3\cdot C:N\cdot N\cdot C_6H_5 \end{array}$$

For action of hydrazine *v.* Curtius and Kastner, J. pr. Chem. 1911, 83, 215.

(3) Hydroxylamine yields *mono-* or *di-*oximes, the former can exist in two, the latter in three modifications, even when the original diketone is symmetrical in structure:



$$\begin{array}{ll} \begin{array}{l} C_6H_5\cdot C\text{——}C\cdot C_6H_5 \\ \quad HO\ddot{N} \qquad \ddot{O} \end{array} & \begin{array}{l} C_6H_5\cdot C\text{——}C\cdot C_6H_5. \\ \quad \ddot{N}OH\ \ \ddot{O} \end{array} \\ \begin{array}{l} C_6H_5\cdot C\text{——}C\cdot C_6H_5 \\ \quad HO\ddot{N} \qquad \ddot{N}OH \end{array} & \begin{array}{l} C_6H_5\cdot C\text{——}C\cdot C_6H_5 \\ \quad \ddot{N}OH\ \ \ddot{N}OH \end{array} \\ \quad \textit{Anti.} & \quad \textit{Amphi.} \end{array}$$

$$\begin{array}{c} C_6H_5\cdot C\text{———}C\cdot C_6H_5 \\ \ddot{N}OH\ HO\ddot{N} \\ \textit{Syn.} \end{array}$$

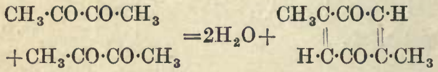
(K. Auwers and V. Meyer, Ber. 1888, 21, 810; 1889, 22, 705; A. Hantzsch and A. Werner, Ber. 1890, 23, 11). The *syn*dioximes are characterised by the ease with which they lose water yielding furazane derivatives.

(4) Semicarbazide gives *mono-* and *di-*semicarbazones and cyclic condensation products (*see* Thiele, Annalen, 1894, 283, 37; Posner, Ber. 1901, 34, 3973; Biltz and Arnd, *ibid.* 1902, 35, 344; Diels, *ibid.* 1902, 35, 347).

(5) With caustic potash the aromatic α-diketones yield diaryl glycollic acids (Liebig, Annalen, 1838, 25, 25; Zinin, *ibid.* 1839, 31, 329):

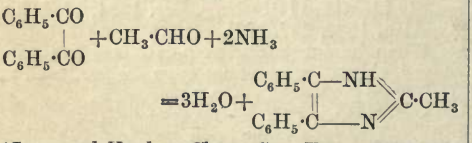
$$C_6H_5\cdot CO\cdot CO\cdot C_6H_5 + KOH = (C_6H_5)_2C(OH)COOK.$$

The aliphatic α-diketones, however, when warmed in alkaline solution undergo condensation with formation of quinones; thus diacetyl gives xyloquinone (v. Pechmann, Ber. 1888, 21, 1417):



$$\begin{array}{l} CH_3\cdot CO\cdot CO\cdot CH_3 \\ +CH_3\cdot CO\cdot CO\cdot CH_3 \end{array} = 2H_2O + \begin{array}{l} CH_3C\cdot CO\cdot C\cdot H \\ \quad\ \| \qquad\quad \| \\ H\cdot C\cdot CO\cdot C\cdot CH_3 \end{array}$$

(6) With aldehydes and ammonia, glyoxalines are formed amongst other products:



(Japp and Hooker, Chem. Soc. Trans. 1884, 45, 672; Japp and Wynne, *ibid.* 1886, 49, 464).

1 : 3- or β- *Diketones.*

The lowest member of the series, acetylacetone, or 2 : 4-pentanedione, was obtained by Combes by the action of aluminium chloride on acetyl chloride and decomposition of the resulting crystalline substance $C_{12}H_{14}O_6Al_2Cl_8$ with water (Compt. rend. 1886, 103, 814).

The usual method of preparation of the 1 : 3-diketones is given under general reaction 17 of monoketones (*vide supra*). As condensing agents for bringing about the reaction

$$R\cdot CO\cdot OC_2H_5 + CH_3\cdot CO\cdot R' \rightarrow R\cdot C(ONa):CH\cdot COR' \rightarrow R\cdot CO\cdot CH_2\cdot CO\cdot R',$$

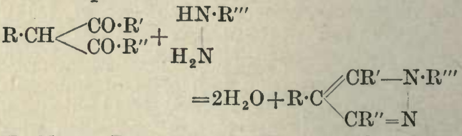
Claisen has found that alcoholic sodium ethoxide works most feebly and in order of increasing activity, are anhydrous sodium ethoxide, metallic sodium (Annalen, 1894, 277, 168), and sodium amide (Ber. 1905, 38, 695).

General properties and reactions.—(1) The 1 : 3-diketones form stable metallic derivatives. Acetylacetone, for example, forms compounds of the types $M^{II}(C_5H_7O_2)_2$, $M^{III}(C_5H_7O_2)_3$, &c., many of which are volatile without decomposition, and may be used for vapour density determinations, thus controlling the valencies of several metals; *e.g.* divalent Gl and Cu, and trivalent Al, Fe, Mn, Co, and Cr (A. Combes, Compt. rend. 1896, 119, 1221; Bull. Soc. chim. 1889, [iii.] 1, 345; Urbain and Debierne, Compt. rend. 1899, 129, 302; Claisen, Ber. 1889, 22, 1010; Annalen, 1893, 277, 170). The metallic radicle may be replaced by acyl groups, branched triketones resulting from the reaction:

$$C_6H_5\cdot C(ONa):CH\cdot CO\cdot C_6H_5 + C_6H_5COCl = NaCl + (C_6H_5CO)_3CH.$$

(v. Baeyer and Perkin, Ber. 1883, 16, 2128; L. Claisen, Ber. 1894, 27, 111; Annalen, 1896, 291, 25; Ber. 1904, 36, 3674).

(2) On warming with arylhydrazines, pyrazoles are produced:

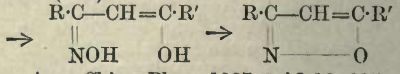


(L. Knorr, Ber. 1885, 18, 311; Annalen, 1887, 238, 37). This reaction can be utilised as the basis of a colour test for β-diketones since pyrazoles are reduced by sodium in boiling alcoholic solution to pyrazolines. If when solution of the metal is complete, water be added and the alcohol boiled off, the pyrazoline may be extracted with ether, and is left when the solvent is evaporated. If the residue be dissolved in fairly concentrated sulphuric acid, addition of a drop of solution of sodium nitrite or potassium dichromate produces a beautiful colouration varying from fuchsine red to blue. This reaction, which can be carried out in test tubes, is general for all pyrazoles derived from phenylhydrazine, not, however, for those obtained from hydrazine itself (L. Knorr, Ber. 1885, 18, 2259; 1893, 26, 101; Annalen, 1887, 238, 200).

(3) Semicarbazide gives similar pyrazole derivatives (T. Posner, Ber. 1901, 34, 3973).

(4) With hydroxylamine the 1 : 3-diketones behave as if one of the ketonic groups were enolised and furnish isoxazoles:

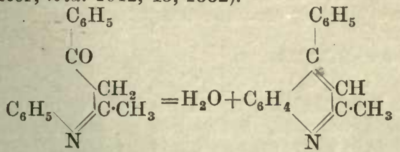
$$R\cdot CO\cdot CH:C(OH)\cdot R'$$



(Combes, Ann. Chim. Phys. 1887, [vi.] 12, 215; Zedel, Ber. 1888, 21, 2178; Claisen, *ibid.* 1891, 24, 3907).

(5) Aniline and benzoylacetone lose 1 molecule of water at 150°, a second molecule of water is removed by heating with concentrated sulphuric

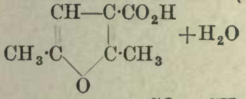
acid, α-methyl-γ-phenylquinoline being formed (C. Beyer, Ber. 1887, 20, 1770; Rügheimer a. Ritter, *ibid.* 1912, 45, 1332).



(6) β-Diketones and β-ketonic esters condense with esters of acetylenic acids, giving unsaturated diketones or ketonic esters. From these, pyrone derivatives have been obtained (Ruhemann, Chem. Soc. Trans. 1899, 75, 245, 411; 1908, 93, 431).

1 : 4- *or γ-Diketones.*

Preparation.—(1) The lowest member of the series, acetonylacetone or 2 : 5-hexanedione was obtained by Paal by heating pyrotritaric acid with water at 150°–160° (Ber. 1885, 18, 58):

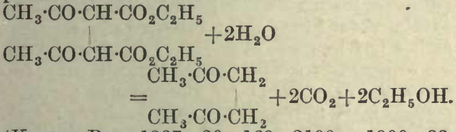


$$=CO_2+CH_3·CO·CH_2·CH_2·CO·CH_3.$$

(2) α-Halogenised ketones react normally with the sodium derivative of ethyl acetoacetate: on hydrolysis 1 : 4-diketones are produced (Paal, Ber. 1883, 16, 2865):

$$CH_3·CO·CH(COOC_2H_5)CH_2·CO·C_6H_5+H_2O$$
$$=CO_2+C_2H_5OH+CH_3·CO·CH_2·CH_2·CO·C_6H_5.$$

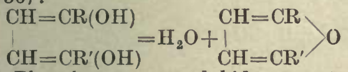
(3) By hydrolysis of compounds of the type of diethyl diacetosuccinate, preferably with potassium carbonate solution:



$$\begin{array}{l}CH_3·CO·CH·CO_2C_2H_5\\ \quad|\\ CH_3·CO·CH·CO_2C_2H_5\end{array}+2H_2O=\begin{array}{l}CH_3·CO·CH_2\\ \quad|\\ CH_3·CO·CH_2\end{array}+2CO_2+2C_2H_5OH.$$

(Knorr, Ber. 1887, 20, 169, 2100; 1900, 33, 1219; Annalen, 1899, 306, 363).

General reactions.—(1) Reacting in the dienolic form, 1 : 4-diketones are dehydrated by fuming hydrochloric acid or acetic anhydride, yielding furfurane derivatives (Paal, Ber. 1884, 17, 2756):



(2) Phosphorus pentasulphide converts them in a similar manner into thiophen compounds.

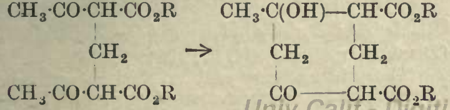
(3) Ammonia similarly yields pyrrole derivatives.

1 : 5-*Diketones, &c.*

Esters of 1 : 5-diketonedicarboxylic acids may be obtained by the condensation of ethyl acetoacetate with aldehydes (P. Rabe, Annalen, 1902, 323, 88; 1904, 332, 11; 1908, 360, 265; Dreckmann a. v. Fischer, Ber. 1911, 44, 966):

$$CH_2O+2CH_3·CO·CH_2·CO_2C_2H_5$$
$$=H_2O+CH_2[CH(COCH_3)·CO_2C_2H_5]_2.$$

Such compounds easily undergo an intramolecular aldol-condensation, yielding 1 : 5-*cyclo*hexanolones:

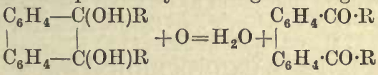


The differentiation of the isomerides is easy, derivatives of dihydropyridine and pyridine being obtained from the 1 : 5-diketonic compounds when treated with ammonia and hydroxylamine respectively.

E. Blaise and A. Koehler (Compt. rend. 1909, 148, 489) have utilised the organo zinc compounds in conjunction with the chlorides of dibasic acids for the synthesis of diketones with far removed carbonyl groups. Whilst succinyl and glutaryl chlorides yield γ- and δ-lactones respectively, the higher acid chlorides react in the sense:

$$COCl(CH_2)_nCOCl+2RZnI$$
$$=ZnCl_2+ZnI_2+R·CO(CH_2)_nCO·R.$$

T. Zincke (Annalen, 1908, 362, 242; 363, 302) has also obtained 1 : 6-diketones by oxidising the ditertiary alcohols obtained from phenanthraquinone by the Grignard reagents:



$$\begin{array}{l}C_6H_4—C(OH)R\\ |\qquad\quad |\\ C_6H_4—C(OH)R\end{array}+O=H_2O+\begin{array}{l}C_6H_4·CO·R\\ |\\ C_6H_4·CO·R\end{array}$$

INDIVIDUAL OPEN-CHAIN DIKETONES.

Diacetyl $CH_3·CO·CO·CH_3$ may be prepared by the method of O. Diels and E. Stephan (Ber. 1907, 40, 4336). Methyl ethyl ketone (850 c.c.) is converted into the *iso*nitroso derivative (diacetyl monoxime) by amyl nitrite (1 litre) and hydrochloric acid (30 c.c., sp.gr. 1·19). The oxime is extracted with dilute sodium hydroxide solution; after acidifying the diacetyl is blown over in a current of steam and the ketone eventually separated from water. 4 kilos. of methyl ethyl ketone give 1300 grams of diacetyl; b.p. 87°–88°.

Diacetyldioxime (dimethylglyoxime)

$$CH_3·C(:NOH)C(:NOH)CH_3$$

has acquired importance as a reagent for nickel. The solution to be tested is treated with an excess of ammonia or sodium acetate and then a little dimethylglyoxime is added and the solution boiled. If nickel is present a scarlet precipitate is produced. Definite results may be obtained with solutions containing 1 part of nickel in 400,000 of water. When cobalt is present, the solution is first shaken with a large excess of ammonia, 0·1mg. of nickel can be detected in the presence of 500 mg. of cobalt (L. Tschugaeff, Ber. 1905, 38, 2520).

Convenient methods for the preparation of dimethylglyoxime have been given by Tschugaeff (*l.c.*), A. Gandarin (J. pr. Chem. 1908, [ii.] 77, 414), and H. Biltz (Zeitsch. anal. Chem. 1909, 48, 164). Biltz's method consists in passing gaseous hydrogen chloride through a well-cooled solution of 50 grams of methyl ethyl ketone in 100 grams of ether, 82 grams of amyl nitrite being added drop by drop. After a few hours the monoxime is extracted by caustic soda solution (150 c.c. iced water and 50 c.c. 33 p.c. caustic soda), the ethereal layer extracted a few times with dilute caustic soda, the alkaline solutions united, extracted with a little ether and somewhat evaporated. After cooling the solution is carefully neutralised with dilute sulphuric acid, and 50 grams of hydroxylamine hydrochloride dissolved in 75 c.c. of water is added. The dioxime crystallises out on standing over-night, and is purified by recrystallisation. The yield amounts to 45–50 grams (*v.* DIMETHYLGLYOXIME).

Benzil $C_6H_5{\cdot}CO{\cdot}CO{\cdot}C_6H_5$ is obtained by the oxidation of benzoïn $C_6H_5{\cdot}CO{\cdot}CH(OH)C_6H_5$, which may be prepared by heating for a short time 200 grams of pure benzaldehyde with 20 grams of potassium cyanide dissolved in 800 grams of 50 p.c. alcohol under reflux. The solution is allowed to cool, benzoïn separates, and is collected, the filtrate yields a further quantity of benzoïn when heated with more potassium cyanide (Zincke, Annalen, 1879, 198, 151). The benzoïn is then heated with twice its weight of nitric acid (sp.gr. 1·4) until red fumes are no longer evolved, the whole is poured into water, and the benzil, which then solidifies, purified by crystallisation from alcohol (Zinin, Annalen, 1840, 34, 188).

Benzil crystallises in six-sided prisms; m.p. 95°; b.p. 346°–348° (corr. with slight decomposition). Easily soluble in alcohol and ether. Is reduced to benzoïn by iron and acetic acid, or zinc and hydrochloric acid (Zinin, Annalen, 1861, 119, 177) and to hydrobenzoïn

$$C_6H_5{\cdot}CH(OH)CH(OH)C_6H_5$$

by sodium amalgam (Zincke and Forst, Ber. 1875, 8, 797). Other reactions have already been mentioned under 1 : 2-diketones.

Benzil yields substitution products with difficulty, it may be nitrated by boiling with fuming nitric acid. Two dinitrobenzils (m.p.'s 131° and 147°) are produced; these may be mechanically separated as crystals. The mixture of dinitrobenzils can be reduced, the resulting diamino-compound (? a mixture), though not isolated, can be used as a component in the preparation of azo dyestuffs (Poirrier and Rosenstiehl, D. R. PP. 44269 and 45789).

OPEN CHAIN TRI- AND TETRA-KETONES.

Triketones. *Preparation.*—(1) F. Sachs and H. Barschall (Ber. 1901, 34, 3047) obtained triketopentane by condensation of nitrosodimethylaniline with acetylacetone and hydrolysis of the resulting azomethine compound:

$$\begin{aligned} &CH_3{\cdot}CO{\cdot}CH_2{\cdot}CO{\cdot}CH_3+ON{\cdot}C_6H_4{\cdot}N(CH_3)_2 \\ &\qquad =H_2O+CH_3{\cdot}CO{\cdot}C[:N{\cdot}C_6H_4N(CH_3)_2]CO{\cdot}CH_3 \\ &CH_3{\cdot}CO{\cdot}C[:N{\cdot}C_6H_4N(CH_3)_2]CO{\cdot}CH_3+H_2O \\ &\qquad =H_2N{\cdot}C_6H_4{\cdot}N(CH_3)_2+CH_3{\cdot}CO{\cdot}CO{\cdot}CO{\cdot}CH_3. \end{aligned}$$

(Later papers by Sachs, Ber. 1902, 35, 3307; 1903, 36, 3221; 1907, 40, 2714.)

(2) Aromatic triketones with open chain have been obtained by Wieland and Bloch (Ber. 1904, 37, 1524). By the action of nitrous gases evolved from a mixture of arsenious oxide and nitric acid (sp.gr. 1·38) on an ethereal solution of dibenzoylmethane, the bisnitroso derivative of the latter compound and diphenyltriketone are obtained. The latter crystallises with water, probably of constitution; in fact the colourless hydrates give coloured triketones by loss of water. The same behaviour is observed in the case of cyclic triketones: Ruhemann (Chem. Soc. Trans. 1910, 2025; 1911, 792, 1306, 1486) finds that the coloured triketohydrindene not only forms a colourless monohydrate, but also gives colourless addition products with guanidine, benzamidine, and hydrogen cyanide.

Tetraketones are also known.

2 : 4 : 5 : 7-*Octanetetrone*

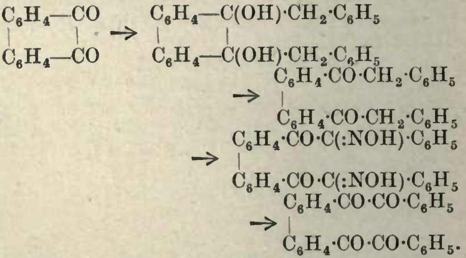
$$CH_3{\cdot}CO{\cdot}CH_2{\cdot}CO{\cdot}CO{\cdot}CH_2{\cdot}CO{\cdot}CH_3$$

is obtained by adding sodium ethoxide (free from alcohol) to an ethereal solution of acetone and diethyl oxalate (Claisen and Stylos, Ber. 1888, 21, 1142). With acetophenone, &c., corresponding aromatic compounds can be prepared.

o-o'-**Dibenzil**

$$C_6H_5{\cdot}CO{\cdot}CO{\cdot}C_6H_4{\cdot}C_6H_4{\cdot}CO{\cdot}CO{\cdot}C_6H_5$$

has been obtained by Zincke and Tropp (Annalen, 1908, 363, 302). Phenanthraquinone is treated with magnesium benzyl halide, the resulting di-tertiary alcohol oxidised to dibenzyldiphenylene diketone, the latter converted into a di*iso*nitroso compound and hydrolysed:



$$\begin{array}{l} C_6H_4{-}CO \\ |\qquad\quad | \\ C_6H_4{-}CO \end{array} \rightarrow \begin{array}{l} C_6H_4{-}C(OH){\cdot}CH_2{\cdot}C_6H_5 \\ | \\ C_6H_4{-}C(OH){\cdot}CH_2{\cdot}C_6H_5 \end{array}$$

$$\rightarrow \begin{array}{l} C_6H_4{\cdot}CO{\cdot}CH_2{\cdot}C_6H_5 \\ | \\ C_6H_4{\cdot}CO{\cdot}CH_2{\cdot}C_6H_5 \end{array} \rightarrow \begin{array}{l} C_6H_4{\cdot}CO{\cdot}C(:NOH){\cdot}C_6H_5 \\ | \\ C_6H_4{\cdot}CO{\cdot}C(:NOH){\cdot}C_6H_5 \end{array} \rightarrow \begin{array}{l} C_6H_4{\cdot}CO{\cdot}CO{\cdot}C_6H_5 \\ | \\ C_6H_4{\cdot}CO{\cdot}CO{\cdot}C_6H_5. \end{array}$$

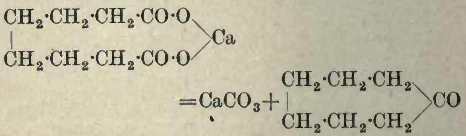
Possessing two 1 : 2-diketo- groups, the compound condenses with 2 molecules of *o*-phenylenediamine to form the corresponding *di*quinoxaline.

CYCLIC KETONES.

In the cyclic ketones the carbonyl groups form members of a closed ring; the properties are very similar to those of the aliphatic ketones as a rule, but in the case of the ortho- and paraquinones, such special characteristics are exhibited that they will be treated in a separate article (*q.v.*).

Preparation.—The cyclic ketones may frequently be prepared by the general methods already given; the following syntheses, or special methods, resulting in the formation of closed chain ketones, may be mentioned.

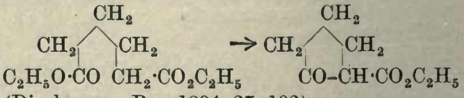
(1) The distillation of the calcium salts of certain dibasic acids gives cyclic ketones. The earliest example is the preparation of suberone from calcium suberate:



$$\begin{array}{l} CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CO{\cdot}O \\ | \\ CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CO{\cdot}O \end{array} \!\!> Ca \;=CaCO_3+\begin{array}{l} CH_2{\cdot}CH_2{\cdot}CH_2 \\ | \\ CH_2{\cdot}CH_2{\cdot}CH_2 \end{array}\!\!> CO$$

(Boussingault, Annalen, 1836, 19, 308; Tilley, *ibid.* 1841, 39, 166; Dale and Schorlemmer, *ibid.* 1879, 199, 147). *Cyclo*pentanone, *cyclo*hexanone, and *cyclo*octanone can be obtained by similar methods from the calcium salts of adipic, pimelic, and azelaïc acids (Wislicenus, Annalen, 1893, 275, 312, 364; v. Baeyer, *ibid.* 1875, 178, 112; Ber. 1893, 26, 229).

(2) The esters of certain dicarboxylic acids undergo intramolecular condensation when acted on by sodium:

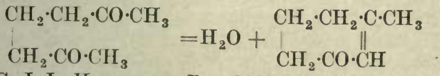


(Dieckmann, Ber. 1894, 27, 102).

(3) *Cyclo*hexanone and its derivatives may be obtained by the reduction of phenols. When

phenol vapour mixed with an excess of hydrogen is passed over reduced nickel at 215°–230°, *cyclo*hexanol and *cyclo*hexanone are obtained. The mixed product may be entirely converted into the latter compound by passing the vapour over copper heated to 330° (Sabatier and Senderens, Compt. rend. 1904, 137, 1025; 138, 457, 1257).

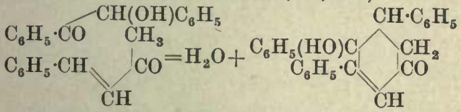
(4) 3-Methyl-Δ^2-*cyclo*hexenone is a product of the interaction of ethyl sodioacetoacetate and methylene iodide. Apparently the first formed 2 : 6-heptanedione undergoes intramolecular condensation:



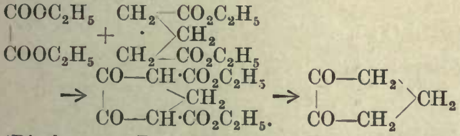
(C. J. L. Hagemann, Ber. 1893, 26, 876).

*iso*Butylidene *di*acetoacetic ester undergoes a similar internal condensation, giving an ester from which 3-methyl-5-*iso*propyl-Δ^2-*cyclo*-hexenone may be obtained (Knoevenagel, Annalen, 1896, 289, 131).

(5) Open chain ketones will condense with unsaturated aldehydes or unsaturated ketones of the type of benzalacetone. Thus the latter compound, condensed with benzoïn, gives 3 : 4 : 5-triphenyl-4-hydroxy-Δ^2-*cyclo*hexenone (Garner, Amer. Chem. J. 1904, 31, 143):

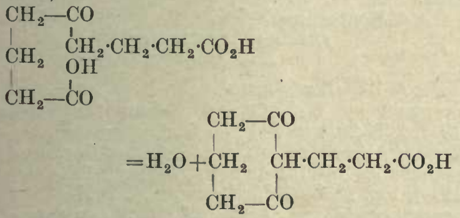


(6) Cyclic 1 : 2-diketones may be obtained by the condensation of diethyl glutarate and its derivatives with diethyl oxalate in presence of sodium ethoxide:

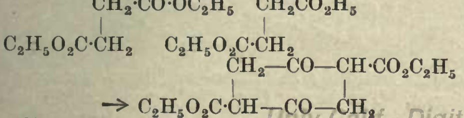


(Dieckmann, Ber. 1897, 30, 1470; 1899, 32, 1933; *cf.* papers by W. H. Perkin, jun., and co-workers, Chem. Soc. Trans. 1906, 89, 1640; 1908, 93, 1943; 1909, 95, 2010).

(7) A derivative of *cyclo*hexane-1 : 3-dione is obtained by dehydration of acetonedipropionic acid (v. Pechmann and Sidgwick, Ber. 1904, 37, 3816):



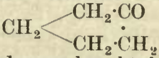
(8) Two molecules of diethyl succinate are condensed by Claisen's reaction (Herrmann, Annalen, 1882, 211, 311):



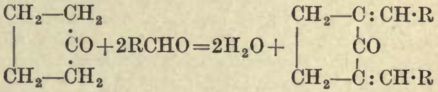
The resulting ester yields *cyclo*hexanedione (*vide infra*).

Individual Cyclic Ketones.

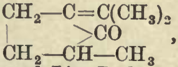
I. *Monocyclic Monoketones.*

*cyclo***Pentanone** 
$CH_2<\begin{matrix}CH_2\cdot CO\\ CH_2\cdot CH_2\end{matrix}$ occurs in raw wood spirit, and may be obtained by the distillation of calcium adipate (J. Wislicenus and Hentzschel, Annalen, 1893, 275, 312, 318). The oil of wood spirit is distilled, and the fraction boiling at 120°–140° shaken with syrupy sodium bisulphite. The resulting crystalline bisulphite compound is well pressed, decomposed with warm saturated sodium carbonate solution, and the oil freed from pyridine bases by shaking with a saturated solution of oxalic acid. The compound obtained is identical with the 'Dumasin' obtained by Kane from acetone oil (J. pr. Chem. 1838, 13, 69).

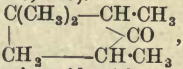
Mobile oil smelling like peppermint; b.p. 130°–130·5°; sp.gr. 0·9416 at 21·5°/4°. *Oxime* $C_5H_8 : NOH$, m.p. 56·5°; b.p. 196°. Condenses with 2 molecules of aromatic aldehydes in presence of alkalis (Vorländer and Hobohm, Ber. 1896, 29, 1836):



Since the resulting compounds crystallise well, and ketones and aliphatic aldehydes do not react with *cyclo*pentanone, Mentzel recommends the reaction for the recognition of aromatic aldehydes (Ber. 1903, 36, 1499). Vorländer and Hobohm have shown that the 'pyroxanthin' obtained by Scanlan, Apjohn and Gregory (Annalen, 1837, 21, 143), by the action of alkalis on raw wood spirit is difural-*cyclo*pentanone.

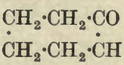
Camphophorone 
$\begin{matrix}CH_2-C=C(CH_3)_2\\ |\qquad\qquad >CO\\ CH_2-CH-CH_3\end{matrix}$, first obtained by Gerhardt and Lies-Bodart (Annalen, 1849, 72, 293) by distillation of calcium camphorate, smells like peppermint; b.p. 200°–205°; sp.gr. 0·9305 at 20°/4°.

Pulegenone is isomeric with camphophorone, both compounds give 2-methyl-5-*iso*propyl*cyclo*pentanone (dihydrocamphorone, dihydropulegenone) on reduction. *Dihydrocamphorone*, b.p. 184°–185°; *oxime*, m.p. 77°–78°; *semicarbazone*, m.p. 193°–195° (Semmler, Ber. 1902, 35, 1022; Wallach, Annalen, 1903, 327, 125).

Dihydrocamphoketone 
$\begin{matrix}C(CH_3)_2-CH\cdot CH_3\\ |\qquad\qquad >CO\\ CH_2-CH\cdot CH_3\end{matrix}$, results on fusion of camphoric acid with potash (W. H. Perkin, jun., and A. W. Crossley, Chem. Soc. Trans. 1898, 73, 26). Smells like peppermint, b.p. 180°–181°; *semicarbazone*

$C_9H_{16} : N\cdot NH\cdot CO\cdot NH_2$,

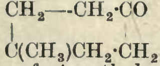
m.p. 202°–203°.

*cyclo***Hexanone** 
$\begin{matrix}CH_2\cdot CH_2\cdot CO\\ CH_2\cdot CH_2\cdot CH_2\end{matrix}$ occurs with other cyclic ketones in wood oil (Looft, Ber. 1894, 27, 1544); it may be obtained by distillation of calcium pimelate (*v.s.*); by the oxidation of synthetic *cyclo*hexanol (v. Baeyer, Ber. 1893,

26, 229; Annalen, 1894, 278, 88); or by the reduction of phenol by alternate current (Drechsel, J. pr. Chem. 1888, [ii.] 38, 65); or by reduction in presence of nickel (*v.s.*), the last method being used technically.

Mobile oil, somewhat soluble in water, smells like peppermint; b.p. 155·4°; sp.gr. 0·9471 at 22°/4°. Gives a bisulphite compound; condenses with 2 molecules of benzaldehyde (Vorländer and Hobohm, Ber. 1896, 29, 1840); yields a di*iso*nitroso derivative (W. Borsche, Festschrift Otto Wallach, 1909, 31).

Oxime $C_6H_{10}:NOH$, m.p. 88°; *phenylhydrazone* $C_6H_{10}:N\cdot NH\cdot C_6H_5$, m.p. 74°–77°.

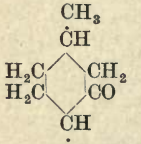


$\begin{array}{l} CH_2\text{—}CH_2\cdot CO \\ | \\ C(CH_3)CH_2\cdot CH_2 \end{array}$

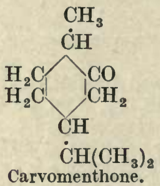
4-Methyl*cyclo*hexanone is obtained by the oxidation of 4-methyl*cyclo*hexanol with nitric acid. Oxidation of methylcyclohexanone with alkaline permanganate gives β-methyladipic acid, a compound which finds employment in the manufacture of dyes and pharmaceutical products (Farbenf. vorm. Fr. Bayer & Co., D. R. P. 221849).

Menthanones $C_{10}H_{18}O$. Ordinary menthone was first obtained in an inactive form by Moriya (Chem. Soc. Trans. 1881, 39, 77) by the oxidation of natural menthol; Atkinson and Yoshida obtained a strongly dextrorotatory variety (*ibid.* 1882, 41, 50). Beckmann has examined the stereochemistry of the menthones at length (Annalen, 1889, 250, 325; 1896, 289, 362; J. pr. Chem. 1897, [ii.] 55, 14).

Carvomenthone (tetrahydrocarvone) was discovered nearly simultaneously by v. Baeyer (Ber. 1893, 26, 822; 1895, 28, 1588; 1896, 29, 27) and Wallach (Annalen, 1893, 277, 133; 1895, 286, 102; 1899, 305, 266; 1900, 312, 302; Ber. 1895, 28, 1961). Ordinary menthone and carvomenthone can each exist in four stereoisomeric forms, their structures are given by:



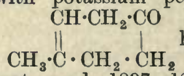
Ordinary menthone.



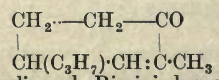
Carvomenthone.

Δ²-*cyclo*Hexenone C_6H_8O has been obtained from *cyclo*hexanone (A. Kötz and T. Grethe, J. pr. Chem. 1909, [ii.] 80, 473).

Methyl*cyclo*hexenone $CH_3\cdot C_6H_7O$. In addition to the compound synthesised from ethyl sodioacetoacetate by methylene iodide (Hagemann, Ber. 1893, 26, 876), and formaldehyde (Knoevenagel, *ibid.* 1090), an isomeride (m.p. 12°, b.p. 192°) has been discovered in wood tar. Since this gives acetic and lævulic acids on oxidation with potassium permanganate the constitution has been deduced (Béhal, Compt. rend. 1897, 125, 1036; 1901, 132, 342).

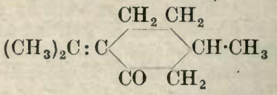


$\begin{array}{l} CH\cdot CH_2\cdot CO \\ \| \qquad\qquad | \\ CH_3\cdot C\cdot CH_2\cdot CH_2 \end{array}$



$\begin{array}{l} CH_2\text{—}CH_2\text{—}CO \\ | \qquad\qquad\qquad | \\ CH(C_3H_7)\cdot CH:C\cdot CH_3 \end{array}$

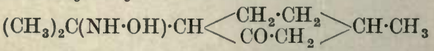
*iso***Camphor** was obtained by Angeli and Rimini by acting on camphoroxime with nitrous acid and decomposing the resultant nitrimine with ice-cold sulphuric acid (Gazz. chim. ital. 1896, ii. 26, 34).



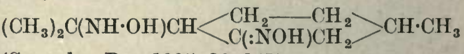
Pulegone ($\Delta^{4(8)}$-3-menthenone) is the most important of the seven possible structurally different *p*-menthenones. (Each of these exhibits stereoisomerism.) Beckmann and Pleissner (Annalen, 1891, 262, 1) obtained pulegone from oil of pennyroyal (*Mentha Pulegium* [Linn.]) of which it constitutes about 80 p.c. It is also found in the ethereal oils of *Hedeoma pulegioides* (Pers.) and *Pycnanthemum lanceolatum* (Pursh.). It is isolated from oil of pennyroyal by fractional distillation and conversion into the sodium bisulphite derivative. The synthesis from citronellal has been effected by Tiemann and Schmidt (Ber. 1897, 30, 22); b.p. 221°–222°; sp.gr. 0·936: $[\alpha]_D +22{\cdot}89°$.

The crystalline hydrochloride $C_{10}H_{17}OCl$ (m.p. 24°–25°) and hydrobromide $C_{10}H_{17}OBr$ (m.p. 40·5°) give pulegone on treatment with alcoholic potash.

Semicarbazone $C_{10}H_{16}:N\cdot NH\cdot CO\cdot NH_2$, m.p. 172°; *oxime* $C_{10}H_{16}:NOH$, m.p. 118°–119°. Addition of hydroxylamine at the double linkage gives 8-*hydroxylaminomenthone* (m.p. 157°, $[\alpha]_D$ −83·44°) which may be successively oxidised to 8-*nitrosomenthone* (chromic acid) and 8-*nitromenthone*, m.p. 80° (nitric acid, sp.gr. 1·16) (Harries and Roeder, Ber. 1899, 32, 3364). The so-called pulegone dioxime, m.p. 118°, has the constitution (Semmler, Ber. 1905, 38, 147).

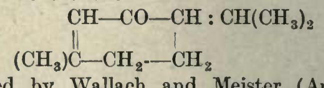


$(CH_3)_2C(NH\cdot OH)\cdot CH\left\langle\begin{array}{l} CH_2\cdot CH_2 \\ CO\cdot CH_2 \end{array}\right\rangle CH\cdot CH_3$



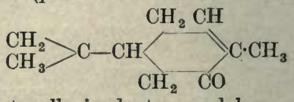
$(CH_3)_2C(NH\cdot OH)CH\left\langle\begin{array}{l} CH_2\text{——}CH_2 \\ C(:NOH)CH_2 \end{array}\right\rangle CH\cdot CH_3$

For the identification of pennyroyal, v. Baeyer and Henrich recommend conversion into the *bis*nitroso compound $(C_{10}H_{15}O_2N)_2$. 2 c.c. pulegone, 2 c.c. petroleum spirit, and 1 c.c. amyl nitrite are mixed, and very little concentrated hydrochloric acid added; the mixture becomes milky in 20–25 seconds, and solidifies to a paste of fine long needles of the nitroso compound. This compound cannot be recrystallised, it dissolves in cold ammonia with a yellow colour (Ber. 1895, 28, 654).



$\begin{array}{l} CH\text{—}CO\text{—}CH:CH(CH_3)_2 \\ \qquad \| \qquad\qquad\quad | \\ (CH_3)C\text{—}CH_2\text{—}CH_2 \end{array}$

Δ′-3-Menthenone prepared by Wallach and Meister (Annalen, 1908, 362, 261) from 1:3:4-trihydroxyterpane has been identified as a constituent of Japanese peppermint oil (Schimmel's Bericht, October, 1910), b.p. 235°–237°. *Oxime*, m.p. 107°–109°; *oxaminooxime*, m.p. 164°–165°; two *semicarbazones* α, m.p. 224°–226°; β, m.p. 171°–172°.



Carvone (p-$\Delta^{6,\,8(9)}$-menthadiene-2-one) occurs naturally in dextro- and lævo- rotatory forms. The former (b.p. 224°, sp.gr. 0·9598 at

20°/4° $[\alpha]_D +62{\cdot}07°$) occurs in the oils of carraway (*Carum Carvi* [Linn.]), fennel (*Fœniculum vulgare* (Mill.), and dill (*Peucedanum graveolens* [Benth. et Hook.]). The lævorotatory form (b.p. 223°–224°; sp.gr. 0·9593 at 20°/4°; $[\alpha]_D -62{\cdot}41°$) occurs in spear mint (*Mentha viridis* [Linn.]) and kuromoji (*Lindera sericea* [Blume]). The isolation of carvone from oils is effected by conversion into the compound with hydrogen sulphide $(C_{10}H_{14}O)_2H_2S$, and subsequent decomposition with alcoholic potash. When heated, carvone yields carvacrol $C_6H_3(OH)(CH_3)(i\text{-}C_3H_7)$. The active *carvoximes* melt at 72°, the inactive at 93°. Carvoxime was first obtained by Tilden by the action of alcoholic potash on limonene nitrosochloride (J. 1877, 428). *d*-α- and *d*-β-Limonene nitrosochlorides correspond to *l*-carvone, the *l*α- and *l*-β-nitrosochlorides to *d*-carvone, whilst α- and β-dipentene nitrosochlorides give the oxime of *r*-carvone (Wallach, Annalen, 1888, 245, 256; 246, 226; 1892, 270, 171).

Harries has described a method for preparation of the carvoximes (Meyer-Jacobson's Lehrbuch, 1902, II. 939).

Hydrochlorocarvoxime $C_{10}H_{15}Cl : NOH$ melts at 135° (*d*- or *l*-) or 125·5° (*r*-). The melting-points of the *hydrobromocarvoximes*

$$C_{10}H_{15}Br : NOH$$

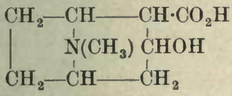
are 133°–134° (*d*- or *l*-) and 128°–129° (*r*-).

d-Carvone yields *m*- and *p*-nitrophenylhydrazones $C_{10}H_{14} : N{\cdot}NH{\cdot}C_6H_4{\cdot}NO_2$, which melt at 105°–106° and 174°–175° respectively (W. Borsche, Annalen, 1908, 359, 49).

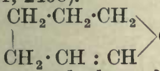
Suberone $C_7H_{12}O$ (Preparation, General Method 1), smells like peppermint; b.p. (742 mm.) 178·5°, sp.gr. 0·9685 at 0°.

Oxime $C_7H_{12} : NOH$, m.p. 23·3°, b.p. 230°; *semicarbazone*, $C_7H_{12}:N{\cdot}NH{\cdot}CO{\cdot}NH_2$, m.p. 163°; *dibenzal derivative* $C_7H_8O(:CH{\cdot}C_6H_5)_2$, m.p. 107°–108°; *sulphonal* $C_7H_{12}(SO_2C_2H_5)_2$ (by the action of mercaptan in presence of hydrogen chloride and oxidation of the resultant mercaptol), m.p. 136°–139°. Suberone gives ζ-hydroxyœnanthoïc acid by oxidation with Caro's acid (v. Baeyer, Ber. 1900, 33, 862).

Willstätter obtained suberone as a degradation product of ecgonine :

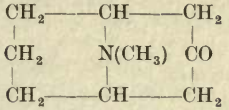


(Ber. 1898, 31, 2498).

Tropilene  CO, an oil of high refractive power and odour of bitter almonds, is difficultly soluble in water, and boils at 186°–188°. It is obtained from tropine by exhaustive methylation (Ladenburg, Ber. 1881, 14, 2403; Annalen, 1883, 217, 132, 138; Merling, Ber. 1891, 24, 3123); its constitution was correctly recognised by Willstätter (Ber. 1898, 31, 1545; 1901, 34, 133).

*cyclo***Octanone** $C_8H_{14}O$ was obtained by Mager (Annalen, 1893, 275, 363) by distilling the calcium salt of azelaïc acid, b.p. about 205°.

*pseudo***Pelletierine** or *methylgranatonine* is an alkaloid obtained from the pomegranate tree (*Punica Granatum* [Linn.]). Its constitution has been determined as:



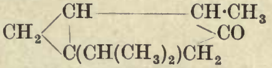
by Willstätter and Veraguth (Ber. 1905, 38, 1975, 1984).

II. *Bicyclic Monoketones.*

Of the numerous monoketones derived from bicyclic hydrocarbons only a few can be mentioned.

Thujone (Tanacetone) $C_{10}H_{16}O$ is known in stereoisomeric forms, it occurs in *Arbor vitæ* (*Thuya occidentalis* [Linn.]), tansy (*Tanacetum vulgare* [Linn.]), *Artemisia* and *Salvia*. α-Thujone predominates in thuja oil, $[\alpha]_D -10{\cdot}23°$; *oxime* $C_{10}H_{16} : NOH$, $[\alpha]_D -25{\cdot}25°$ in ethereal solution, *semicarbazone* $C_{10}H_{16} : N{\cdot}NH{\cdot}CO{\cdot}NH_2$ $[\alpha]_D +59{\cdot}9°$ in methyl alcoholic solution. β-Thujone is found in tansy oil $[\alpha]_D$ about +70°, *oxime*, m.p. 54°–55°, $[\alpha]_D +105{\cdot}1°$ in methyl alcoholic solution; *semicarbazone*, dimorphic, hexagonal, m.p. 174°–175°, rhombic, m.p. 170°–172°. Other derivatives *v.* Kijner, J. Russ. Phys. Chem. Soc. 1910, 42, 1198; 1911, 43, 577, 951, 1132.

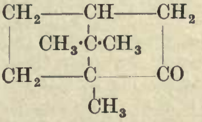
Artemisia oil seems to contain a third feebly dextro-rotatory thujone (Wallach, Annalen, 1893, 275, 179; 1894, 279, 383; 1895, 286, 90; 1904, 336, 247). Thujone probably possesses the structure :

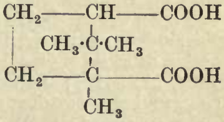


(Tschugaeff, Ber. 1900, 33, 3122; Semmler, *ibid.* 1900, 33, 275; 1903, 36, 4367; D. Thomson, Chem. Soc. Trans. 1910, 97, 1502).

Carone $C_{10}H_{16}O$, obtained by the action of alcoholic potash on the hydrobromide of dihydrocarvone, is also probably bicyclic (v. Baeyer, Ber. 1894, 27, 2715; 1895, 28, 639, 1586; 1896, 29, 3, 2796; 1898, 31, 1401, 2067).

Camphor $C_{10}H_{16}O$ (*q.v.*) occurs in the dextrorotatory form ($[\alpha]_D +44{\cdot}22°$ in 20 p.c. alcoholic solution) in *Cinnamomum Camphora* (Nees and Eberm.) and other plants, m.p. 178·4°, b.p. 209°. The lævo- form occurs in the oils of *Matricaria*, *Salvia*, and *Tanacetum*. Bredt gives the following formulæ for camphor and its oxidation product, camphoric acid (Ber. 1893, 26, 3047; Annalen, 1896, 292, 55):—

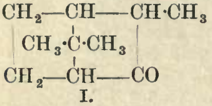


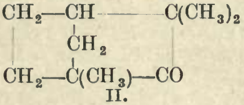


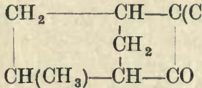
Camphor has been obtained by distillation of the lead (Haller) and calcium (Bredt and Rosenberg) salts of homo- camphoric acid; respecting the synthesis of camphoric acid see Kommpa (Ber. 1903, 36, 4332), Blanc and Thorpe (Chem. Soc. Trans. 1910, 97, 836), and Kommpa (Chem. Soc. Trans. 1911, 99, 29).

Fenchone $C_{10}H_{16}O$ occurs in nature as optical antipodes. The dextro-rotatory modification was found by Wallach and Hartmann (Annalen, 1890, 259, 324) in the portion of fennel oil boiling at 190°–195°, whilst *l*-fenchone is a constituent of the corresponding fraction of thuja oil. The two fenchones melt at 5°–6°, boil at 192°–193°; sp.gr. 0·9465 at 19°. *d*-Fenchone gives $[\alpha]_D + 71{\cdot}97^\circ$, the *l*-fenchone a slightly lower value (*see* also Bertram and Helle, J. pr. Chem. 1900, [ii.] 61, 293). Fenchone does not combine with sodium bisulphite; the *oximes* melt at 161°. Many derivatives have been prepared by Wallach; much *m*-cymene is produced on heating to 115°–130° with phosphorus pentoxide (Annalen, 1891, 263, 129; 1892, 269, 326; 1893, 272, 99; 1893, 275, 145; 1895, 284, 324; 1901, 315, 291).

Of the following formulæ for fenchone:

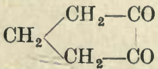
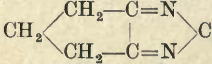

I.


II.

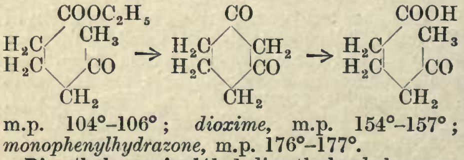

III.

the first was proposed by Wallach, the other two by Semmler (Ber. 1906, 39, 2577). L. Bouveault and F. Levallois prefer formula II. above (Semmler's first formula), and have brought forward considerable evidence in its favour (Compt. rend. 1908, 146, 180; 1909, 148, 1399, 1524; Bull. Soc. chim. 1910, [iv.] 7, 542, 683, 736, 807, 963, 968; Wallach, Annalen, 1911, 379, 182, 215).

III. *Monocyclic Diketones, &c.*

1 : 2-*cyclo*Pentanedione  $CH_2<\begin{array}{l}CH_2-CO\\ \quad\ |\\ CH_2-CO\end{array}$ (preparation, *v.s.*) is easily soluble in water, the solution reddens litmus, and is coloured violet by ferric chloride. In some respects it behaves as if one $\cdot CH_2\cdot CO\cdot$ group were enolised, giving a phenylurethane $C_5H_5O{\cdot}O{\cdot}CO{\cdot}NH{\cdot}C_6H_5$, m.p. 122°, and benzoyl ester $C_5H_5O{\cdot}O{\cdot}CO{\cdot}C_6H_5$, m.p. 72°–73°. As a 1 : 2-diketone it yields a *dioxime* $C_5H_6(:NOH)_2$, m.p. 210°; an *osazone* $C_5H_6(:N{\cdot}NH{\cdot}C_6H_5)_2$, m.p. 146°; and a *quinoxaline*  $CH_2<\begin{array}{l}CH_2-C=N\\ \qquad\ |\\ CH_2-C=N\end{array}>C_6H_4$, m.p. 102°–103°.

1 : 3-*cyclo*Hexanedione (Dihydroresorcinol) $C_6H_8O_2$ was obtained by Merling by the reduction of resorcinol in boiling alcoholic solution with sodium amalgam, carbon dioxide being led in during the operation (Annalen, 1894, 278, 28). Vorländer synthesised the diketone by the action of sodium on ethyl γ-acetobutyrate (Ber. 1895, 28, 3428); barium hydroxide breaks the ring, giving γ-acetobutyric acid:



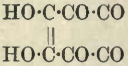
m.p. 104°–106°; *dioxime*, m.p. 154°–157°; *monophenylhydrazone*, m.p. 176°–177°.

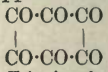
Dimethylresorcinol (1 : 1-dimethyl*cyclo*-hexanedione-3 : 5 has been obtained by D. Vorländer (Annalen, 1898, 304, 15) and A. W. Crossley (Chem. Soc. Trans. 1899, 75, 771); the latter chemist has examined it exhaustively (*see* later papers).

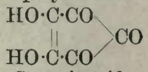
1 : 4-*cyclo*Hexanedione $C_6H_8O_2$ is obtained in small quantity by the dry distillation of calcium succinate (Feist, Ber. 1895, 28, 738). v. Baeyer (Annalen, 1894, 278, 91) obtains a good yield of the ketone in the following manner: 100 grams of diethyl diacetosuccinate are dissolved in 420 c.c. of concentrated sulphuric acid, the solution being meanwhile cooled and then poured on to ice (1450 grams). After addition of 40 c.c. of alcohol the mixture is boiled for 16 hours, the alcohol distilled off and the residue nearly neutralised with calcined sodium carbonate. The sodium sulphate is frozen out, the filtrate saturated with ammonium sulphate, and the diketone extracted with chloroform, m.p. 78°; *dioxime*, m.p. 192°; *dicyanhydrin*, m.p. 180°.

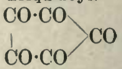
Phloroglucinol $C_6H_3(OH)_3$1 : 3 : 5 behaves tautomerically as *cyclo*hexanetrione, giving a *trioxime* $C_6H_6(:NOH)_3$, m.p. 155°.

A few cyclic polyketones may be mentioned. The potassium carboxide $(KCO)_n$ prepared by Liebig (Annalen, 1834, 11, 182), and which forms a by-product in Brunner's method of manufacturing potassium (Brodie, Annalen, 1860, 113, 358), is the potassium derivative of hexahydroxybenzene (Nietzki and Benckiser, Ber. 1885, 18, 499; 1886, 19, 293, 772). Treatment with dilute alcohol gives rhodizonic acid $C_6H_2O_6$ (Heller, Annalen, 1837, 24, 1; 1840, 34, 232; 1862, 124, 32; Will, *ibid.* 1861, 118, 189). Rhodizonic acid, as well as hexahydroxybenzene, when oxidised, give triquinoyl $C_6H_{16}O_{14}$ or $C_6O_6{\cdot}8H_2O$. Alkalis convert rhodizonic acid into croconic acid $C_5H_2O_5$ (*see* Zincke, Ber. 1887, 20, 1267, footnote), and the latter compound can be oxidised to leuconic acid. All four compounds appear to be cyclic polyketones:


Rhodizonic acid.

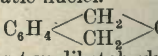

Triquinoyl.

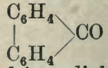

Croconic acid.

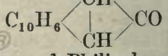

Leuconic acid.

IV. *Aromatic Cyclic Ketones.*

Only the briefest reference can be made to the cyclic ketones, in which both ends of the closed chain containing carbonyl groups are united to aromatic nuclei.

Hydrindene  $C_6H_4<\begin{array}{l}CH_2\\ CH_2\end{array}>CH_2$ gives rise to two hydrindones, two diketohydrindenes, and one triketohydrindene. The properties of these compounds are those to be expected of monoketones, α- and β-diketones and triketones respectively.

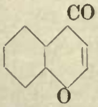
Fluorene ketone  $\begin{array}{l}C_6H_4\\ \ |\\ C_6H_4\end{array}>CO$ is obtained by the distillation of calcium diphenate with lime (Fittig and Ostermayer, Annalen, 1873, 166, 373); by oxidation of phenanthraquinone with alkaline permanganate (Anschütz and Japp, Ber. 1878, 11, 212); and by oxidation of fluorene alcohol. Yellow rhombic tablets, m.p. 83·5°–84°.

Pyrene ketone  $C_{10}H_6<\begin{array}{l}CH\\ \ |\\ CH\end{array}>CO$ was obtained by Bamberger and Philip by distillation of pyrenic acid $C_{15}H_8O_5$ with slaked lime, m.p. 83°, b.p. 235°–250° (Annalen, 1887, 240, 178).

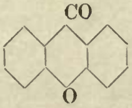
The ketonic properties of the carbonyl group are usually profoundly modified when it forms one of the members of a heterocyclic chain. This is observed in the following well-known examples :—

Pyridone.

Pyrone.



Chromone.



Xanthone.

Ketonic Acids and Esters.

Whilst a few ketonic acids (*e.g.* pyruvic and lævulic) are obtained by special reactions, these substances are generally obtained as esters by condensation of simpler esters or esters and ketones under the influence of sodium, sodium ethoxide, &c.

α-Ketonic Monobasic Acids.

Pyruvic acid (*Pyroracemic* or *Propanonic acid*) $CH_3{\cdot}CO{\cdot}CO_2H$ can be obtained by the distillation of tartaric or racemic acids (Berzelius, Pogg. Ann. 1835, 36, 1) ; of glyceric acid (Moldenhauer, Annalen, 1864, 131, 338) ; and from α-dichloro- or α-dibromopropionic acids or their esters by the action of moist silver oxide (Beckurts and Otto, Ber. 1877, 10, 264 ; 1885, 18, 228). Claisen and Shadwell hydrolysed acetyl cyanide with hydrochloric acid (Ber. 1878, 11, 620, 1563), and Beilstein and Wiegand oxidised calcium lactate with potassium permanganate (*ibid.* 1884, 17, 840) (*v.* Pyruvic acid).

Pyruvic acid is prepared by distilling 500 grams of tartaric acid and 780 grams of commercial potassium bisulphate from a copper retort of 2 litres capacity. The process is complete in 30 minutes, and a 60 p.c. yield is obtained after rectifying the product under reduced pressure, b.p. 59°–60° at 12 mm. (A. Wohl and R. Maag, Ber. 1910, 43, 2188).

The salts crystallise when prepared in the cold ; the solutions, if boiled, only yield gummy masses.

Pyruvic acid shows the reaction of a (methyl) ketone as well as an acid, *e.g.*

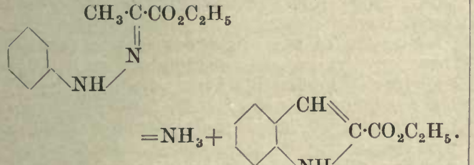
$$CH_3{\cdot}C(OH)(SO_3Na)CO_2H$$

and $CH_3{\cdot}C(OH)(SO_3Na)CO_2Na,H_2O$ are known.

Pyruvic acid phenylhydrazone

$$CH_3{\cdot}C(:N{\cdot}NH{\cdot}C_6H_5)CO_2H$$

forms shining needles, m.p. 192°. The *ethyl ester* $C_9H_9O_2N_2{\cdot}C_2H_5$, m.p. 116°–117°, when heated 3 or 4 minutes with its own weight of zinc chloride, yields ethyl indole carboxylate (E. Fischer, Annalen, 1886, 236, 142) :



Benzoylformic acid $C_6H_5{\cdot}CO{\cdot}CO_2H$ is obtained by the hydrolysis of benzoyl cyanide with hydrochloric acid (Claisen, Ber. 1877, 10, 845), m.p. 65°–66° ; easily soluble in water ; reduced by sodium amalgam to mandelic acid, and by hydriodic acid and amorphous phosphorus to α-toluic acid. *Phenylhydrazone*

$$C_6H_5{\cdot}C(:N{\cdot}NH{\cdot}C_6H_5)CO_2H,$$

m.p. 153° (with decomposition into carbon-dioxide and benzalphenylhydrazone).

β-Ketonic Monobasic Acids.

The β-ketonic acids are extremely unstable, decomposing very readily into carbon dioxide and a ketone :

$$R{\cdot}CO{\cdot}CH_2{\cdot}COOH = CO_2 + R{\cdot}CO{\cdot}CH_3.$$

Owing to the reactivity of the methylene group, the esters of these acids are valuable synthetic agents ; they are prepared by the action of sodium (sodium ethoxide, &c.) on esters or mixtures of esters and decomposition of the resultant sodium derivatives with dilute acetic acid :

$$R{\cdot}COOC_2H_5 + CH_3{\cdot}COOC_2H_5 + NaOC_2H_2$$
$$= 2C_2H_5OH + R{\cdot}C(ONa):CH{\cdot}COOC_2H_5.$$
$$R{\cdot}C(ONa):CH{\cdot}COOC_2H_5 + H{\cdot}C_2H_3O_2$$
$$= Na{\cdot}C_2H_3O_2 + R{\cdot}CO{\cdot}CH_2{\cdot}COOC_2H_5.$$

Ethyl acetoacetate $CH_3{\cdot}CO{\cdot}CH_2{\cdot}COOC_2H_5$ is obtained by the action of sodium on ethyl acetate (Geuther, J. 1863, 323 ; Zeitsch. Chem. 1866, 5 ; Wislicenus, Annalen, 1877, 186, 161 ; Matthews and Hodgkinson, Ber. 1882, 15, 2679) ; b.p. 180·6°–181·2° ; sp.gr. at 20°/4° 1·0256 (Brühl, Annalen, 1880, 203, 27) ; b.p. 71° at 12·52 mm. (Kahlbaum). Free acetoacetic acid is described by Ceresole as a thickish liquid, miscible with water, reacting strongly acid, and decomposing violently below 100° into carbon dioxide and acetone. Ceresole obtained the acid by allowing 4·5 parts of ethyl acetoacetate, 2·1 parts of caustic potash, and 80 parts of water to stand for 24 hours, then acidifying with sulphuric acid and extracting with ether (Ber. 1882, 15, 1327, 1872).

Ethyl acetoacetate reacts tautomerically as :

$$CH_3{\cdot}C(OH):CH{\cdot}CO_2C_2H_5 \text{ and } CH_3{\cdot}CO{\cdot}CH_2{\cdot}CO_2C_2H_5.$$

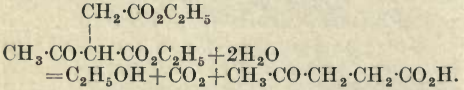
The question of this tautomerism has been much discussed, some of the papers bearing on this matter which have appeared since 1890 are as follows :—

J. U. Nef (Annalen, 1891, 266, 52 ; 1893, 276, 239) ; W. H. Perkin, sen. (Chem. Soc. Trans. 1892, 61, 800) ; J. W. Brühl (Ber. 1894, 27, 2378 ; J. pr. Chem. 1894, [ii.] 50, 119) ; L. Claisen (Annalen, 1893, 277, 162 ; Ber. 1892, 25, 1763) ; A. Michael (Amer. Chem. J. 1892, 14, 481 ; Ber. 1905, 38, 22 ; *cf.* H. Goldschmidt, *ibid.* 1096) ; A. Lapworth (Chem. Soc. Trans. 1902, 81, 1491, 1499 ; 1903, 83, 1114 : 1904, 85, 46) ; E. C. C. Baly and C. H. Desch (*ibid.* 1904, 85, 1029 ; 1905, 87, 766) ; R. S. Morrell (Chem. Soc. Proc. 1898, 14, 121 ; Chem. Soc. Trans. 1903, 83, 1292) ; R. Schenck and E. Ellenberger (Ber. 1904, 37, 3443) ; F. Giolitti (Gazz. chim. ital. 1904, 34, ii. 208) ; S. F. Acree (Amer. Chem. J. 1907, 37, 71) ; A. E. Dunstan and J. A. Stubbs (Chem. Soc. Trans. 1908, 93, 1919) ; A. Hantzsch (Ber. 1910, 43, 3049) ; Knorr (*ibid.* 1911, 44, 1138, 2767) ; Kurt Meyer (Annalen, 1911, 380, 212 ; Ber. 1911, 44, 2718, 2725, 2729).

In addition to the use of acetoacetic ester in the laboratory, it is employed in the preparation of pyrazolone derivatives, *e.g.* antipyrine and pyrazolone dyestuffs (*see* Farbenfab. vorm. Fr. Bayer & Co., Eng. Pat. 532 of 1910) (*v.* PYRAZOLONE).

γ-Ketonic Monobasic Acids.

Lævulic acid $CH_3\cdot CO\cdot CH_2\cdot CH_2\cdot CO_2H$ is obtained synthetically from diethyl acetosuccinate (b.p. 254°–256°, sp.gr. 1·08809 at 15°), produced from ethyl chloroacetate and the sodium derivative of ethyl acetoacetate by boiling with twice its volume of dilute hydrochloric acid (Conrad, Annalen, 1877, 188, 222):

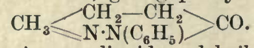


$$\begin{array}{l} \quad CH_2\cdot CO_2C_2H_5 \\ \quad | \\ CH_3\cdot CO\cdot CH\cdot CO_2C_2H_5+2H_2O \\ \qquad =C_2H_5OH+CO_2+CH_3\cdot CO\cdot CH_2\cdot CH_2\cdot CO_2H. \end{array}$$

It is obtained from various carbohydrates by boiling with acids, *e.g.* lævulose, glucose, cane sugar, milk sugar, inulin (Tollens, Annalen, 1875, 175, 181; 1881, 206, 231; 1885, 227, 228); pine shavings, Carragheen moss and gum arabic (Bente, Ber. 1875, 8, 416, 1157). Conrad and Guthzeit (*ibid.* 1885, 18, 1442) recommend warming 20 grams of cane sugar with 50 grams of water containing 9·43 grams of hydrogen chloride for 17 hours on the water-bath. The liquid is filtered, evaporated on the water-bath, and extracted with ether; the ethereal extract is concentrated and distilled under reduced pressure.

W. A. van Ekenstein and J. J. Blanksma find the conversion of hexoses into lævulic acid takes place in two stages, hydroxyfurfuraldehyde which is first formed, giving lævulic and formic acids subsequently (Chem. Weekblad. 1910, 7, 387).

Lævulic acid has m.p. 33·5°, b.p. 250° (with slight decomposition); sp.gr. 1·135 at 15°. Easily soluble in water, alcohol, and ether. Reduced by sodium amalgam in alcoholic solution to γ-hydroxyvaleric acid. Yields iodoform with iodine and caustic soda in the cold and forms *oxime* and *phenylhydrazone*, m.p. 108°. The latter compound loses water above 160°, giving phenylmethylpyridazolone



The *methyl* and *ethyl esters* are liquid, and boil at 191°–191·5° (743 mm.) and 205·2° (corr. 756 mm.) respectively.

Lævulic acid is used in cotton printing.

A number of ε-ketonic acids have been prepared, starting with adipic acid (E. E. Blaise and A. Kochler, Bull. Soc. chim. 1910, [iv.] 7, 215).

Carboxylic acids of cyclic ketones are also known, *e.g. cyclo*hexanone-2-carboxylic acid, and *l*-methyl*cyclo*hexane-2-one-3-carboxylic acid (H. D. Gardner, W. H. Perkin, jun., and H. Watson, Chem. Soc. Trans. 1910, 97, 1756).

Dibasic Ketonic Acids.

Mesoxalic acid (dihydroxymalonic acid) $C(OH)_2(COOH)_2$ or $CO(COOH)_2,H_2O$ was obtained by Liebig and Wöhler by the hydrolysis of alloxan (Annalen, 1838, 26, 298); from aminomalonic acid by Baeyer (*ibid.* 1864, 131, 298) and from dibromomalonic acid by Petriew (J. Russ. Phys. Chem. Soc. 1878, 10, 72). M. Conrad and C. Brückner (Ber. 1891, 24, 2993) obtained the diethyl ester (m.p. 57°) by the action of bromine on diethyl acetyltartronate $CH_3CO\cdot O\cdot CH(CO_2C_2H_5)_2$, whilst H. Filippo, jun., obtained a practically quantitative yield of the ester by the action of bromine on diethyl tartronate (Rec. trav. chim. 1910, [ii.] 14, 113).

Mesoxalic acid melts at 119°–120° (E. Fischer), is easily soluble in water, fairly so in alcohol and ether. The aqueous solution, when boiled, gradually decomposes into carbon dioxide and glyoxylic acid.

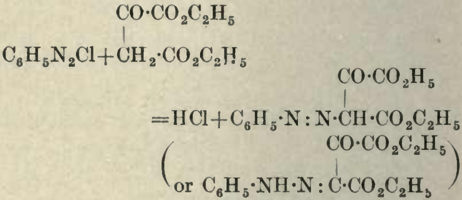
Diethyl oxalacetate

$$C_2H_5O_2C\cdot CO\cdot CH_2\cdot CO_2C_2H_5$$

is obtained by Claisen's method from diethyl oxalate and ethyl acetate, and by the action of concentrated sulphuric acid on diethyl acetonedicarboxylate. It is a colourless oil giving an intense dark red colouration with ferric chloride, and is sufficiently acid in character to be titrated with phenolphthaleïn as indicator (H. Gault, Compt. rend. 1910, 150, 1608; L. J. Simon, *ibid.* 1760).

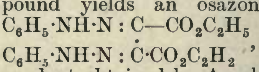
Hydrolysis with dilute sulphuric acid gives alcohol, carbon dioxide, and pyruvic acid (ketonic fission); with alkalis, salts of oxalic and acetic acids are produced.

The ester reacts with phenyldiazonium chloride, giving a product identical with the monophenylhydrazone of diethyl diketosuccinate (m.p. 72°–73°):



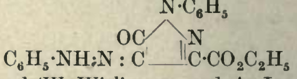
$$\begin{array}{l} \qquad\qquad CO\cdot CO_2C_2H_5 \\ \qquad\qquad | \\ C_6H_5N_2Cl+CH_2\cdot CO_2C_2H_5 \\ \qquad\qquad\qquad\qquad\qquad\qquad CO\cdot CO_2H_5 \\ \qquad\qquad\qquad\qquad\qquad\qquad | \\ \qquad\qquad =HCl+C_6H_5\cdot N:N\cdot CH\cdot CO_2C_2H_5 \\ \qquad\qquad \left(\begin{array}{r} CO\cdot CO_2C_2H_5 \\ | \\ \text{or } C_6H_5\cdot NH\cdot N:C\cdot CO_2C_2H_5 \end{array}\right) \end{array}$$

The action of phenylhydrazine on this compound yields an osazone (m.p. 119°–120°)



$$\begin{array}{l} C_6H_5\cdot NH\cdot N:C\text{—}CO_2C_2H_5 \\ C_6H_5\cdot NH\cdot N:C\cdot CO_2C_2H_2 \end{array}$$

, identical with the product obtained by Anschütz and Geldermann from phenylhydrazine and diethyl diketosuccinate (Annalen, 1891, 261, 130). When this osazone is boiled with three or four parts of glacial acetic acid, ethyl alcohol is eliminated, and ethyl phenylketopyrazolonephenylhydrazone carboxylate



is produced (W. Wislicenus and A. Jensen, Ber. 1892, 25, 3448). Orange needles, m.p. 152°–153°; also obtained by Anschütz and Parlato (*ibid.* 1892, 25, 1975).

The pyrazolone compound described is of tartrazine type, and it is evident that mixed tartrazines may be prepared from ethyl oxalacetate, using hydrazines and diazo compounds derived from different aromatic amines. The constitution of the original tartrazine derived from phenylhydrazine-*p*-sulphonic and dihydroxytartaric acids has been fully investigated by Anschütz (Annalen, 1897, 294, 219), who recognised definitely the existence of the pyrazolone ring in the dyestuff. In the preparation of this colouring matter from diethyl oxalacetate, 9·4 kilos. of the ester, 9·5 kilos. of phenylhydrazine sulphonic acid, and 7·5 kilos. of crystallised sodium acetate are stirred with 50 litres of water at 50° until complete solution is effected. The solution is cooled to ordinary temperature, 8–10 kilos. of calcined soda are added (reaction alkaline), and after completion of the pyrazolone condensation, the tartrazinogen ester sulphonic acid precipitated by dilute sulphuric acid, pressed and dried. After the hydrolysis with caustic soda, diazotised sulphanilic acid is added, and the tartrazine salted out when coupling is completed (B. A. S. F., Eng. Pats. 5693 of 1893 and 765 of 1897; *cp.* R. Grehm and L. Benda, Annalen, 1898, 299, 100, and Farbenfab. vorm. Fr. Bayer & Co., Eng. Pat. 532 of 1910).

Dihydroxytartaric acid (Diketosuccinic acid) $HO_2\cdot C\cdot C(OH)_2C(OH)_2\cdot CO_2H$ or

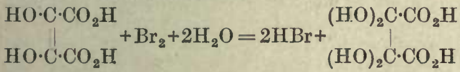
$$HO_2C\cdot CO\cdot CO\cdot CO_2H+2H_2O$$

was first obtained from protocatechuic acid (Gruber, Ber. 1879, 12, 514) and catechol (Barth, Monatsh. 1880, 1, 869) by the action of nitrous gases (N_2O_3). Kekulé obtained it from dinitrotartaric acid

$$HO_2\cdot C\cdot CH(O\cdot NO_2)\cdot CH(O\cdot NO_2)\cdot CO_2H$$

(Annalen, 1883, 221, 247). The dinitrotartaric acid is obtained by dissolving tartaric acid in 4½ parts of fuming nitric acid, shaking with an equal volume of concentrated sulphuric acid, and drying the precipitate on porous earthenware. This compound is then mixed with an equal amount of ether, some crude ethyl nitrite added, and the mixture allowed to stand for some days. On shaking with water and adding sodium carbonate, the nearly insoluble sodium dihydroxytartrate is precipitated.

H. J. H. Fenton and E. S. St. B. Sladen (Eng. Pat. 27032 of 1897) obtain the acid by adding to a mixture of 1 part of dihydroxymaleïc acid and 4 parts of glacial acetic acid, bromine and water drop by drop in quantities slightly greater than that required by the equation:



$$\begin{array}{l}HO\cdot C\cdot CO_2H\\ \quad|\\ HO\cdot C\cdot CO_2H\end{array}+Br_2+2H_2O=2HBr+\begin{array}{l}(HO)_2C\cdot CO_2H\\ \quad|\\ (HO)_2C\cdot CO_2H\end{array}$$

During the addition the mixture is well cooled.

Dihydroxytartaric acid generally reacts as diketosuccinic acid, and is very unstable; its employment in the production of tartrazines has already been mentioned.

Acetonedicarboxylic acid

$$HO_2C\cdot CH_2\cdot CO\cdot CH_2\cdot CO_2H$$

is obtained by heating citric and sulphuric acids on the water-bath until carbon dioxide begins to be evolved:

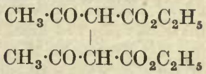
$$HO_2C\cdot CH_2\cdot C(OH)(CO_2H)CH_2\cdot CO_2H$$
$$=HO_2C\cdot CH_2\cdot CO\cdot CH_2\cdot CO_2H+H\cdot COOH(CO+H_2O).$$

The mixture is then diluted with water, and the acetonedicarboxylic acid extracted with ether (v. Pechmann, Ber. 1884, 17, 2543).

Heated with phenylhydrazine and hydrochloric acid in aqueous solution, methylphenylpyrazolone carboxylic acid is produced. The latter compound, when heated to 160°, and then distilled under reduced pressure, gives Knorr's phenylmethylpyrazolone (Ber. 1883, 16, 2597; Annalen, 1887, 238, 147; v. Pechmann and Jenisch, Ber. 1891, 24, 3252).

Acetonedicarboxylic acid is obtained crystalline from ethyl acetate; it decomposes on fusion into carbon dioxide and acetone, the same reaction occurring on boiling with water or warming with acids or alkalis. Ferric chloride gives a violet colouration.

Diethyl diacetosuccinate



$$\begin{array}{c}CH_3\cdot CO\cdot CH\cdot CO_2C_2H_5\\ |\\ CH_3\cdot CO\cdot CH\cdot CO_2C_2H_5\end{array}$$

is obtained by the action of iodine on the sodium derivative of ethyl acetoacetate (Rugheimer, Ber. 1874, 7, 892; Harrow, Annalen, 1880, 201, 144); rhombic tables, m.p. 78°. The free acid seems incapable of existence; when boiled with 20 p.c. sodium carbonate solution carbon dioxide escapes and acetonylacetone is produced. Like the latter compound, the ester readily condenses with ammonia, giving pyrrolderivatives.

Ethyl oxalyl-succinate, b. p. 170°–175°/12–13 mm. Blaise a. Gault. Bull. Soc. Chim. 1911, 9, 451, 458, 588. J. T. H.

KHAYA or **KAYA** *v.* Caïl-cedra.

KIDNEY IRON ORE *v.* Iron.

KIESELGUHR, *Diatomite*, *Diatomaceous earth*, *Infusorial earth*, or *Tripolite*. A white or greyish, pulverulent material of low sp.gr., consisting chiefly of the minute silicious shields of diatomaceæ. Large deposits of fossil diatoms have been traced in many parts of the world, but the chief amount of kieselguhr is obtained from Naterleuss, between Hamburg and Hanover. It is found there from the surface down to a depth of about 150 feet. The upper stratum supplies the white kieselguhr. It contains very little organic matter, but some sand; on washing, it gives a very pure and porous product. The second stratum produces grey kieselguhr, containing very little sand, but sufficient organic matter for calcining it. After calcination it forms kieselguhr of the highest quality. The lowest and by far the largest stratum, varying from 50 to 100 feet in thickness, supplies the green kieselguhr, which contains up to 30 p.c. of organic matter. When dry this material glows when heated like peat. It is calcined in small furnaces about 15 feet high and 6 feet wide; these are filled and lighted at the bottom, and no additional fuel is needed. The furnaces are continually replenished at the top, and the calcined product, which has a reddish colour due to ferric oxide, is taken out from the grates underneath.

Deposits of diatomite are found with peat at several places in Scotland (W. I. Macadam, Min. Mag. 1884, 6, 87; 1886, 7, 30, 35; 1889, 8, 135), and beds up to 40 feet in thickness are now being worked in the Isle of Skye. (On the kieselguhr of County Antrim, *see* J. H. Pollok, Sci. Proc. R. Dublin Soc. 1899, 9, 33.) Enormous deposits, sometimes as much as 1000 feet in thickness, are found at several places in the United States. The more compact, laminated variety known as tripolite is from Tripoli and from Bilin in Bohemia.

Kieselguhr varies much in composition, containing silica, 70–80 p.c.; water and organic matter, 10–20 p.c.; together with small amounts of alumina, ferric oxide, lime, &c. The silica is largely in the soluble form of opal (hydrated silica).

The high degree of porosity of the material makes it very valuable as an absorbent of nitroglycerin in the manufacture of dynamite. Its high non-conducting power makes it useful for the coating of steam boilers and pipes. It is used by safe makers, cooking stove and kitchener manufacturers, for making fireproof rooms, and for filling up bulkheads in steamships, &c. It has been made into fireproof bricks of low sp.gr. for the setting of steam boilers, the lining of blast furnaces and the hot-air pipes connected with them, and for the backs of fireplaces. It has also been suggested as an absorbent for bromine to be used for disinfecting purposes, and for sulphuric acid. What is termed ‘ dry sulphuric acid ’ is prepared by saturating calcined kieselguhr with three or four times its weight of sulphuric acid. The product, containing 75 p.c. of its weight of sulphuric acid, is said to retain the pulverulent form, and can be transported by land or sea in iron vessels without damage or breakage. Kieselguhr is used by manufacturers of ultramarine and by soap makers. A composition for preventing rot and fungus in buildings is made of it; it is also used for polishing metals, &c., and for the manufacture of imitation meerschaum.

References.—Diatomaceous Earths (kieselguhr) and their Utilisation, Bull. Imperial Inst. 1905, 3, 88–103; Haacke, J. Soc. Chem. Ind. 3, 132. L. J. S.

KIESERITE. Hydrated magnesium sulphate $MgSO_4,H_2O$, of rare occurrence as colourless monoclinic crystals, but as granular masses abundant in the potash-salt deposits of Stassfurt in Prussia. It is also found at Hallstadt in Austria, and Kalusz in Galicia (*v.* POTASSIUM). (On the artificial production of kieserite, *see* van ’t Hoff, Sitz.-Ber. Akad. Wiss. Berlin, 1901, 1034.)

L. J. S.

KILLAS. A local name used by Cornish miners for the clay-slates of their country (*v.* SLATE).

KINETITE *v.* EXPLOSIVES.

KING’S BLUE, KING’S YELLOW, *v.* PIGMENTS.

KINO. Kino is the red, astringent, jelly-like juice obtained by incisions made in the trunks of several trees, and dried without the application of artificial heat. The variety originally introduced by Fothergill in 1757 (Med. Observ. and Inq. 1, 358) came from the river Gambia in tropical West Africa, where it was derived from the *Pterocarpus erinaceus* (Lam.). This *African* or *Gambia kino* was, however, soon replaced by other similar products from Jamaica, the East Indies, and Australia. *Jamaica, West Indian,* or *Caracas kino* is obtained from the *Coccoloba uvifera* (Linn.), a tree inhabiting Florida and the West Indian Islands. The only important kinos at the present day are, however, those which come from India and Australia. The *official, East Indian,* or *Malabar kino* is the product of the *Pterocarpus Marsupium* (Roxb.) (Corom. Pl. plate 116; Bentl. a. Trim. plate 81), a tree which attains a height of 40 to 80 feet, and occurs throughout Southern India and Ceylon. In the Madras Presidency it is one of the trees the felling of which is restricted by the Government. It affords valuable timber. The allied *P. indicus* (Willd.) was the source of the kino exported from Moulmein in Lower Burma. Another variety of Indian kino is that furnished by the *Butea frondosa* (Roxb.) and other allied species of *Butea*, and known as *Butea kino, Butea guru, Bengal kino, Palas* or *Pulas kino,* or *Dhak gum.* It closely resembles official kino, and is largely substituted for it in India. *Australian, Botany Bay,* or *Eucalyptus kino* is the product of numerous species of *Eucalyptus* (Mueller, Pharm. J. [iii.] 16, 898; Maiden, J. Soc. Chem. Ind. 1888, 38; Pharm. J. [iii.] 20, 221, 321). Eucalyptus kino is gradually becoming more important, and the better varieties are quite equal in all respects to the kino of Malabar (*cf.* Flück a. Hanb. 199).

The dried juices from the bark of several Asiatic species of *Myristica* show but little difference from official Malabar kino, but the crude inspissated fresh juice contains calcium tartrate suspended in and depositing from it, which serves to distinguish it from other kinos of commerce (Schaer, Pharm. J. [iv.] 3, 117).

Kino consists of small glistening, angular, brittle, garnet-like fragments, heavier than water, and transparent when in thin layers. When chewed it tastes astringent and colours the saliva blood-red. It is partly soluble in water, entirely soluble in rectified spirit, and almost insoluble in ether. The weak spirituous solution of kino used in medicine sometimes becomes gelatinous. Methods to obviate this have been much discussed (*v.* Indexes Ph.). Fused with potash it yields the trihydroxybenzene *phloroglucinol* (Hlasiwetz, Annalen, 134, 122), and the dihydroxybenzoic acid, *protocatechuic acid* (Stenhouse, *ibid.* 177, 187). When it is distilled alone, *o*-dihydroxybenzene or *catechol* is formed (Eisfeldt, *ibid.* 92, 101).

Treatment of Malabar, Butea, or Eucalyptus kino with ether extracts a small quantity of *catechol*, and perhaps in the case of Eucalyptus kino traces also of *catechin* (Eisfeldt, Annalen, 92, 101; Flückiger, Ber. 5, 1; Flück. a. Hanb.; Wiesner, Pharm. J. [iii.] 2, 102). When dilute mineral acids are added to an aqueous solution of kino, a bulky precipitate falls of a substance which has been described as *kinotannic acid.* This compound constitutes the greater part of kino, but it has not hitherto been isolated in a state of purity. It differs from other tannins in its behaviour towards reagents. It is sparingly soluble in water, soluble in alcohol, and insoluble in ether (*v.* Berzelius, Lehrbuch, 3 Aufl. 6, 258; Gerding, Arch. Pharm. [ii.] 65, 283; Hennig, *ibid.* 73, 129; 77, 260; 85, 150; Eisfeldt). By boiling kino with dilute hydrochloric acid (1 in 5), a crystalline compound, *kinoïn*, $C_{14}H_{12}O_6$, is extracted, which is taken up by ether from the acid solution and may be purified by recrystallisation from water (Etti, Ber. 11, 1879; 17, 2241; Flück. a. Hanb. 197). It forms colourless prisms which are sparingly soluble in cold, easily soluble in hot water, very soluble in alcohol, and less so in ether. With ferric chloride it gives a red colour. It does not precipitate gelatin solution. Heated with concentrated hydrochloric acid at 120°–130°, it breaks up into *methyl chloride, gallic acid,* and *catechol*, which indicates that kinoïn is probably *methylcatechol gallic ether*, $C_{14}H_{12}O_6$ or $C_6H_2(OH)_3CO\cdot OC_6H_4\cdot OMe$. Heated at 120°–130°, two molecules of kinoïn lose a molecule of water, and are converted into the anhydride *kino red* $C_{28}H_{22}O_{11}$, identical with that described by Gerding, and which is also obtained from the residue after extraction of the kinoïn from kino by treatment with dilute acid (Etti). Kino red is a resinous compound difficultly soluble in water, easily so in alcohol and in alkalis. Ferric chloride colours it dirty green. It gives a precipitate with gelatin solution. It melts at 160°–170°, losing a molecule of water, and forming the *anhydride*, $C_{28}H_{20}O_{10}$, a compound resembling kino red. Among the products of the dry distillation of kino red are *catechol* and *phenol* (*cf.* Catechu). A. S.

KINO RED, KINOÏN, KINOTANNIC ACID, *v.* Kino.

KIRSCHWASSER or **KIRSCH** is a strong spirituous liquor made by distillation of the fermented juice of ripe Morella or wild cherries. It is prepared chiefly in Germany (particularly in the Black Forest), in Switzerland, and in the Vosges district in France.

The cherries are crushed and the juice collected in vats, the kernels added and the whole allowed to ferment for about 5 days, when the liquor is drawn off and distilled by steam.

The strength of the spirit is usually about 50 p.c. alcohol by volume or approximately 10 under proof; and its peculiar taste and flavour are due largely to the presence of hydrocyanic (prussic) acid derived from the kernels of the cherry stones.

In properly made kirschwasser, the hydrocyanic acid does not exceed 0·015 gram per litre, but in crude varieties, made by prolonged fermentation of unripe or unsound fruit, and distilled over an open fire, it occasionally reaches almost poisonous proportions.

Kirschwasser is sometimes made from grain, grape, molasses, or other spirit flavoured with ‘essence of kirschwasser’ or with peach blossom, oil of bitter almonds or its substitute nitrobenzene. Traces of copper are frequently found as an impurity, due no doubt to the copper vessels used for distillation.

Genuine kirschwasser improves greatly by keeping, either in flasks or bottles with porous stoppers or in casks. The latter are made of ash in preference to oak, as the liquor should remain perfectly bright and colourless.

Various imitations of kirschwasser are made, the characteristic flavour being derived from the kernels of stone fruit, apricots, peach kernels or oil of bitter almonds. The following recipe (Spon's Encyclopædia) is one of the best: cherry seeds, 9 kilos; apricot seeds, 3 kilos; dried peach leaves, 625 grams; myrrh, 150 grams; alcohol at 85°, 62 litres. The seeds are bruised and digested with about 30 litres of water for 24 hours, and the whole distilled until about 60 litres have come over, when the distillate is reduced to about 50° alcohol. A little glycerin or sugar (not more than 15 grams per 100 litres) is usually added to soften the flavour.

Kirschwasser is occasionally heavily sweetened, when it greatly resembles ‘noyeau’ (*v.* Liqueurs and Cordials). J. C.

KISH. An ironworker's name for the masses of impure graphite which are occasionally found in blast furnaces, and which separate out from molten cast iron.

KLIACHITE *v.* Bauxite.

KOHLRABI. *Brassica oleracea* f. *caulo-rapa.* A plant of the cabbage tribe producing a great enlargement on the stem. This ‘bulb,’ which sometimes weighs as much as 12 or 15 lbs., is the valued portion of the crop, and furnishes an excellent substitute for swedes or turnips as food for cattle and sheep.

It is very hardy and more resistant to drought and frost than the turnip.

König gives as the average composition of the “bulb”—

Water	Protein	Fat	Sugar	Other *N*-free subst.	Crude fibre	Ash	Organic sulphur
86·9	2·9	0·2	0·4	7·8	1·7	1·2	0·06

Of the total nitrogen, from which the “protein” in the above analysis is calculated, only about 44 p.c. is present as true proteid, about 8 p.c. as amides, and the remainder in other forms of combination.

The leaves and stalks contain—

Water	Protein	Fat	Sugar	Other *N*-free subst.	Crude fibre	Ash	Organic sulphur
86·0	3·0	0·4	0·5	6·8	1·6	1·7	0·08

The ash contains—

	K_2O	Na_2O	CaO	MgO	Fe_2O_3	P_2O_5	SO_3	SiO_2	Cl	
‘Bulb’	35·3	6·5	11·0	6·8	3·0	21·9	8·8	2·5	4·9	p.c.
Leaves	18·5	4·9	30·1	4·6	6·0	8·3	10·9	9·0	8·0	,,

H. I.

KOLA. Kola nuts, the fruit of *Cola acuminata,* (Schott and Endl.) are imported from the West Coast of Africa, and are made into a paste which contains about 2 p.c. of caffeïne, in addition to betaïne (Polstorff, Chem. Zentr. 1909, ii. 1014; *cf.* Desvignes, J. Pharm. Chim. 1910, 2, 20; Allard, *ibid.* 2, 122). According to Heckel and Schlagdenhauffen, the fruit of *Heritiera littoralis* (Dryand), a tree growing in India, in the Philippines, and Molucca, is often found mixed with kola nuts. This fruit belongs to the same family (*Sterculiaceæ*) as those which give the kola nuts, and is said to possess the same waste-repairing properties as the kola nut, although it contains no caffeïne. It is used as a foodstuff in India.

KORALLENERZ *v.* Cinnabar.

KOSIN or **KOUSSEIN RESIN** *v* Resins.

KOUMISS *v.* Milk.

KRANTZITE. A variety of retinite (*v.* Resins).

KREMS or **KREMSER WHITE, CREMNITZ WHITE,** *v.* Pigments.

KREOSAL, KREOTOSAL, KRESALOL, KRYOGENIN *v.* Synthetic drugs.

KREOSOL *v.* *Guaiacum,* art. Resins.

KRYOFINE. Trade name for phenetidine-methyl-glycollate $CH_3OCH_2CONH{\cdot}C_6H_4OC_2H_5$. Used as an antipyretic and anti-neuralgic. White crystalline needles, m.p. 98°, odourless and tasteless, sparingly soluble in water (*v.* Synthetic drugs).

KRYPTON. Sym. Kr. At.wt. 82·9 (Moore, Watson, *v. infra*).

An inert gas, discovered by Ramsay and Travers (Proc. Roy. Soc. 1898, 63, 405; British Assoc. Rep. 1898, 828) in the last portions of gas collected after evaporating considerable quantities of liquid air. When the latter is allowed to evaporate quietly in a vacuum vessel, the last traces of liquid consist almost entirely of oxygen, with small quantities of nitrogen, argon, krypton, and xenon. The liquid is allowed to evaporate, the gas is mixed with hydrogen and passed through a heated iron tube to remove oxygen. Nitrogen is absorbed by means of lime and magnesium (*cf.* ARGON), and after removing traces of hydrogen and carbon monoxide by means of heated copper oxide, the mixture of argon, krypton, and xenon is separated into its components by liquefaction and fractional evaporation. At the temperature of liquid air, krypton has a vapour pressure of 17 mm., whilst that of xenon is only 0·17 mm. (*v.* Travers, Study of Gases, 218; Ladenburg and Krügel, Sitzungber K. Preuss. Akad. Wiss. 1900, 212, 727; Ramsay and Travers, Proc. Roy. Soc. 1901, 67, 329; Moore, Chem. Soc. Trans. 1908, 93, 2181). The separation of a mixture of argon, krypton, and xenon has been effected by absorbing the gases in charcoal cooled in liquid air, allowing the temperature to rise slowly and collecting the evolved gas in fractions (Valentiner and Schmidt, Sitzungber. K. Akad. Wiss. Berlin, 1905, 38, 816).

The proportion of krypton in the atmosphere is about 1 part in twenty millions by volume (Ramsay, Proc. Roy. Soc. 1903, 71, 421; 1908, 80, A. 599). Krypton also occurs in the gases evolved from many thermal springs (Moureu and Lepape, Compt. rend. 1909, 149, 1171).

Krypton is a colourless, odourless, tasteless gas. It is only slightly soluble in water, the absorption coefficient at 20° being 0·0729 (Antropoff, Proc. Roy. Soc. 1910, 83, A. 474). One litre of the gas at N. T. P. weighs 3·708 grams; its density is therefore 41·506 (O=16) (Moore, Chem. Soc. Trans. 1908, 93, 2181; Watson, *ibid.* 1910, 97, 833). Krypton boils at −151·7° and melts at −169°; its critical temperature is −62·5°, and the critical pressure is 54·3 atmospheres. One cub. cm. of liquid krypton at its boiling-point weighs 2·155 grams; the molecular volume is 37·84 (Ramsay and Travers, Proc. Roy. Soc. 1901, 67, 329). At N. T. P. the refractive index of the gas for the green mercury line ($\lambda=5461$) is 1·0004287 (Cuthbertson and Cuthbertson, Proc. Roy. Soc. 1908, 81, A. 440; 1910, 84, A. 13). (For the viscosity of krypton, *v.* Rankine, *ibid.* 1910, 83, A, 516; for its spectrum, *v.* Baly, Phil. Trans. 1903, 202, A. 183; Liveing and Dewar, Proc. Roy. Soc. 1901, 68, 389.)

Krypton is completely inactive, no compounds of the element being known. The gas is monatomic, since the ratio of its specific heats is 1·66 (Ramsay and Travers).

KUNKUR. An argillaceous limestone used in India for the preparation of mortar. It forms an excellent hydraulic mortar (E. Nicholson, Chem. News, 32, 82).

KUNZITE. A transparent, violet, or lilac-coloured variety of the mineral spodumene, $LiAlSi_2O_6$ (*q.v.*), used as a gem-stone. It is found with pink tourmaline in the gem-mines of San Diego Co., California, and in Madagascar.

L. J. S.

KUS-KUS ROOT. The rhizome of *Andropogon squarrosus* (Linn.), a marsh plant of the Gramineæ, growing in India, the Philippines, &c., and cultivated in Jamaica; gives an ethereal oil, *oleum æther vetiveriæ*, used in perfumery.

KUTEERA GUM *v.* GUMS.

KYANISING. A process for preserving timber, due to Kyan, of New York, in which a solution of mercuric chloride is forced into the pores of the wood.

KYANITE or **CYANITE.** An aluminium silicate $Al_2O_3 \cdot SiO_2$ found in triclinic prisms; generally of a pale blue colour, sometimes white, or blue with white edges; also grey, green, and black. Occurs usually in gneiss or mica schist.

KYANOL. Runge's term for aniline.

KYNITE *v.* EXPLOSIVES.

L

LABDANUM or **LADANUM** *v.* OLEO-RESINS.

LABEL VARNISH *v.* VARNISH.

LABRADORITE *v.* FELSPAR.

LAC DYE. Lac dye is produced by an insect, the *Coccus lacca* or *ficus*, living on the twigs of various kinds of trees, particularly the *Ficus religiosa* (Linn.), the *Zizyphus Jujuba* (Lam.), and the *Butea frondosa* (Roxb.). These insects appear usually in November, and subsequently fasten themselves to the fleshy portions of the young branches. Gradually the abdomen of the insects becomes covered by a viscous fluid, which slowly forms a cellule surrounding the animal. The substance composing this cellule is the *stick lac.* The cellule attains its full size in March, and the insect then exhibits the appearance of a red oval-shaped, smoothly polished lifeless sack entirely filled with a beautifully red liquid; its size is then the same as the full-grown cochineal (Crookes, Dyeing and Calico Printing, 354). Commercial stick lac is chiefly gathered on the hilly banks of the Ganges in India, that for dyeing purposes possessing a deep red colour, whereas the pale perforated kind in which no insects exist is employed for varnish making, and constitutes the material for *shellac.*

Of *lac*, the following varieties occur: *stick lac*, the crude product together with the twigs upon which it is formed; *grained lac*, the material removed from the twigs; and *caked lac* the latter variety fused and cast into moulds.

Such a resinous material is not suitable for dyeing purposes, and a simple process is adopted to remove the colouring matter from the resin, or at least to obtain it in a more concentrated form. This consists in extracting stick lac with hot dilute sodium carbonate, evaporating the extract, and moulding the residue into square cakes. The product, which is *lac dye*, according to Crookes (*l.c.*) contains on an average about 50 p.c. of colouring matter, 25 p.c. of resin, and 22 p.c. of earthy impurities.

Lac dye is an extremely ancient dyestuff, and was employed by the East Indians for many centuries before it was known in Europe. It appears to have been introduced into this country about 1790. Early in the last century, lac dye was a very important article of commerce, so much so that at that time shellac was practically a bye-product of its manufacture. The position of these products has now been reversed, for whereas the dyestuff is almost defunct, the shellac industry is of considerable importance.

According to the older writers, the colouring matter of lac dye was considered to be identical with that of cochineal, but that this is not the case has been clearly indicated by Schmidt (Ber. 20, 1285).

Laccaic acid. Finely powdered lac dye, after treatment with dilute hydrochloric acid to remove mineral matter, is extracted with boiling water, and the colouring matter is precipitated from this solution by means of lead acetate. The lead precipitate suspended in water is decomposed with sulphuretted hydrogen, and the filtrate which contains the free colouring matter is evaporated to dryness. The residue thus obtained is extracted with alcohol and ether is then added to the solution until a precipitate no longer separates. The filtered liquid on gradual evaporation deposits crystals of laccaic acid. According to Schmidt, the amount of pure colouring matter which can be isolated by this method from a kilo. of lac dye is 20 grams.

Thus prepared, laccaic acid consists of a brownish-red crystalline powder, soluble in water with a blood-red colour, and insoluble in ether. When heated it decomposes at about 180°. Schmidt's analyses indicate $C=58{\cdot}00$, $H=41$ p.c., and correspond to the formula $C_{16}H_{12}O_8$. When heated with concentrated hydrochloric acid at 180°, *methyl chloride* and a red-brown amorphous substance, $C_{26}H_{16}O_{11}$, are produced. Dilute nitric acid at 160° gives *picric acid*, but no crystalline compounds resembling the α- and β-bromcarmines so readily prepared from carminic acid are produced from it by the action of bromine. On the other hand, although no distinction is to be observed in the absorption spectra of the aqueous and alkaline solutions of laccaic and carminic acids, it is possible when the colouring matters are dissolved in sulphuric acid to thus discriminate between them. When fused with potassium hydroxide, laccaic acid gives, in addition to a substance (*a*) volatile in steam, colourless needles, m.p. 142°–143°; a compound (*b*) $C_{10}H_6O_6$ or $C_{10}H_8O_6$, m.p. 285°, readily soluble in water; a compound (*c*) $C_8H_8O_3$, m.p. 169°, possibly a *hydroxytoluic acid*; and (*d*) an easily soluble substance, the aqueous solution of which gives with ferric chloride a black colouration.

Dyeing properties.—The dyeing properties of lac dye are practically identical with those of cochineal, although the shades obtained are somewhat faster. Owing to the resinous and mineral impurities accompanying the colouring matter, it is not readily dissolved by water, and before use it is therefore ground to a paste with the requisite quantity of tin spirit together with a little hydrochloric acid, and allowed to stand overnight. Cochineal and lac dye can be used together with advantage, or after the wool is dyed with lac it may be entered into a fresh bath with cochineal. Its employment at the present time is, however, extremely limited.

A. G. P.

LACMOID $C_{12}H_9NO_4$ (?)

Preparation.—(1) A mixture of resorcinol (20 parts), sodium nitrite (1 part), and water (1 part) is slowly heated to 110°, when a vigorous reaction sets in; the mass is then kept at 115°–120° until it has become quite blue and no more ammonia is evolved. The product is dissolved in water and the lacmoid precipitated with hydrochloric acid (Traub and Hock, Ber. 1884, 17, 2615). (2) By fusing resorcinol (5 parts) with potassium nitrite (6 parts) (Benedict and Julius, Monatsh. 1884, 5, 534). (3) By the action of H_2O_2 on ammoniacal resorcinol solution (Wurster, Ber. 1887, 20, 2938).

To purify the substance, extract it almost completely with boiling water, cool, filter, and acidify the blue solution with hydrochloric acid. Filter off the precipitated lacmoid, wash with cold water and dry it below 100°. An alternative method is to warm gently powdered lacmoid (8 parts) with 20 p.c. alcohol (100 parts) for 15 minutes, cool and filter (Foerster, Zeitsch. angew. Chem. 1890, 3, 163).

Properties.—A glistening brown powder, easily soluble in methyl, ethyl, or amyl alcohol, acetone, acetic acid, or phenol, less easily in ether or water, insoluble in benzene or petroleum spirit. It dissolves in concentrated HCl or H_2SO_4, yielding a blue solution. Heated below 200° it decomposes.

Lacmoid differs from the colouring matter of litmus in being soluble in strong alcohol. Its absorption spectrum resembles that of azolitmin (Hartley, Proc. Roy. Dublin Soc. 5, 159).

For the use of lacmoid as an indicator, *v.* Thomson (Chem. News, 1885, 52, 18, 29) and ACIDIMETRY AND ALKALIMETRY.

LACQUER (*Urushi, Ki-urushi*). A varnish obtained from the juice of *Rhus vernicifera* (DC.), a tree indigenous to China, whence in early times it was introduced into Japan (Bull. Imp. Inst. 1910, 8, 32; J. Soc. Chem. Ind. 1910, 639).

Chinese lacquer. The tree is abundant in Central China, growing wild or under cultivation at altitudes of 3000 to 7500 feet. It is tapped in June or early July; shallow incisions are made in the bark of the stem and the greyish-white, milky juice collected in shells, bamboos, &c., and covered with oiled paper to prevent oxidation. The tapping is repeated seven times at intervals of 7 days, and the tree is then left for 5–7 years to recover. Much of the varnish is sent to Japan. The lacquer is frequently adulterated with tung oil.

Japanese lacquer. The lacquer tree grows abundantly all over Japan, and is cultivated largely in the district north of Tokyo. Tapping takes place when the tree is 10 years old and is continued from June to October, each tree yielding from 27 to 54 grams of lacquer. Usually the tree is left to recover, but sometimes it is cut down. In the latter case, a further yield of lacquer is obtained from the branches by steeping them in water for 10–20 days, and then making incisions and heating the water to cause the sap to exude. The varnish thus obtained, called *seshine-urushi*, is harder and of poorer quality, and is used only for groundwork and for cheap articles. The best quality is obtained from between the inner and outer bark of trees from 14 to 15 years old. It is called *ki-urushi* (Pudor, Zeitsch. öffentl. Chem. 1910, 16, 315). A very inferior quality, known as *Moku-yshi*, is used mixed with the better kinds in varying proportions.

The raw varnish is packed in wooden tubs and covered with oiled paper to prevent oxidation. It is prepared for use by various processes, the quality and value of the varnish and of the lacquered ware produced depending upon the time and care spent upon the purification.

The juice is strained from particles of bark, &c., and is allowed to stand in wooden vessels until it separates into various layers, when the lighter and finer qualities are decanted from the heavier and inferior varnish. The product is finally filtered through hempen or cotton cloth and exposed in shallow wooden pans to the heat of the sun or to artificial warmth. It thus becomes syrupy and of a dark-brown colour, the change being due principally to loss of water. It is thinned with camphor or oil of turpentine or other suitable solvent.

Coloured lacquers are prepared from *ki-urushi* during the exposure to the sun (*v.s.*) by mixing in appropriate pigments, those most commonly employed being as follows (Miyama, J. Coll. Engineering, Imp. Univ. Tokyo, 1908, 4, 201; J. Soc. Chem. Ind. 1909, 318):—

White.—Barium sulphate; bismuth oxychloride.

Red.—Cinnabar; rouge.

Blue.—Prussian blue; ultramarine.

Yellow.—Cadmium sulphide; lead chromate; orpiment.

Green.—Chromic oxide (or by the addition of indigo from *Polygonum tinctorum* (Ait.) to the yellow lacquer).

Black.—Lampblack; iron powder or compounds of iron.

Brown.—Mixture of red and black.

The so-called 'pear-ground' lacquer, used with gold-dust, is prepared with gamboge.

Use of the lacquer.—The prepared surface of the article to be lacquered first receives several coats of the poorer quality mixed with a special clay called *ching-chu*, or in some cases with an inferior clay or with pottery dust. After each coat, the article is kept for several days in a moist atmosphere until the lacquer has set, and it is then rubbed down with pumice to a dull, smooth surface before another coat is given. The final coat is of the better quality lacquer, and the article may be further decorated with a pattern in coloured lacquer. Any joint in the wood is scraped down below the general level of the surface and then filled up with alternate layers of silk and lacquer.

Lacquering is applied to small articles, *e.g.* card-cases, vases, images, &c., either for ornamental purposes or for practical use. Hollow articles of lacquer are made by building up a layer of lacquer and silk on a clay model which is afterwards washed out with water through a hole left for that purpose. (For full details of the manufacture of lacquered ware, *see* Nightingale, J. Indust. and Engineering Chem. 1911, 3, 59; also Workshop Receipts, 3rd series, 306.)

The drying of lacquer at ordinary temperatures is caused by an enzyme (an oxydase) called *laccase*, contained in the sap (Tschirch and Stevens, Arch. Pharm. 1905, 243, 504; J. Soc. Chem. Ind. 1906, 81). During the drying it absorbs 5·75 p.c. of oxygen.

It may also be dried by heat, this process being specially applicable to lacquered articles of glass, porcelain, and papier-mache (Miyama, J. Soc. Chem. Ind. 1909, 318). At 100° it dries in 4–5 hours, at 150° in 30 minutes, and at 180° in 10 minutes. The drying by heat is attended by absorption of oxygen and some decomposition, giving a dark-coloured coating which is harder and more durable than the cold-dried lacquer. Coloured lacquers cannot usually be dried by heat because of the darkening of the lacquer. For a similar reason it is not the practice to use 'driers' in lacquers.

Composition of lacquer.—The main constituent of lacquer, to which its peculiar properties are due, is an unsaturated polyhydric phenol, *urushiol*, having the formula $C_{20}H_{28}O_2$ (Majima, Ber. 1909, 42, 3664).

Miyama gives the following analyses of typical specimens of the juice (J. Coll. Eng. Tokyo, 1908, 4, 89; J. Soc. Chem. Ind. 1908, 456):—

	Japanese	Chinese	Indian
Moisture .	17·81–27·62 p.c.	—	—
Urushiol .	64·14–77·63 ,,	36·88 p.c.	26·39 p.c.
Gum .	2·62–7·57 ,,	23·5 ,,	37·78 ,,
Nitrogenous matter .	1·78–2·47 ,,	—	—

Sun-dried Japanese lacquer contains 94·5 p.c. urushiol.

Urushiol forms a compound with barium hydroxide, and is estimated by titrating with a solution of that base, using phenolphthalein as indicator.

Urushiol may be obtained from lacquer by repeated extraction with alcohol, and is purified by treatment with petroleum spirit. It is a light-brown, viscous fluid, sp.gr. 0·9687 at 21·5°/4°, and is readily soluble in most organic solvents. It forms a dimethyl ether and an easily hydrolysable acetyl derivative. On dry distillation it yields various hydrocarbons and polyhydric phenols, but no simple alicyclic hydrocarbon or ordinary terpene (Majima and Cho, Ber. 1907, 40, 4390; Majima, *ibid.* 1909, 42, 1418, 3664). Tschirch and Stevens (*l.c.*) found in the lac an irritant poison, named by them *verniciferol.*

LAC RESIN *v.* Resins.

LACTANIN *v.* Synthetic drugs.

LACTARIC ACID $C_{14}H_{29}COOH$ is obtained by extracting the fungus *Agaricus integer* with alcohol (Chuit, Bull. Soc. chim. [iii.] 2, 153); m.p. 69·5°–70°.

LACTASE is the enzyme decomposing lactose (milk sugar) to dextrose and galactose. The distribution in animals is limited, being confined entirely to the intestine and generally of young animals only. Plimmer (J. physiol. 1906, 35, 20) found lactase in the cat and the pig during the whole of their lives, but only in the young guinea pig. The gastro-intestinal sac of snails contains a lactase (Bierry, Compt. rend. 1909, 148, 949). It is present in a few torula (*S. fragilis*, *S. kayser*, *S. adametz*, &c.) and in kephir. Lactose is also hydrolysed by the emulsin derived from almonds, which accordingly contains a lactase. There is apparently a difference between kephir and almond lactase, since the hydrolytic activity of the former is restricted mainly by galactose, that of the latter mainly by glucose (Armstrong, Proc. Roy. Soc. 1908, B, 80, 321). Lactase also hydrolyses β-methylgalactoside and melibiose. The optimum activity is about 37°. Lactase is precipitated by alcohol, and behaves very similarly to emulsin: its rate of action is governed by the same laws. It has not been fully investigated.

E. F. A.

LACTIC ACID or α-**HYDROXYPROPIONIC ACID** (Ger. *Milchsäure*) $CH_3CH(OH)COOH$ was first obtained by Scheele in 1780 from sour milk. Its exact constitution was, however, first ascertained by Liebig and Mitscherlich (Annalen, 7, 47) and by Gay-Lussac and Pelouze (*ibid.* 7, 40). It is widely distributed in nature, occurring in the lesser centaury (*Erythræa Centaurium* [Pers.]) (Habermann, Chem. Zeit. 30, 40); in the sap of the vine; and in most fermented liquids of vegetable origin, especially in sour milk; it is not, however, present in fresh milk. It is found in beet molasses, and owes its origin to the boiling of the sucrose solution with lime in the process of defecation (Schöne and Tollens, J. Soc. Chem. Ind. 1901, 54; Weisberg, *ibid.* 375; Beythien, Parcus and Tollens, Annalen, 255, 228). It has also been found in small quantities in saliva; in the brain and under certain conditions in the gastric juice; in the blood and in urine. The acid obtained by Braconnot, and termed *nanceic acid*, as well as the *thebolactic* acid obtained from opium, have been proved to be identical with common lactic acid. On the other hand, the acid obtained by Berzelius from flesh, and further investigated by Liebig, differs from the ordinary lactic acid in certain of its properties, and is therefore distinguished as *paralactic acid.* This will be described later on.

Lactic acid is formed in the fermentation of various sugars, of mannitol, and of dextrin (*v.* FERMENTATION), and also by the action of caustic alkalis on the sugars. It has also been obtained synthetically in a number of ways, the three most important of which are the following:—

(1) Aldehyde unites with hydrogen cyanide, forming the nitrile

$$CH_3{\cdot}CHO+HCN=CH_3{\cdot}CH(OH)CN,$$

and this on treatment with acids is converted into lactic acid (Wislicenus, Annalen, 128, 13, 22).

(2) By the action of alkalis on α-chloropropionic acid (Friedel and Machuca, Annalen, 120, 285)

$$CH_3{\cdot}CHCl{\cdot}COOH+2KOH \\ =CH_3{\cdot}CH(OH)COOH+KCl+H_2O.$$

(3) By the reduction of pyruvic acid with sodium amalgam, hydriodic acid (Wislicenus, Annalen, 126, 227), zinc (Debus, *ibid.* 127, 332), or electrolytically (Tafel and Friedrichs, Ber. 1904, 3187)

$$CH_3{\cdot}CO{\cdot}COOH+H_2=CH_3{\cdot}CH(OH)COOH.$$

These syntheses clearly show that the acid is α-hydroxypropionic acid.

In order to distinguish lactic acid from the allied acids it is frequently called *ethylidene-lactic* or *fermentation lactic acid.*

Preparation.—Lactic acid is usually prepared by the fermentation of sugar. McLauchan (J. Soc. Chem. Ind. 1909, 734) recommends the following method: 400 grams of commercial glucose are dissolved in 1200 c.c. of hot water, and to this is added 170 grams of whitening or well powdered calcium carbonate and 20 grams of malt, previously boiled for a few minutes with 100 c.c. of water. The solution is kept simmering for 30 minutes, then cooled to 60°–70°, and after stirring is poured into a narrow-necked bottle, of 2½ litres capacity. The calcium carbonate is rinsed out with water and the solution made up to 1800 c.c. The bottle is placed in an air-bath at 45°, a small quantity of sour milk or caseïn added to start fermentation, and a wad of cotton used to stopper the bottle. The bottle is shaken every few hours for 6 days and when the unfermented sugar is less than 0·4 p.c. the solution is filtered. The final filtrate after concentration should be one litre of 25 p.c. acid. Kassner (Chem. Zentr. 1897, ii. 20) dissolves 300 grams of cane sugar and 15 grams of tartaric acid in 1700 grams of boiling water and allows the solution to stand for several days, the temperature being maintained at 60°; 100 grams of old cheese and a little more than the calculated quantity of finely powdered chalk are then added and fermentation is allowed to proceed with daily stirring for about 3 weeks. Brensch (Annalen, 61, 177) proceeds in a similar manner, but during fermentation keeps the temperature at 30°–35°. Lautemann (*ibid.* 113, 142) replaces the chalk in the original mixture by 2 kilos. zinc white. After about 10 days a magma of zinc lactate together with some mannitol is formed, which may be recrystallised from water. The purified salt obtained by any of these methods is dissolved in boiling water, and precipitated with H_2S, the filtrate evaporated to a syrup, cooled, and separated from mannitol and any undecomposed salt by extraction with ether. The syrup which remains after evaporation of the ether is then warmed on the water-bath.

A large number of micro-organisms are capable of causing lactic fermentation of sugar, one of which has, however, a much greater intensity of action than the remainder, and is known therefore as *Bac. acid. lactici.* The solution must be kept neutral, and access of air must be allowed, as well as the necessary nitrogenous food. Its form in a highly nitrogenous saccharine solution, is a double truncated cone, and it has the tendency of all lactic bacteria to link itself together in pairs or short chains (Claflin, J. Soc. Chem. Ind. 1897, 516). (For further particulars of the micro-organisms, *v.* Andreasch, J. Soc. Chem. Ind. 1897, 53; Leichmann and Bazarewski, *ibid.* 1900, 698; Harden, Chem. Soc. Trans. 1901, 624; J. Soc. Chem. Ind. 1901, 921; Hashimoto, *ibid.* 1902, 506; Beijerinck, *ibid.* 1903, 106; Henneberg, *ibid.* 1904, 332; Buchner and Meisenheimer, Annalen, 349, 125; Wehmer, Chem. Zeit. 30, 1033; Heinemann, J. Biol. Chem. 1907, 2, 603.) Lactolase is an enzyme which causes the formation of lactic acid in plant cells (Stoklasa, Chem. Zentr. 1905, i. 265; 1907, i. 828). Malic, succinic, tartaric, and citric acids are all readily converted into lactic acid by certain moulds such as *Pencillium glaucum*, *Aspergillus niger*, and *Botrytis cinera* (Bied. Zentr. 1908, 37, 215).

For the preparation of the acid from sugar by the action of caustic alkalis, Kiliani (Ber. 1882, 699) recommends the following method. 500 grams cane sugar are mixed with 250 c.c. water, and 10 c.c. of the sulphuric acid employed later on, and warmed in a flask of 2 litres capacity to 50° for 2 hours. To the well-cooled solution 400 c.c. of caustic soda solution (1 part of caustic to 1 part water) are gradually added, the mixture being constantly cooled. The exact quantity of sulphuric acid necessary is then allowed to flow in; the acid is prepared by adding 3 parts H_2SO_4 to 4 parts water, and previously directly compared with the caustic soda solution by titration. A crystal of Glauber's salt is added to facilitate crystallisation, the whole being cooled and well shaken, and allowed to stand 24 hours. The mass is then extracted with 93 p.c. alcohol, filtered on the pump, and half the filtrate neutralised with $ZnCO_3$ on the water-bath, then mixed with the other portion, and the whole allowed to stand 36 hours. The separated zinc salt is filtered off, well pressed, recrystallised from water, and converted into the acid as before.

Just as lactic acid may be obtained by boiling hexoses and hexobioses with caustic alkalis, so it may be obtained from pentoses such as arabinose and xylose (Katsuyama, Ber. 1902, 669; Araki, Zeitsch. physiol. Chem. 19, 463) and from cane sugar and raffinose (Beythien, Parcus, and Tollens, Annalen, 255, 222). Meisenheimer (Ber. 1908, 1009) states that lactic acid is formed in small quantities when glucose, fructose, or galactose are allowed to stand in dilute sodium hydroxide for many months in the dark.

Manufacture.—There are three stages in the manufacture of lactic acid, the preparation of the saccharine solution, the fermentation process, and the conversion of the fermented liquid into commercial lactic acid. The saccharine solution, which should have a sp.gr. of about 1·075, *i.e.* a saccharine content of 7½–11 p.c., and which should be faintly alkaline or neutral but not acid, is sterilised either by boiling for an hour, or by blowing live steam into the solution for one hour at 95°. It is advantageous to have about 10–15 p.c. of the saccharine matter in the form of cane sugar and the remainder as glucose. After sterilisation, the liquid is conveyed to the fermentation tank, cooled to between 45° and 55°, and impregnated. Where continuous manufacture of lactic acid is carried on, impregnation takes place from a previously fermented liquor where a lively fermentation is in progress; for an original fermentation, milk, which has been kept until it is slightly sour, is used. For efficient working, the lactic acid ferment must be well nourished with nitrogenous matter, the most convenient sources being vegetable matter, *e.g.* as extracted from bran by the action of boiling water and dilute acid. If mineral food is employed, ammonium salts should be in excess of nitrates. As the fermentation proceeds, the temperature is allowed to decrease and the solution is neutralised with milk of lime or chalk in suspension, as the lactic acid bacteria are only healthy in solutions containing between 0·02 and 0·5 p.c. of acid: the fermentation is best completed in from 3 to 6 days. The fermented liquid, which contains calcium lactate with a layer of dead bacteria floating on it, is evaporated and filtered. For a commercial acid, decomposition of the syrupy solution of calcium lactate with sulphuric acid gives an acid of sufficient purity. If a pure acid is required, the solution of calcium lactate is set to crystallise; the solid crystals are pressed to remove mother liquor, and may be recrystallised if required (Claflin, J. Soc. Chem. Ind. 1897, 516; Dreher, *ibid.* 1898, 1070; McLauchan; *ibid.* 1907, 734; *cf.* Just, U.S. Pat. 868444; J. Soc. Chem. Ind. 1907, 1211; D. R. P. 203306; Chem. Zentr. 1908, ii. 1843). Various methods have been patented for the manufacture of lactic acid, differing mainly as to the source of the saccharine solution. Mislin and Lewin (Eng. Pat. 10436; Fr. Pat. 355520; J. Soc. Chem. Ind. 1905, 1248) place alternate layers of malt and rye in a suitable apparatus until saccharification of the starch is complete. The must is removed by pressure and fermented as in above method (*cf.* Brookes, Eng. Pat. 5780; J. Soc. Chem. Ind. 1885, 116; Avery, Pharm. J. Aug. 5, 1882). Jean and Bougard obtain lactic acid from powdered grain or oil-free cake (Fr. Pats. 315325, 315326, 321374; J. Soc. Chem. Ind. 1903, 225), and Claflin uses as the starting material a wort containing about 10 p.c. of fermentable material (U.S. Pat. 861163; J. Soc. Chem. Ind. 1907, 985). Boullanger acts on starch or sugar containing substances with a mould such as *Rumex acetosella*, and then proceeds as above (D. R. P. 118083; Chem. Zentr. 1901, i. 650).

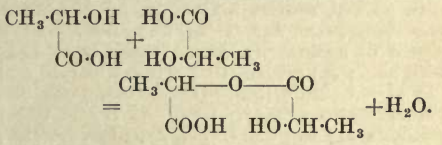
Boehringer states that calcium lactate and sulphuric acid form a paste which is very difficult to work up. The method recommended is to take 300 litres of calcium lactate solution (10° B.), obtained from fermentation process, and evaporated to 50 litres; 50 kilos. of a 50 p.c. solution of lactic acid is added and then the calcium lactate is decomposed by sulphuric acid. The solution of lactic acid thus obtained is 50 p.c. (Eng. Pat. 7094; Fr. Pat. 401395; D. R. P. 221112; J. Soc. Chem. Ind. 1909, 674).

Patents have been granted for processes to recover lactic acid from brewers' and distillers' slop and from the waste water of jam factories. One such method consists in neutralising the liquid with milk of lime, partly evaporating and causing the albuminoid substances to coagulate, filtering and allowing the calcium lactate to separate out from the filtrate (Beckers, D. R. P. 104281; Chem. Zentr. 1899, ii. 926; *v.* also Beckers, D. R. P. 113383; Chem. Zentr. 1900, ii. 702; Roehr, U.S. Pat. 823366; J. Soc. Chem. Ind. 1906, 901).

Several processes have been patented for the purification of the acid thus obtained. Waite (Eng. Pat. 13403; D. R. P. 140319; J. Soc. Chem. Ind. 1901, 931) washes the crude acid with amyl alcohol and distils off the solvent from the alcoholic solution of the acid, or washes this solution with water and concentrates the aqueous solution. Blumenthal and Chain (D. R. P. 169992; J. Soc. Chem. Ind. 1907, 279) mix the crude acid with aniline (150 parts 60 p.c. acid with 93 of aniline) and cool to —5°; the precipitate is recrystallised from a small quantity of water, decomposed with steam, and the acid concentrated *in vacuô*. Noerdlinger (Eng. Pat. 26415; Fr. Pat. 364468; D. R. P. 221786; U. S. Pat. 924494; J. Soc. Chem. Ind. 1908, 245) distils the crude acid in a current of inert gas. The water is first expelled and then pure lactic acid passes over. Erdmann (D. R. P. 217846; Chem. Zentr. 1910, i. 701) obtains pure lactic acid from copper lactate and water, heated at 150°–250°.

Properties.—The acid thus obtained forms a syrup of sp.gr. 1·21–1·24, and is soluble in all proportions in water and alcohol, less readily in ether. It is hygroscopic, colourless, and inodorous, but has a very sharp acid taste. The syrup is, however, not the pure acid, but a mixture of the latter with small quantities of water and the anhydride. The pure acid cannot be obtained by evaporation of the aqueous solution, as formation of the anhydride commences before all the water is driven off. Krafft and Dyës (Ber. 1895, 2589; Chem. Zentr. 1896, i. 742) have obtained lactic acid in the form of very hygroscopic white crystals, m.p. 18°, by the distillation of the commercial acid under reduced pressure. Lactic acid is slightly volatile at the ordinary temperatures, lactide is less volatile, and lactic anhydride practically non-volatile (Müller, Bull. Soc. chim. 1896, 15, 1206); lactic acid is volatile in steam, but not sufficiently volatile to be quantitatively separated from aqueous solutions by this means (Utz, Chem. Zeit. 1905, 29, 363). Lactic acid contains an asymmetric carbon atom, and hence can exist in two optically active modifications (*v. infra*). The fermentation lactic acid is optically inactive, but the acid obtained from the works is sometimes optically active. According to McKenzie (Chem. Soc. Trans. 1905, 1377), this is due to the fact that the action of the pure culture on sugar is to produce equal amounts of *d*- and *l*-isomerides. On converting these into the calcium salts and recrystallising, the crop of crystals which separate are mostly calcium *r*- salt, the active salt remaining in solution. If crystallisation takes place from a concentrated solution and the precipitate is not washed free from mother liquor, the acid obtained will be optically active. This would also be the case if the bacterial action had been such as to produce an excess of one isomeride (*cf.* Pottevin, J. Soc. Chem. Ind. 1899, 700). Wehmer recommends the use of *Oidium lactis* and two mycoderma to decompose lactic acid in liquids where its presence is not desirable (Chem. Zentr. 1903, i. 891). An aqueous solution of lactic acid decomposes in sunlight into acetaldehyde, pyruvic acid, carbon dioxide, and water (Ganassini, Boll. Chim. Farm. 48, 785). Oxidation of lactic acid with hydrogen peroxide yields pyruvic acid (Fenton and Jones, Chem. Soc. Trans. 1900, 71); with potassium permanganate, pyruvic acid (Aristoff, J. Russ. Phys. Chem. Soc. 1884, 2, 249), acetaldehyde and malic acid (Schoorl, Zeitsch. angew. Chem. 1900, 15, 367); with dilute sulphuric acid at 130°, or by heating alone at 440°–460°, acetaldehyde and formic acid (Nef, Annalen, 335, 296); with chromic acid, acetic acid, and carbon dioxide (Dossios, Zeitsch. Chem. 1866, 451; Chapman and Smith, *ibid.* 1867, 477.) Oxidation of the ammonium salt with hydrogen peroxide yields acetaldehyde, acetic acid, and carbon dioxide (Dakin, J. Biol. Chem. 4, 91). Reduction with hydriodic acid yields propionic acid. Electrolysis of the sodium salt results in the production of acetaldehyde and carbon dioxide (Walker, Chem. Soc. Trans. 1896, 1278; Ber. 1894, 467; Kolbe, Annalen, 113, 244). Phosphorus pentachloride converts lactic acid into α-chlorpropionic acid (Walden, Ber. 1895, 1293; Le Bel, *ibid.* 1895, 1923); bleaching powder converts it into chloroform and formic acid (Eberhard, Chem. Soc. Abstr. 1901, i. 357). Lactic acid reduces the nitrates of the heavy metals, *e.g.* bismuth, silver, mercury, cadmium, &c.; cobalt and nickel yield strongly magnetic powders (Vanino and Hauser, Zeitsch. anal. Chem. 1900, 29, 506). When the silver salt is treated with alkyl iodides, the hydrogen of the hydroxyl and carboxyl groups are both attacked (Purdie and Lander, Chem. Soc. Trans. 1898, 296, 300). For thermo-chemical data, *v.* Berthelot and Delépine, Compt. rend. 1899, 129, 920; dielectric constant, electrical conductivity, Drude, Zeitsch. physikal. Chem. 23, 349; Walden, *ibid.* 46, 103; 54, 129.

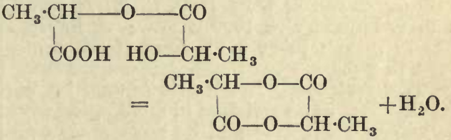
Lactic anhydride, which has been mentioned above, is formed by the elimination of a molecule of water from two molecules of the acid in the following manner, the one molecule acting as an alcohol and the other as an acid:—



$$\begin{array}{l}\mathrm{CH_3{\cdot}CH{\cdot}OH\quad HO{\cdot}CO}\\ \quad | \qquad\quad + \qquad\ | \\ \quad\mathrm{CO{\cdot}OH\quad HO{\cdot}CH{\cdot}CH_3}\end{array} = \begin{array}{l}\mathrm{CH_3{\cdot}CH—O—CO}\\ \quad | \qquad\qquad\ \ | \\ \mathrm{COOH\quad HO{\cdot}CH{\cdot}CH_3}\end{array} + \mathrm{H_2O}.$$

This compound, *lactic anhydride* or *lactolactic acid*, is at the same time an alcohol, an acid, and an ethereal salt. It is a light-yellow amorphous mass, easily soluble in alcohol and ether, insoluble in water, and is decomposed by alkalis, forming salts of lactic acid.

On further heating, another molecule of water is driven off, forming a second anhydride called lactide



$$\begin{array}{l}\mathrm{CH_3{\cdot}CH—O—CO}\\ \quad | \qquad\qquad\ \ | \\ \mathrm{COOH\quad HO—CH{\cdot}CH_3}\end{array} = \begin{array}{l}\mathrm{CH_3{\cdot}CH—O—CO}\\ \quad | \qquad\qquad\ \ | \\ \mathrm{CO—O—CH{\cdot}CH_3}\end{array} + \mathrm{H_2O}.$$

This substance, which is a double ethereal salt, is very slightly soluble in water, and forms white needles melting at 124·5° (Bischoff and Walden, Annalen, 279, 71; Nef, *ibid.* 335, 296; Raper, J. Physiol. 32, 216).

Detection and estimation.—On heating lactic acid with potassium chromate and sulphuric acid it is decomposed into formic acid and acetaldehyde. The mixture is distilled and vapours collected in Nessler's solution, giving a yellow precipitate or opalescence (Lassar-Cohn, Annalen, 284, 226; Windisch, J. Soc. Chem. Ind. 1887, 262). Thoms (Apoth. Zeit. 1907, 22, 206) recommends treating a few cc. of the liquid with 3 or 4 drops of 30 p.c. solution of chromic acid sufficient to impart a bright-yellow tint. In the presence of free lactic acid a reddish-brown colouration is produced on warming the solution on the water-bath for 10 minutes. Denigès (Ann. Chim. Phys. 18, [viii.] 191) treats the solution with bromine water, and then after the addition of acetic acid a red-violet colour is produced on adding sodium nitroprusside. Other methods, *v.* Denigès, Bull. Soc. chim. 1909, 5, 647; Croner and Cronheim, J. Soc. Chem. Ind. 1905, 1258; Herzog, Annalen, 1907, 351, 263. The following process has been recommended by Jean (Ann. Chim. Anal. Appl. 1900, 5, 285) for estimating the commercial acid. (i.) Total acidity is determined as H_2SO_4; (ii.) free acids by evaporating three times to dryness on the water-bath; (iii.) lactic acid by evaporating 10 c.c. to dryness several times, and dissolving the residue in water. The solution is heated to boiling, neutralised with barium carbonate, and then filtered and evaporated to dryness in a platinum dish. The residue is incinerated to carbonate, extracted with boiling water, collected on a filter, well washed, and dissolved in a known volume of decinormal hydrochloric acid. The solution is heated to remove the carbon dioxide, titrated with decinormal alkali, and the volume of N/10-hydrochloric acid neutralised by the carbonate formed by subtraction. This number of c.c. × 0·009 gives weight of lactic acid originally present. To estimate the amount of lactic acid and lactic anhydride present in a sample of lactic acid, the following process is used: (i.) dilute sample with water and titrate with normal sodium hydroxide, using phenolphthalein as an indicator; (ii.) add a known excess of sodium hydroxide and titrate back with acid; (i.) gives actual amount of acid and (ii.) of anhydride (Philip, Collegium, 1906, 88; Kunz, Chem. Zentr. 1901, i. 791). Other methods, *v.* Ulzer and Seidel, Monatsh. 18, 138; Paessler, Collegium, 1907, 388, 396. Estimation in wines, *v.* Kunz, Chem. Soc. Abstr. 1901, ii. 700; 1903, ii. 701; Sostegni and Prandi, Chem. Zentr. 1903, ii. 469; Müller, Bull. Soc. chim. 1896, 15, [iii.] 1203; Parthiel, Chem. Soc. Abstr. 1903, ii. 189; Arch. Pharm. 241, 401; Paris, Chem. Zentr. 1908, i. 773; Trummer, Chem. Zentr. 1908, ii. 101; Heiduschka and Quincke, Arch. Pharm. 245, 458. In milk, *v.* Thörner, Chem. Zeit. 16, 1469, 1519. In urine, *v.* Proc. Physiol. Soc. 1909, v.–vii.; J. Physiol. 39. In gastric juice, *v.* De Jong, Chem. Zentr. 1896, ii. 806.

Technical uses.—Lactic acid is used by the woollen dyer as an assistant in mordanting with potassium dichromate and its advantages over tartaric and oxalic acids are its greater reducing power, the greater solubility of itself and its salts, and the fact that it is less corrosive. It gives the wool a very fine, soft 'handle' and a beautiful lustre. *Lactolin,* which consists of equal parts of lactic acid and potassium lactate is stated to be superior to lactic acid, which is in itself superior to tartar (Claflin, *l.c.*; Norton and Tuttle, J. Soc. Chem. Ind. 1891, 362; Hoffmann, *ibid.* 1896, 196, 540; Dreher, *ibid.* 1896, 448; 1898, 1070; 1899, 491; Kielmeyer, *ibid.* 1899, 368; Kapff, *ibid.* 1900, 659; Fuchs, Chem. Zentr. 1897, i. 1183; Archer, J. Soc. Chem. Ind. 1897, 140; Düring, Bull. Soc. Ind. Mulhouse, 1902, [v.] 3; Paessler and Appelius, Collegium, 1903, 152, 153, 164, 169). Aniline lactate is used in producing aniline black on cotton (Goldovsky, Bull. Soc. Ind. Mulhouse, Jan. 9, 1900; Schener and Schoellkopf, *ibid.* 1901, 102; Düring, Chem. Zentr. 1905, i. 1515; D. R. P. 96600; J. Soc. Chem. Ind. 1899, 1119). The double lactate of calcium and antimony is used in mordanting cotton, and as a substitute for glycerin and tartaric acid in printing fabrics (Dreher, J. Soc. Chem. Ind. 1898, 919, 921). For methods of obtaining double lactates of antimony and calcium or of antimony and alkalis or alkaline earths, *v.* Moritz, Zeitsch. angew. Chem. 17, 1143; Akt. Ges. Revaler Chem. Fab. R. Mayer, D. R. P. 136135; Chem. Zentr. 1902, ii. 1286; Ch. Fab. von Heyden, D. R. P. 184202; Chem. Soc. Abstr. 1907, i. 888; Boehringer, D. R. P. 98939; Chem. Zentr. 1898, ii. 1231; Ch. Werke Schuster and Wilhelmj, D. R. PP. 216158, 217806; Chem. Zentr. 1909, ii. 1908; 1910, i. 701.

A solution containing the lactates of aluminium, calcium, and tin has been used instead of the above (Oswald, Bull. Soc. Ind. Mulhouse, 1900, 343), whilst Boehringer (D. R. P. 91230; Chem. Zentr. 1897, i. 1189) employs zinc lactate for the same purpose. Lactolin and sulphuric acid are used in hat dyeing (Düring, J. Soc. Chem. Ind. 1900, 660; 1901, 470) and lactic acid, free from traces of iron, is used as a discharge for Turkey red (Düring, *ibid.* 1900, 1013). It has also been used as a solvent for dyestuffs insoluble in water (Dreher, *ibid.* 1897, 1014; 1898, 919, 921).

Lactic acid is used in tanning for colouring, bating, and plumping. In preparing the skins it completely removes the lime, ensures a fine even grain, and does not dissolve the hide substance. It is easier to control than the bran drench, which is also used for this purpose, and which owes its efficiency to the lactic acid produced during the fermentation of the bran (Claflin, J. Soc. Chem. Ind. 1901, 210, 596, 730, 913; Paessler and Appelius, *ibid.* 1902, 1461, 57; 1903, 1201). It is also used in the preparation of yeast (Büchler, *ibid.* 1901, 376) and in the distillery, *e.g.* to check the bacterial development in the 'Hefengut' mash (Moritz, *ibid.* 1899, 778).

Lactic acid is also used for medicinal purposes in cases of laryngeal tuberculosis and of infantile diarrhœa. It dissolves false membrane and a solution of 1 part of acid in 6 parts of water is employed in the local treatment of diphtheria and croup. Local applications are used in stopping the growth of venereal worts and in treatment of tuberculous ulcers, lupus, and epithelioma. Calcium lactate is used in the treatment of rheumatism. For pharmaceutical purposes, the acid must be colourless and inodorous, and have a sp.gr. of at least 1·21, and should leave scarcely any residue on ignition. It should not be affected by NH_3 and $(NH_4)_2S$, and should give, at most, only a faint opalescence with $BaCl_2$, $AgNO_3$, $(NH_4)_2C_2O_4$, and should give no precipitate on boiling with Fehling's solution.

Esters. The esters of lactic acid may be prepared by treating a salt of lactic acid with sulphuric acid or gaseous hydrogen chloride and the corresponding alcohol. The product is distilled *in vacuô,* whereby the pure ester is obtained. By treating the pure ester with steam, distilling off the alcohol and concentrating, the pure acid is obtained (Ch. Fab. Güstrow, Hillringhaus and Heilmann, D. R. P. 171835; Chem. Zentr. 1906, ii. 470).

Methyl ester. Colourless liquid, b.p. 144·8°; sp.gr. 1·0898 at 19° (Schreiner, Annalen, 197, 12).

Ethyl ester. Colourless liquid, b.p. 154–5°; sp.gr. 1·0308 at 19° (Schreiner, *l.c.*; Friedel and Wurz, Ann. Chim. Phys. [iii.] 63, 102; Brüggen, Annalen, 148, 227).

Ethylidene ester. Prepared by heating acetaldehyde and lactic acid at 120°–170° for some hours: colourless liquid, b.p. 150°–151·5° (Leipen, Monatsh. 9, 45).

Glyceryl mono- and di-lactates (*v.* Kalle & Co. D. R. P. 216917; Chem. Zentr. 1910, i. 214).

Salts. The salts of lactic acid are all soluble in water, many so readily that they are very difficult to obtain crystalline. They are obtained by direct neutralisation of the free acid, or by double decomposition from the calcium salt.

The K, Na, NH_4 salts are very hygroscopic, and only the last two have been obtained crystalline (Wislicenus, Annalen, 125, 49; Engelhardt and Maddrell, *ibid.* 63, 88; Brüning, *ibid.* 104, 192).

Calcium lactate $(C_3H_5O_3)_2Ca,5H_2O$ is usually obtained direct from sugar in the preparations of lactic acid (*v. supra*). In small quantities it is sometimes prepared by neutralising lactic acid with chalk. It forms cauliflower-like aggregates of microscopic rhombic needles, which are soluble in 9·5 parts of cold, much more readily in hot water, and also soluble in alcohol. It loses its water of crystallisation at 100°, and at 250°–275° loses another molecule of water, forming *calcium dilactate* $(CH_3{\cdot}CH)_2{\cdot}O(CO_2)_2Ca$. The product is a vesicular mass, from which alcohol extracts some unaltered calcium lactate, and leaves the new compound behind as a very slightly soluble substance (Friedel and Würtz, Ann. Chim. Phys. [iii.] 63, 114).

Barium lactate $(C_3H_5O_3)_2Ba,4H_2O$ crystallises with great difficulty, forming cauliflower-like aggregates. It does not lose all its water of crystallisation at 100° (Meyer, Ber. 1886, 2454).

Magnesium lactate $(C_3H_5O_3)_2Mg,3H_2O$ is prepared by dissolving lactic acid syrup in 10 times its bulk of water, and neutralising with basic magnesium carbonate. The solution is evaporated until a skin forms, and then allowed to crystallise. It forms small light prismatic crystals, which frequently unite to form crusts. It dissolves in 28 parts of cold and 6 parts of hot water, forming a neutral very bitter solution. It loses its water of crystallisation at 100°.

Zinc lactate $(C_3H_5O_3)_2Zn,3H_2O$ is best obtained direct from sugar by neutralising the lactic acid produced with zinc carbonate or zinc white (Lautemann, Annalen, 113, 142; Kiliani, Ber. 1882, 659). It crystallises better than any other lactate, and forms colourless, well-developed, four-sided rhombic prisms. It loses its water of crystallisation *in vacuô* or at 100°. It dissolves in 53 parts of water at 15°, and in 6 parts at 100°, forming an acid, bitter-tasting solution. It is very slightly soluble in alcohol (Strecker, Annalen, 105, 316).

Ferrous lactate $(C_3H_5O_3)_2Fe,3H_2O$. This salt was introduced into pharmacy by Gélis and Conté in 1840, and was again recommended in 1847 by Engelhardt and Maddrell (*l.c.*). It is best prepared from crude calcium lactate in the following manner. The crude salt is recrystallised from water to which a little lime has been added, and if necessary the operation repeated. To the conc. aqueous solution of the purified salt the theoretical quantity of ferrous chloride is added, and the mixture allowed to stand for 3 days in a cool place. When no more crystals form the precipitated salt is filtered off, washed with a little alcohol, and dried at 50°.

Ferrous lactate forms greenish-white crusts of needles, or a similarly coloured crystalline powder. It dissolves at the ordinary temperature in 48 parts, and at 100° in 12 parts of water, forming an acid solution with a sweetish chalybeate taste. The solution becomes yellow, and then brown, in the air, ferric lactate being formed, and also undergoes alteration on evaporation in the air, leaving a hygroscopic residue containing ferrous and ferric lactates and some free acid. The dry salt is unaltered in the air, and loses its water of crystallisation when heated at 100° in a current of hydrogen.

Silver lactate $C_3H_5O_3Ag,\frac{1}{2}H_2O$ is prepared by treating freshly prepared lactic acid, after cooling, with silver oxide, evaporating the solution in the dark *in vacuô* at the ordinary temperature. It forms colourless needles, soluble in 20 parts of cold water, insoluble in cold, but readily soluble in hot alcohol. On heating the salt in the dark for 3 hours at 80°, anhydrous silver lactate is obtained (Klimenko, J. Russ. Chem. Soc. 12, 97; Berthelot and Delépine, Compt. rend. 129, 920).

Bismuth lactate $BiC_6H_9O_6,7H_2O$ is prepared by the slow dissolution of freshly precipitated bismuth hydroxide in lactic acid slightly diluted with water. The solution gradually deposits needles of the hydrated salt; on heating to 105° this yields the anhydrous salt, which is very sparingly soluble in water. The latter may be obtained by digesting freshly precipitated bismuth hydroxide in lactic acid at 100°. It forms rhombic tablets which decompose slightly when boiled with water for some time (Telle, Arch. Pharm. 1908, 246, 484).

Mercury lactates. *Mercurous lactate*

$$(C_3H_5O_3)_2Hg,HgO$$

is prepared by dissolving freshly precipitated mercurous oxide in dilute lactic acid, which has previously been heated with water to destroy the anhydride which it contains. The solution is allowed to evaporate in a desiccator over sulphuric acid, when the salt separates in short white prismatic needles. It is not completely soluble in water, hydrolysis occurring with the formation of a basic lactate, which then decomposes into mercuric lactate and mercury. *Mercuric lactate* $(C_3H_5O_3)_2Hg$, prepared in a similar manner from lactic acid and mercuric oxide, forms colourless prismatic needles, readily soluble in water. On boiling the aqueous solution, mercurous lactate, acetaldehyde, lactic acid, and carbon dioxide are produced (Guerbet, Bull. Soc. chim. 1902, 27, [iii.] 803).

Glucinium lactate (*v.* Tanatar and Kurowski, J. Russ. Phys. Chem. Soc. 39, 936; Glassmann, Ber. 1908, 33).

Cerous lactate (*v.* Morgan and Cahen, Pharm. J. 1907, 78, 428).

Optically active acids. As has already been stated, lactic acid can be resolved into two optically active components. This resolution has been effected by the fractional crystallisation of zinc ammonium lactate (Purdie and Walker, Chem. Soc. Trans. 1893, 1143; 1895, 616); of the strychnine salts (Purdie and Walker, *ibid.* 1892, 754); morphine salts (Irvine, *ibid.* 1906, 935); and of the quinine salts (Jungfleisch, Compt. rend. 1904, 139, 56, 203; 1905, 140, 719; 1906, 142, 515). Asymmetric syntheses have been made by the reduction of the *l*-menthyl (McKenzie, Chem. Soc. Trans. 1905, 1373), *l*-bornyl (McKenzie and Wren, *ibid.* 1906, 688), and *d*-amyl (McKenzie and Müller, *ibid.* 1909, 544) salts of pyruvic acid.

Paralactic acid (Sarcolactic acid, *d*-lactic acid) is present in flesh, in the blood, in muscles, in the thymus and thyroid and other animal organs (Berlinbauer, Chem. Zentr. 1888, 757; Salomon, Chem. Soc. Abstr. 1889, 64; Asker and Jackson, Zeit. Biol. 41, 393; Moscatelli, Zeitsch. physiol. Chem. 12, 416; Griffiths, Chem. News, 91, 147; Werther, Chem. Soc. Abstr. 1890, 348; Inouye and Kondo, Zeitsch. physiol. Chem. 54, 481; Frew, *ibid.* 60, 15; Moriya, *ibid.* 43, 397).

It is obtained from extract of meat by dissolving in 4 parts of warm water, adding 3 times the volume of 90 p.c. alcohol, and evaporating the filtrate to a syrup. This is again precipitated with alcohol, filtered, and evaporated, then acidified with H_2SO_4, and extracted with ether (Wislicenus, Annalen, 167, 302). The crude acid may be purified by conversion into the zinc salt. If *Penicillium glaucum* is allowed to grow in the solution of the inactive ammonium lactate, the *d*- modification alone will remain (Lewkowitsch, Ber. 1883, 2720; Linossier, Bull. Soc. chim. [iii.] 6, 10). *Micrococcus acidi paralacti*, an anaërobic micrococcus formed in the preparation of the *Rauschbrand bacillus*, is found to convert sugar into paralactic acid (Nencki and Sieber, Monatsh. 10, 532).

Paralactic acid is a syrup which can only be distinguished from lactic acid by the fact that it rotates the plane of polarisation to the right, whereas lactic acid is inactive. The salts strongly resemble the lactates, but are somewhat more soluble in water. The methyl ester boils at 143°–145° and has sp.gr. 1·1017 at 15°/16°; and the ethyl ester, b.p. 152°–154°, sp.gr. 1·0414 at 15°/16° (Frankland, Chem. Soc. Proc. 1895, 54). Further details as to rotatory power of acid and derivatives, *v.* Walker, Chem. Soc. Trans. 1895, 914; Purdie and Williamson, *ibid.* 1896, 827; Guye and Melikian, Compt. rend. 123, 1291; Henderson and Prentice, Chem. Soc. Trans. 1902, 658; 1903, 259; Wassmer and Guye, J. Phys. Chem. 1903, i. 257; Purdie and Irvine, Chem. Soc. Trans. 1899, 484; Walker, J. Phys. Chem. 13, 574.

l-**Lactic acid** has not been found in nature. It is prepared by the resolution of the inactive acid (*q.v.*); by the fermentation of sugar with *Bacillus acidi lævolacti* (Schardinger, Monatsh. 11, 545) or with a lævolactic ferment obtained from pears (Tate, Chem. Soc. Trans. 1893, 1263). It is similar in properties to *d*-lactic acid, with the exception that it rotates the plane of polarisation to the left.

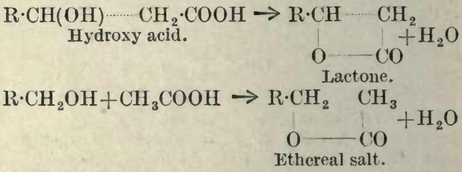
Besides these acids, another isomeric acid remains to be described. *Hydracrylic acid, ethylene-lactic acid* or *β-hydroxypropionic acid* $CH_2(OH)CH_2CO_2H$ is prepared by the action of moist silver oxide on β-iodopropionic acid (Sokolow, Annalen, 150, 167; Wislicenus, Annalen, 166, 10); by heating the sodium salt of acrylic acid with sodium hydroxide at 100° (Linnemann, Ber. 1875, 1095); and by the action of prussic acid on ethylene chlorhydrin and saponification of the resulting nitrile (Wislicenus, Annalen, 128, 1; 167, 346; Erlenmeyer, *ibid.* 191, 268). It forms a syrup which decomposes into water and acrylic acid on heating. Chromic acid oxidises it into oxalic acid and carbon dioxide, and silver oxide converts it into glycollic acid. Wislicenus also obtained from flesh, in addition to paralactic acid, an acid which he believed to be identical with this ethylene-lactic acid, but it has been shown (Siegfried, Ber. 1889, 2713) that this is in reality *acetyllactic acid.*

Atrolactinic acid (*αα-phenylhydroxypropionic acid*) $CH_3{\cdot}C(C_6H_5)OH{\cdot}CO_2H$. Prepared by the action of fuming hydrochloric acid on acetophenone hydrocyanide (Spiegel, Ber. 1881, 14, 1353; Tiemann and Köhler, *ibid.* 1980); colourless needles, m.p. (anhydrous) 93°–94°.

LACTIC FERMENTATION GUM *v.* GUMS.

LACTOLIN. Trade name for potassium di-lactate used as a mordant.

LACTONES. Generally speaking a lactone is formed by the elimination of water from a hydroxyl group and a carboxyl group present in the same molecule. They may therefore be regarded as internal salts corresponding with the external salts which are known as the ethereal salts or esters:



$$R{\cdot}CH(OH)\text{······}CH_2{\cdot}COOH \rightarrow \begin{array}{c} R{\cdot}CH\text{······}CH_2 \\ |\qquad\quad| \\ O\text{——}CO \end{array} + H_2O$$

$$R{\cdot}CH_2OH + CH_3COOH \rightarrow \begin{array}{c} R{\cdot}CH_2\quad CH_3 \\ |\qquad\quad| \\ O\text{——}CO \end{array} + H_2O$$

The lactones are therefore derived from that class of organic compounds known as the hydroxy acids. The hydroxy acids are divided into several series depending on the position of the hydroxyl group in respect to the carboxyl group and are named α-, β-, γ-, &c., hydroxy acids according as the hydroxyl group is in the α-, β-, γ-, &c., position in respect to the acid group, thus:

$R{\cdot}CH(OH){\cdot}COOH$
(α) — α-Hydroxy acid

$R{\cdot}CH(OH){\cdot}CH_2{\cdot}COOH$
(β) (α) — β-Hydroxy acid

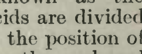
$R{\cdot}CH(OH){\cdot}CH_2{\cdot}CH_2{\cdot}COOH$
(γ) (β) (α) — γ-Hydroxy acid

$R{\cdot}CH(OH){\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}COOH$
(δ) (γ) (β) (α) — δ-Hydroxy acid

$R{\cdot}CH(OH){\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}COOH$
(ε) (δ) (γ) (β) (α) — ε-Hydroxy acid

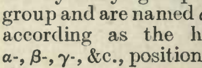
$R{\cdot}CH(OH){\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2COOH$
(ζ) (ε) (δ) (γ) (β) (α)—ζ-Hydroxy acid

The lactones derived from these acids are named accordingly α-, β-, γ-, &c., lactones and thus a γ-lactone would be constituted



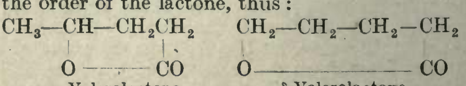
$$\begin{array}{c} R{\cdot}CH{\cdot}CH_2CH_2 \\ |\qquad\qquad| \\ O\text{——}CO \end{array}$$

and a δ-lactone would have the structure



$$\begin{array}{c} R{\cdot}CH{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2. \\ |\qquad\qquad\qquad| \\ O\text{————}CO \end{array}$$

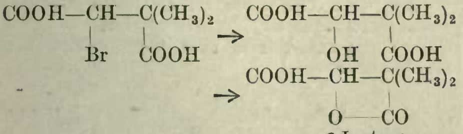
Nomenclature.—The name of the lactones is usually taken from the trivial name of the acid from which the corresponding hydroxy acid is derived, as for example, butyrolactone from γ-hydroxybutyric acid, valerolactone from γ-hydroxyvaleric acid. In those cases where the formation of two isomeric lactones is possible the prefix γ- or δ- is added to indicate the order of the lactone, thus:



$$\begin{array}{c} CH_3\text{—}CH\text{—}CH_2CH_2 \\ |\qquad\quad| \\ O\text{——}CO \end{array} \qquad \begin{array}{c} CH_2\text{—}CH_2\text{—}CH_2\text{—}CH_2 \\ |\qquad\qquad\qquad\qquad| \\ O\text{————————}CO \end{array}$$

γ-Valerolactone. δ-Valerolactone.

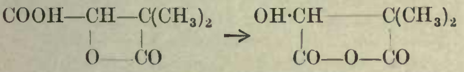
α-Lactones are not known, and in only a few exceptional cases has the formation of β-lactones been observed. Thus Baeyer and Villiger (Ber. 1897, 30, 1954; compare also Fichter and Hirsch, *ibid.* 1900, 33, 3273) have shown that when α-bromo-α′α′-dimethylsuccinic acid is treated with moist silver oxide the β-lactone of dimethylmalic acid is formed:



$$\underset{\mathrm{Br}\quad\ \mathrm{COOH}}{\mathrm{COOH{-}CH{-}C(CH_3)_2}} \rightarrow \underset{\mathrm{OH}\quad\ \mathrm{COOH}}{\mathrm{COOH{-}CH{-}C(CH_3)_2}} \rightarrow \underset{\mathrm{O}\ \text{——}\ \mathrm{CO}}{\mathrm{COOH{-}CH{-}C(CH_3)_2}}$$

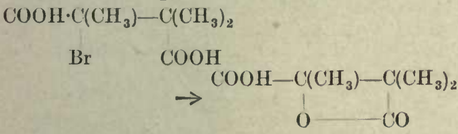
β-Lactone.

This compound crystallises in rhombic plates containing 1 mol. of water, and melts at 54°–55°; it loses this water of crystallisation at 45° in a vacuum. When distilled under diminished pressure it passes by rearrangement into the anhydride of αα-dimethylmalic acid

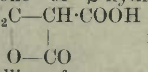


$$\underset{\mathrm{O}\ \text{—}\ \mathrm{CO}}{\mathrm{COOH{-}CH{-}C(CH_3)_2}} \rightarrow \underset{\mathrm{CO{-}O{-}CO}}{\mathrm{OH{\cdot}CH\ \text{——}\ C(CH_3)_2}}$$

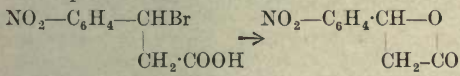
In the same way, trimethylbromosuccinic acid is converted into the β-lactone of trimethylmalic acid (Komppa, Ber. 1902, 35, 534)



$$\underset{\mathrm{Br}\qquad\quad \mathrm{COOH}}{\mathrm{COOH{\cdot}C(CH_3){-}C(CH_3)_2}} \rightarrow \underset{\mathrm{O}\ \text{———}\ \mathrm{CO}}{\mathrm{COOH{-}C(CH_3){-}C(CH_3)_2}}$$

The formation of a similar compound has been recorded by Meldrum (Chem. Soc. Trans. 1908, 93, 598) who finds that when acetone is condensed with malonic acid in the presence of acetic anhydride containing a little sulphuric acid, the β-lactone of β-hydroxy*iso*propylmalonic acid  $\underset{\mathrm{O{-}CO}}{\mathrm{(CH_3)_2C{-}CH{\cdot}COOH}}$ is formed. This substance crystallises from acetone in transparent four-sided plates melting at 97°.

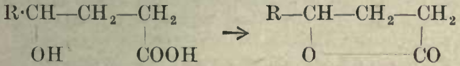
β-Lactone formation occurs in the aromatic series from β-hydroxy acids having a phenyl-group, in which strongly negative groups are present, attached to the β-carbon atom. Thus the lactones of *o*-, *m*-, and *p*-nitrophenyl-β-lactic acids are formed when the corresponding nitrophenyl-β-bromopropionic acids are treated with cold aqueous sodium carbonate



$$\underset{\mathrm{CH_2{\cdot}COOH}}{\mathrm{NO_2{-}C_6H_4{-}CHBr}} \rightarrow \underset{\mathrm{CH_2{-}CO}}{\mathrm{NO_2{-}C_6H_4{\cdot}CH{-}O}}$$

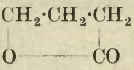
o-Nitrophenyllactic acid lactone readily passes into indigo when boiled with glacial acetic acid.

γ-Lactones. The remarkable tendency which exists for the formation of the five-membered ring causes the γ-hydroxy acids to be, usually, unstable at the ordinary temperature and to pass, with elimination of water, into the γ-lactone

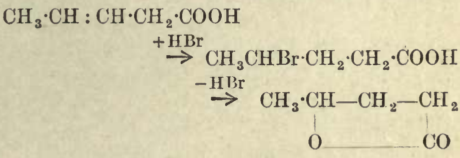


$$\underset{\mathrm{OH}\qquad\quad \mathrm{COOH}}{\mathrm{R{\cdot}CH{-}CH_2{-}CH_2}} \rightarrow \underset{\mathrm{O}\ \text{———}\ \mathrm{CO}}{\mathrm{R{-}CH{-}CH_2{-}CH_2}}$$

γ-Hydroxy acid. γ-Lactone.

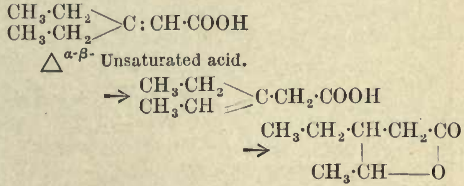
The tendency for the formation of the inner anhydride is so great that the change from the hydroxy acid to the lactone is usually effected by merely raising the temperature of an aqueous solution of the acid and in many cases the lactone exists in aqueous solution at the ordinary temperature. The simplest member of the class, butyrolactone  $\underset{\mathrm{O}\ \text{——}\ \mathrm{CO}}{\mathrm{CH_2{\cdot}CH_2{\cdot}CH_2}}$, was discovered by Saitzew in 1873, although certain naturally occurring lactones, such as coumarin and meconine (*q.v.*), were known before that time. (For a general description of the lactones, compare E. Hzelt, Ahrens' Samm. 1903, 8, 83.)

Formation.—The methods usually adopted for the preparation of γ-hydroxy acids, that is of the γ-lactones, may be briefly summarised as follows: (1) The transformation of the $\Delta^{\beta.\gamma.}$ unsaturated acids by the addition of halogen hydride and its subsequent elimination thus:



$$\mathrm{CH_3{\cdot}CH:CH{\cdot}CH_2{\cdot}COOH} \xrightarrow{+\mathrm{HBr}} \mathrm{CH_3CHBr{\cdot}CH_2{\cdot}CH_2{\cdot}COOH} \xrightarrow{-\mathrm{HBr}} \underset{\mathrm{O}\ \text{————}\ \mathrm{CO}}{\mathrm{CH_3{\cdot}CH{-}CH_2{-}CH_2}}$$

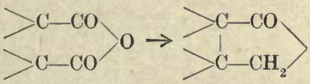
The $\Delta^{\beta.\gamma.}$ unsaturated acids are also transformed into the γ-lactones either by merely heating them alone or by warming them with a mixture of equal volumes of concentrated sulphuric acid and water at 140° (Fittig, Ber. 1894, 27 2667; Annalen, 1894, 283, 51). In the latter instance, the same change is shown by those $\Delta^{\alpha.\beta.}$ unsaturated acids which have two alkyl groups on the β-carbon atom. Thus Fichter, Kiefer, and Bernoulli (Ber. 1909, 42, 4710) find that when ββ-diethylacrylic acid is warmed for a short time with 60 p.c. aqueous sulphuric acid, it is converted into β-ethyl-γ-valerolactone



$$\begin{matrix}\mathrm{CH_3{\cdot}CH_2}\\ \mathrm{CH_3{\cdot}CH_2}\end{matrix}\!\!>\mathrm{C:CH{\cdot}COOH} \quad \Delta^{\alpha\text{-}\beta\text{-}}\ \text{Unsaturated acid.} \rightarrow \begin{matrix}\mathrm{CH_3{\cdot}CH_2}\\ \mathrm{CH_3{\cdot}CH}\end{matrix}\!\!>\mathrm{C{\cdot}CH_2{\cdot}COOH} \rightarrow \underset{\mathrm{CH_3{\cdot}CH}\ \text{——}\ \mathrm{O}}{\mathrm{CH_3{\cdot}CH_2{\cdot}CH{\cdot}CH_2{\cdot}CO}}$$

γ-Lactone.

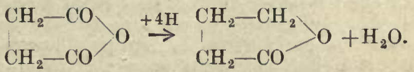
(2) The relation between the anhydrides of the dibasic acids and the γ-lactones, which is illustrated by the expression:



$$\begin{matrix}>\mathrm{C{-}CO}\\ >\mathrm{C{-}CO}\end{matrix}\!\!>\mathrm{O} \rightarrow \begin{matrix}>\mathrm{C{-}CO}\\ >\mathrm{C{-}CH_2}\end{matrix}\!\!>$$

Anhydride. γ-Lactone.

indicates that the last-named compounds can be derived from the anhydrides by reduction. Thus butyrolactone is formed when succinic anhydride is reduced by sodium amalgam (Fichter and Herbrand, Ber. 1896, 29, 1192):

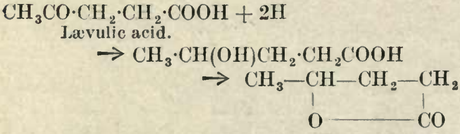


$$\begin{matrix}\mathrm{CH_2{-}CO}\\ \mathrm{CH_2{-}CO}\end{matrix}\!\!>\mathrm{O} \xrightarrow{+4\mathrm{H}} \begin{matrix}\mathrm{CH_2{-}CH_2}\\ \mathrm{CH_2{-}CO}\end{matrix}\!\!>\mathrm{O} + \mathrm{H_2O}.$$

Succinic anhydride. Butyrolactone.

(3) The sodium salts of γ-hydroxy acids are also formed when γ-ketonic acids, such as

lævulic acid, are reduced by sodium amalgam, thus:



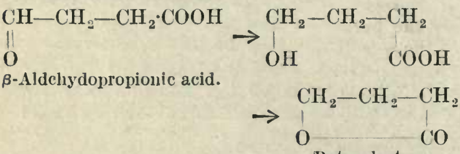
$$\underset{\text{Lævulic acid.}}{\mathrm{CH_3CO{\cdot}CH_2{\cdot}CH_2{\cdot}COOH}} + 2\mathrm{H}$$

$$\rightarrow \mathrm{CH_3{\cdot}CH(OH)CH_2{\cdot}CH_2COOH}$$

$$\rightarrow \begin{array}{ccccccc}\mathrm{CH_3}&—&\mathrm{CH}&—&\mathrm{CH_2}&—&\mathrm{CH_2}\\ &&|&&&&|\\ &&\mathrm{O}&—&—&—&\mathrm{CO}\end{array}$$

γ-Valerolactone.

In a similar manner, β-aldehydo acids, for example, β-aldehydopropionic acid, yield γ-lactones when reduced.



$$\begin{array}{l}\mathrm{CH—CH_2—CH_2{\cdot}COOH}\\ \|\\ \mathrm{O}\end{array} \rightarrow \begin{array}{ccccc}\mathrm{CH_2}&—&\mathrm{CH_2}&—&\mathrm{CH_2}\\ |&&&&|\\ \mathrm{OH}&&&&\mathrm{COOH}\end{array}$$

β-Aldehydopropionic acid.

$$\rightarrow \begin{array}{ccccc}\mathrm{CH_2}&—&\mathrm{CH_2}&—&\mathrm{CH_2}\\ |&&&&|\\ \mathrm{O}&—&—&—&\mathrm{CO}\end{array}$$

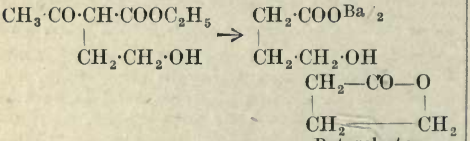
Butyrolactone.

(4) The alkyl salts of γ-hydroxy acids may be formed by the condensation of chlorhydrins of the type $\mathrm{CH_2Cl\,CH_2OH}$ with the sodium compounds of ethyl acetoacetate and its homologues, thus:

$$\mathrm{CH_3{\cdot}CO{\cdot}CHNa{\cdot}COOC_2H_5 + CH_2Cl{\cdot}CH_2OH}$$

$$\rightarrow \mathrm{CH_3{\cdot}CO\,CH(COOC_2H_5)CH_2{\cdot}CH_2OH + NaCl}$$

When this ethyl salt is hydrolysed with baryta, the acetyl group is eliminated and the barium salt of the hydroxy acid, which is then formed, is converted into the γ-lactone by the action of dilute mineral acids:

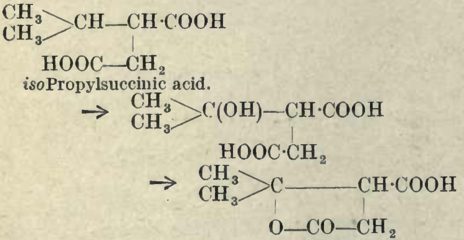


$$\begin{array}{l}\mathrm{CH_3{\cdot}CO{\cdot}CH{\cdot}COOC_2H_5}\\ \qquad\quad |\\ \qquad\mathrm{CH_2{\cdot}CH_2{\cdot}OH}\end{array} \rightarrow \begin{array}{l}\mathrm{CH_2{\cdot}COO^{Ba}/_2}\\ |\\ \mathrm{CH_2{\cdot}CH_2{\cdot}OH}\end{array}$$

$$\begin{array}{ccccc}\mathrm{CH_2}&—&\mathrm{CO}&—&\mathrm{O}\\ |&&&&|\\ \mathrm{CH_2}&—&—&—&\mathrm{CH_2}\end{array}$$

Butyrolactone.

(5) The formation of certain γ-lactones may also be effected by taking advantage of the fact that the tertiary hydrogen atom of the system $\begin{matrix}\mathrm{CH_3}\\ \mathrm{CH_3}\end{matrix}\!\!>\!\overset{*}{\mathrm{C}}\mathrm{H}—$ is readily oxidised to hydroxyl by alkaline permanganate. Thus *iso*propyl-succinic acid passes on oxidation into terebic acid (Lawrence, Chem. Soc. Trans. 1899, 75, 527).



$$\begin{array}{l}\begin{matrix}\mathrm{CH_3}\\ \mathrm{CH_3}\end{matrix}\!\!>\!\mathrm{CH—CH{\cdot}COOH}\\ \qquad\qquad\quad |\\ \qquad\mathrm{HOOC—CH_2}\end{array}$$

*iso*Propylsuccinic acid.

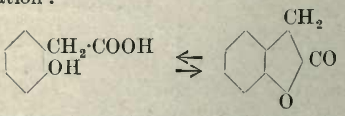
$$\rightarrow \begin{array}{l}\begin{matrix}\mathrm{CH_3}\\ \mathrm{CH_3}\end{matrix}\!\!>\!\mathrm{C(OH)—CH{\cdot}COOH}\\ \qquad\qquad\qquad\quad |\\ \qquad\quad\mathrm{HOOC{\cdot}CH_2}\end{array}$$

$$\rightarrow \begin{matrix}\mathrm{CH_3}\\ \mathrm{CH_3}\end{matrix}\!\!>\!\begin{array}{ccccc}\mathrm{C}&—&—&—&\mathrm{CH{\cdot}COOH}\\ |&&&&|\\ \mathrm{O}&—&\mathrm{CO}&—&\mathrm{CH_2}\end{array}$$

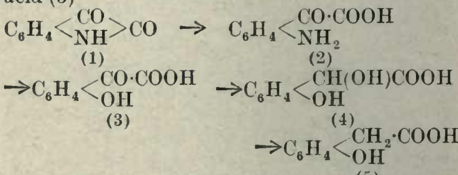
Terebic acid.

(6) The methods of formation of γ-lactones of the aromatic series are similar to those employed with aliphatic compounds, but for the sake of convenience the substances belonging to this class may be divided into three sections. (*a*) The γ-lactones which are derived from hydroxy acids having the hydroxyl group in the ortho- position in the benzene nucleus to a side chain bearing a carboxyl group. (*b*) The γ-lactones which are formed when both the hydroxyl and carboxyl groups are attached to the side chain. (*c*) The γ-lactones formed from compounds having the hydroxyl group in the side chain and the carboxyl group attached to the ortho- position in the benzene nucleus.

o-Hydroxyphenylacetic acid may be given as an illustration of compounds included under section (*a*). This acid, unlike the γ-hydroxy acids of the aliphatic series, can be isolated in the free state, but passes into the γ-lactone on distillation:



The lactone is again converted into the acid on shaking with water. The method employed for the preparation of *o*-hydroxyphenylacetic acid is as follows (Baeyer and Fritsch, Ber. 1884, 17, 973; compare also Stoermer, Annalen, 1900, 313, 83; Ber. 1901, 34, 1807). Isatin (1) is converted into *o*-aminobenzoylformic acid, (2) by the action of alkali, and this substance is then converted into *o*-hydroxybenzoylformic acid (3) by the aid of the diazo reaction. Reduction with sodium amalgam converts this compound into α-hydroxy-α-*o*-hydroxyphenylacetic acid, (4) which, on reduction with hydriodic acid, yields *o*-hydroxyphenylacetic acid (5)



$$\underset{(1)}{\mathrm{C_6H_4}\!<\!\begin{matrix}\mathrm{CO}\\ \mathrm{NH}\end{matrix}\!>\!\mathrm{CO}} \rightarrow \underset{(2)}{\mathrm{C_6H_4}\!<\!\begin{matrix}\mathrm{CO{\cdot}COOH}\\ \mathrm{NH_2}\end{matrix}}$$

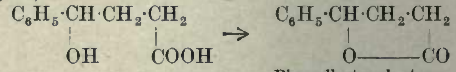
$$\rightarrow \underset{(3)}{\mathrm{C_6H_4}\!<\!\begin{matrix}\mathrm{CO{\cdot}COOH}\\ \mathrm{OH}\end{matrix}} \rightarrow \underset{(4)}{\mathrm{C_6H_4}\!<\!\begin{matrix}\mathrm{CH(OH)COOH}\\ \mathrm{OH}\end{matrix}}$$

$$\rightarrow \underset{(5)}{\mathrm{C_6H_4}\!<\!\begin{matrix}\mathrm{CH_2{\cdot}COOH}\\ \mathrm{OH}\end{matrix}}$$

Under section (*b*) may be given, as illustration, the example of γ-phenyl-γ-hydroxybutyric acid, $\mathrm{C_6H_5{\cdot}CH(OH)CH_2{\cdot}CH_2{\cdot}COOH}$, which can be produced by the reduction of β-benzoylpropionic acid

$$\mathrm{C_6H_5{\cdot}CO{\cdot}CH_2{\cdot}CH_2{\cdot}COOH},$$

and by other methods. Although this substance is more stable than the corresponding γ-hydroxy acids of the aliphatic series, and can be isolated in the free state, it nevertheless passes into the γ-lactone when heated above its melting-point (75°).

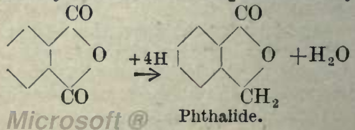


$$\begin{array}{ccc}\mathrm{C_6H_5{\cdot}CH}&\mathrm{{\cdot}CH_2{\cdot}}&\mathrm{CH_2}\\ |&&|\\ \mathrm{OH}&&\mathrm{COOH}\end{array} \rightarrow \begin{array}{ccc}\mathrm{C_6H_5{\cdot}CH}&\mathrm{{\cdot}CH_2{\cdot}}&\mathrm{CH_2}\\ |&&|\\ \mathrm{O}&—&\mathrm{CO}\end{array}$$

Phenylbutyrolactone.

The hydroxy acid may be recrystallised from warm water, but at 80° lactone formation slowly occurs, and when the acid is treated with very dilute hydrochloric acid the transformation into the lactone (m.p. 37°) is complete even at low temperatures.

The γ-lactones included under section (*c*) are known as the *phthalides*, a name which is derived from that of the first member of the series, phthalide. Phthalide itself may be conveniently prepared by the reduction of phthalic anhydride



Phthalide.

Other methods of preparation will be found under the head of *Meconine* (*q.v.*).

General properties of γ-lactones.—As already mentioned, the γ-hydroxy acids of the aliphatic series are, for the most part, unstable, and therefore cannot be isolated in the free state. The corresponding γ-lactone separates in almost every case when the aqueous solution of the salt of the acid is acidified even at low temperatures, and in only one or two instances has it been found possible to isolate the hydroxy acid in the free condition. Thus Fittig and Chanlarow (Annalen, 1884, 226, 325, 334) found that γ-hydroxybutyric acid as well as its ethyl derivatives are stable at very low temperatures. The lactones titrate as monobasic acids, and the salts of the corresponding hydroxy acids can usually be isolated in the crystalline condition; the silver salts, which are mostly well-defined crystalline substances, can be readily obtained by double decomposition from the potassium salt.

The γ-lactones derived from the monohydroxy-mono-carboxylic acids of the aliphatic series, and which therefore have the general formula $C_nH_{2n-2}O_2$, are neutral, colourless liquids or low-melting solids which are volatile with steam, and can be distilled without decomposition under ordinary atmospheric pressure. The lower members of the series are miscible with water in all proportions, but the solubility decreases with increase of molecular weight. The less soluble γ-lactones are frequently characterised by possessing the curious property of being varyingly soluble in water; thus when a concentrated solution of the lactone is warmed, the solution becomes cloudy owing to the partial separation of the dissolved substance; the emulsion again clears above 80°. When the γ-lactones are dissolved in water, a partial conversion into the hydroxy acid takes place, and a state of equilibrium between the two compounds is attained. Thus it has been found by P. Henry (Zeitsch. physikal. Chem. 1892, 10, 96) that a boiling 1 p.c. solution of butyrolactone contains 80 p.c. of the lactone and 20 p.c. of the hydroxy acid. γ-Lactones frequently react with halogen hydrides, yielding the γ-halogen derivatives of the acid, thus:

$$\begin{array}{l} CH_2{\cdot}CH_2{\cdot}CH_2 \\ \vert \qquad\qquad \vert \;\; +HBr \rightarrow CH_2Br{\cdot}CH_2{\cdot}CH_2{\cdot}COOH \\ O\text{———}CO \end{array}$$

but the breaking of the lactone ring in this manner is usually more easily effected by heating the compound with an alcoholic solution of the halogen hydride, whereby the corresponding ester is formed (Henry, Compt. rend. 1886, 102, 368; Cloves, Annalen, 1901, 319, 362). When treated with aqueous ammonia in the cold, the γ-lactones yield the amide of the hydroxy acid, thus:

$$\begin{array}{l} CH_2\text{—}CH_2\text{—}CH_2 \\ \vert \qquad\qquad\quad \vert \;\; +NH_3 \\ O\text{————}CO \\ \qquad\qquad \rightleftarrows CH_2OH{\cdot}CH_2{\cdot}CH_2{\cdot}CONH_2. \end{array}$$

These compounds readily split off ammonia and pass again into the lactone (Fittig and Rasch, Annalen, 1890, 256, 151; Fittig and Dubois, *ibid.* 1890, 256, 153). The γ-lactones react with hydrazine (Blanc and Luttringer, Bull. Soc. chim. 1905, [iii.] 33, 1095) also with potassium cyanide (Wislicenus, Annalen, 1886, 233, 113; Blanc, Bull. Soc. chim. 1905, [iii.] 33, 886, 904).

The more important γ-lactones of the formula $C_nH_{2n-2}O_2$ are:

Butyrolactone $\begin{array}{l} CH_2\text{—}CO \\ \vert \qquad\quad >O \\ CH_2\text{—}CH_2 \end{array}$ Preparation method (3): boils at 204° and solidifies at −42°. It has sp.gr. 1·129 at 16°.

Valerolactones. γ-*Methylbutyrolactone* (*n-valerolactone*) $\begin{array}{l} CH_2\text{—}CO \\ \vert \qquad\quad >O \\ CH_2\text{—}CH{\cdot}CH_3 \end{array}$ Preparation from lævulic acid method (3); occurs in pyroligneous acid (crude acetic acid from the distillation of wood). It boils at 206°–207°, solidifies at −31°, and has sp.gr. 1·072 at 0°. The reduction of lævulic acid to the lactone is very readily effected by hydrogen at 250° (method of Sabatier and Senderens).

α-*Methylbutyrolactone* $\begin{array}{l} CH_3{\cdot}CH\text{—}CO \\ \vert \qquad\qquad >O \\ CH_2\text{—}CH_2 \end{array}$ is a pungent-smelling oil, boiling at 200°–202°.

Caprolactones. γ-*Ethylbutyrolactone* (*n-caprolactone*) $\begin{array}{l} CH_2\text{—}CO \\ \vert \qquad\quad >O \\ CH_2\text{—}CH.C_2H_5 \end{array}$ boils at 220°. α-*Ethylbutyrolactone* $\begin{array}{l} C_2H_5{\cdot}CH\text{—}CO \\ \vert \qquad\qquad >O, \\ CH_2\text{—}CH_2 \end{array}$ boils at 215°. αα-*Dimethylbutyrolactone* $\begin{array}{l} (CH_3)_2C\text{—}CO \\ \vert \qquad\qquad >O \\ CH_2CH_2 \end{array}$ boils at 200°–201°. αγ-*Dimethylbutyrolactone* $\begin{array}{l} CH_3{\cdot}CH\text{—}CO \\ \vert \qquad\qquad >O \\ CH_2\text{—}CH{\cdot}CH_3, \end{array}$ boils at 206°. βγ-*Dimethylbutyrolactone* $\begin{array}{l} CH_2\text{———}CO \\ \vert \qquad\qquad\quad >O \\ CH(CH_3)\text{—}CH{\cdot}CH_3, \end{array}$ boils at 213°, and γγ-*Dimethylbutyrolactone* (*isocaprolactone*) $\begin{array}{l} CH_2\text{—}CO \\ \vert \qquad\quad >O \\ CH_2\text{—}C(CH_3)_2, \end{array}$ boils at 95° (20 mm.), and at 206°–207° under ordinary atmospheric pressure. It melts at +6° and dissolves in 20 parts of water at 0°.

Stearolactone (γ-*tetradecylbutyrolactone*)

$$\begin{array}{l} CH_2\text{—}CO \\ \vert \qquad\quad >O \\ CH_2\text{—}CH(CH_2)_{13}CH_3 \end{array}$$

is formed, in yield of 30–40 p.c., when oleic acid, elaïdic acid, or *iso*-oleic acid is warmed with zinc chloride or concentrated sulphuric acid at 80°–85°. It crystallises from alcohol as leaflets melting at 47°–48°.

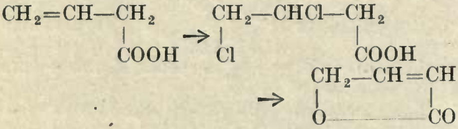
Behenolactone (γ-*octodecylbutyrolactone*)

$$\begin{array}{l} CH_2\text{—}CO \\ \vert \qquad\quad >O \\ CH_2\text{—}CH(CH_2)_{17}CH_3 \end{array}$$

which is formed from erucic acid by the action of sulphuric acid, crystallises from alcohol or ether as plates melting at 63·5°.

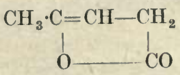
The unsaturated monohydroxymonocarboxylic acids also yield γ-lactones, and the following are important members of this series:—

Crotonolactone $\begin{array}{l} CH_2\text{—}CH:CH \\ \vert \qquad\qquad\quad \vert \\ O\text{————}CO \end{array}$ is formed from vinylacetic acid by converting it into βγ-dichlorobutyric acid by the addition of chlorine and then eliminating hydrogen chloride by heating at 200°–215°. It melts at 4° and boils at 95°–96° (13 mm.):



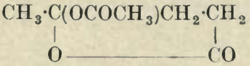
$$\begin{array}{l}\mathrm{CH_2{=}CH{-}CH_2}\\ \qquad\qquad |\\ \qquad\quad \mathrm{COOH}\end{array} \rightarrow \begin{array}{l}\mathrm{CH_2{-}CHCl{-}CH_2}\\ |\qquad\qquad\quad |\\ \mathrm{Cl}\qquad\quad\ \ \mathrm{COOH}\end{array} \rightarrow \begin{array}{l}\mathrm{CH_2{-}CH{=}CH}\\ |\qquad\qquad |\\ \mathrm{O}\text{———}\mathrm{CO}\end{array}$$

Crotonolactone.

$\Delta^{\beta\gamma}$-Angelicalactone 

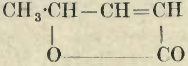
$$\begin{array}{l}\mathrm{CH_3{\cdot}C{=}CH{-}CH_2}\\ |\qquad\qquad\ |\\ \mathrm{O}\text{————}\mathrm{CO}\end{array}$$

is formed, unaccompanied by the $\Delta^{\alpha\beta}$-lactone (*see* below), when acetyllævulic acid



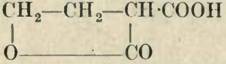
$$\begin{array}{l}\mathrm{CH_3{\cdot}C(OCOCH_3)CH_2{\cdot}CH_2}\\ \quad |\qquad\qquad\qquad |\\ \quad \mathrm{O}\text{——————}\mathrm{CO}\end{array}$$

is distilled under 200–230 mm. pressure. It melts at 18°–18·5°, and distils at 55°–56° (12 mm.).

$\Delta^{\alpha\beta}$-*Angelicalactone* 

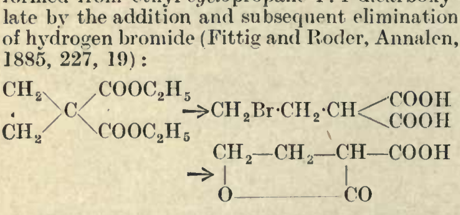
$$\begin{array}{l}\mathrm{CH_3{\cdot}CH{-}CH{=}CH}\\ \quad |\qquad\qquad |\\ \quad \mathrm{O}\text{————}\mathrm{CO}\end{array}$$

is formed from the $\Delta^{\beta\gamma}$ compound by warming it with triethylamine. It does not solidify at −17°, and boils at 89° (15 mm.). The $\Delta^{\alpha\beta}$-lactone is partially converted into the $\Delta^{\beta\gamma}$-lactone on distillation under ordinary pressure (Thiele, Tischbein, and Lossow, Annalen, 1901, 319, 180).

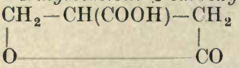
The γ-lactones which are derived from the hydroxydicarboxylic acids are, of course, no longer neutral substances, but contain a free carboxyl group; the following compounds are important members of this class: *Butyrolactone-α-carboxylic acid* 

$$\begin{array}{l}\mathrm{CH_2{-}CH_2{-}CH{\cdot}COOH}\\ |\qquad\qquad\quad |\\ \mathrm{O}\text{—————}\mathrm{CO}\end{array}$$

is formed from ethyl *cyclo*propane-1 : 1-dicarboxylate by the addition and subsequent elimination of hydrogen bromide (Fittig and Roder, Annalen, 1885, 227, 19):

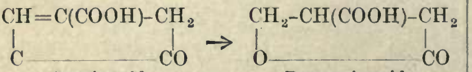


$$\begin{array}{c}\mathrm{CH_2}\\ \mathrm{CH_2}\end{array}\!\!>\mathrm{C}<\!\!\begin{array}{c}\mathrm{COOC_2H_5}\\ \mathrm{COOC_2H_5}\end{array} \rightarrow \mathrm{CH_2Br{\cdot}CH_2{\cdot}CH}<\!\!\begin{array}{c}\mathrm{COOH}\\ \mathrm{COOH}\end{array} \rightarrow \begin{array}{l}\mathrm{CH_2{-}CH_2{-}CH{-}COOH}\\ |\qquad\qquad\quad |\\ \mathrm{O}\text{—————}\mathrm{CO}\end{array}$$

The lactonic acid forms a thick viscid liquid which is readily soluble in water, and when heated at 120° evolves carbon dioxide and passes into butyrolactone. *Butyrolactone-β-carboxylic acid, Paraconic acid* 

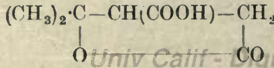
$$\begin{array}{l}\mathrm{CH_2{-}CH(COOH){-}CH_2}\\ |\qquad\qquad\qquad\ |\\ \mathrm{O}\text{——————}\mathrm{CO}\end{array}$$

is formed by the reduction of aconic acid by zinc-dust and acetic acid (Reitter, Ber. 1898, 31, 2722)



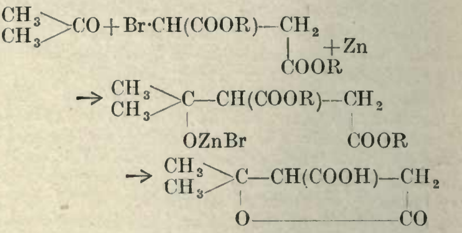
$$\begin{array}{l}\mathrm{CH{=}C(COOH){-}CH_2}\\ |\qquad\qquad\quad\ |\\ \mathrm{C}\text{—————}\mathrm{CO}\end{array} \rightarrow \begin{array}{l}\mathrm{CH_2{-}CH(COOH){-}CH_2}\\ |\qquad\qquad\qquad\ |\\ \mathrm{O}\text{——————}\mathrm{CO}\end{array}$$

Aconic acid. Paraconic acid.

Terebic acid 

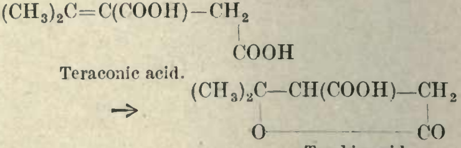
$$\begin{array}{l}\mathrm{(CH_3)_2{\cdot}C{-}CH(COOH){-}CH_2}\\ \quad |\qquad\qquad\qquad\quad |\\ \quad \mathrm{O}\text{——————}\mathrm{CO}\end{array}$$

is a product of the oxidation of oil of turpentine, and has been synthesised by several methods. Thus it is formed by the oxidation of *iso*propylsuccinic acid, as indicated by method (5), and is also produced when the ester, formed by the condensation of ethyl bromosuccinate with acetone in the presence of zinc (Reformatzky's method), is hydrolysed:



$$\begin{array}{c}\mathrm{CH_3}\\ \mathrm{CH_3}\end{array}\!\!>\mathrm{CO}+\begin{array}{l}\mathrm{Br{\cdot}CH(COOR){-}CH_2}\\ \qquad\qquad\qquad\ |\\ \qquad\qquad\quad\ \mathrm{COOR}\end{array}+\mathrm{Zn} \rightarrow \begin{array}{c}\mathrm{CH_3}\\ \mathrm{CH_3}\end{array}\!\!>\begin{array}{l}\mathrm{C{-}CH(COOR){-}CH_2}\\ |\qquad\qquad\qquad |\\ \mathrm{OZnBr}\qquad\quad \mathrm{COOR}\end{array} \rightarrow \begin{array}{c}\mathrm{CH_3}\\ \mathrm{CH_3}\end{array}\!\!>\begin{array}{l}\mathrm{C{-}CH(COOH){-}CH_2}\\ |\qquad\qquad\qquad |\\ \mathrm{O}\text{——————}\mathrm{CO}\end{array}$$

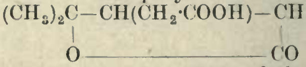
It is also obtained from teraconic acid by warming with sulphuric acid



$$\begin{array}{l}\mathrm{(CH_3)_2C{=}C(COOH){-}CH_2}\\ \qquad\qquad\qquad\qquad\ |\\ \qquad\qquad\qquad\quad \mathrm{COOH}\end{array} \rightarrow \begin{array}{l}\mathrm{(CH_3)_2C{-}CH(COOH){-}CH_2}\\ \quad |\qquad\qquad\qquad\quad |\\ \quad \mathrm{O}\text{——————}\mathrm{CO}\end{array}$$

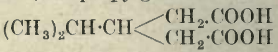
Teraconic acid. Terebic acid.

Terebic acid crystallises from water as needles which melt at 174°–175°.

Two other lactonic acids, which have played an important part in the elucidation of the chemistry of the terpenes, are terpenylic acid and homoterpenylic acid. *Terpenylic acid* 

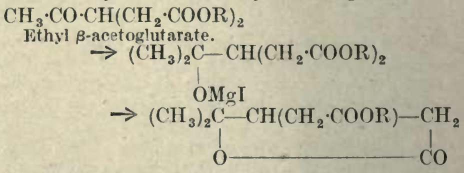
$$\begin{array}{l}\mathrm{(CH_3)_2C{-}CH(CH_2{\cdot}COOH){-}CH_2,}\\ \quad |\qquad\qquad\qquad\qquad\quad |\\ \quad \mathrm{O}\text{———————}\mathrm{CO}\end{array}$$

which occurs frequently as a product of the degradation of the terpenes, was discovered by Hempel and investigated by Fittig and his pupils; its structure was determined by Wallach. The acid has been synthetically prepared by Lawrence (Chem. Soc. Trans. 1899, 75, 529) by the oxidation of β-*iso*propylglutaric acid



$$\mathrm{(CH_3)_2CH{\cdot}CH}<\!\!\begin{array}{c}\mathrm{CH_2{\cdot}COOH}\\ \mathrm{CH_2{\cdot}COOH}\end{array}$$

(compare method (5)), and by Simonsen (Chem. Soc. Trans. 1907, 91, 187) by the action of magnesium methyl iodide on ethyl β-acetoglutarate



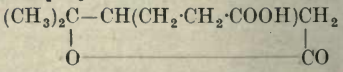
$$\mathrm{CH_3{\cdot}CO{\cdot}CH(CH_2{\cdot}COOR)_2}$$

Ethyl β-acetoglutarate.

$$\rightarrow \begin{array}{l}\mathrm{(CH_3)_2C{-}CH(CH_2{\cdot}COOR)_2}\\ \quad |\\ \quad \mathrm{OMgI}\end{array} \rightarrow \begin{array}{l}\mathrm{(CH_3)_2C{-}CH(CH_2{\cdot}COOR){-}CH_2}\\ \quad |\qquad\qquad\qquad\qquad\quad |\\ \quad \mathrm{O}\text{———————}\mathrm{CO}\end{array}$$

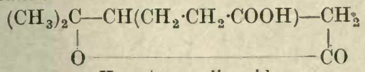
Terpenylic acid crystallises with 1 molecule of water as colourless prisms which melt at 56°. The water of crystallisation is removed by sulphuric acid and the anhydrous substance then melts at 89°.

Homoterpenylic acid



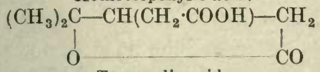
$$\begin{array}{l}\mathrm{(CH_3)_2C{-}CH(CH_2{\cdot}CH_2{\cdot}COOH)CH_2}\\ \quad |\qquad\qquad\qquad\qquad\qquad\quad |\\ \quad \mathrm{O}\text{————————}\mathrm{CO}\end{array}$$

was isolated by Baeyer during his researches on the constitution of pinene—the chief constituent of oil of turpentine: its relation to terpenylic acid and terebic acid is shown by the following formulæ :—



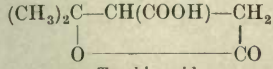
$$\underset{\underset{\displaystyle O}{|}}{(CH_3)_2C}\text{—}CH(CH_2\cdot CH_2\cdot COOH)\text{—}\underset{\underset{\displaystyle CO}{|}}{CH_2}$$

Homoterpenylic acid.



$$\underset{\underset{\displaystyle O}{|}}{(CH_3)_2C}\text{—}CH(CH_2\cdot COOH)\text{—}\underset{\underset{\displaystyle CO}{|}}{CH_2}$$

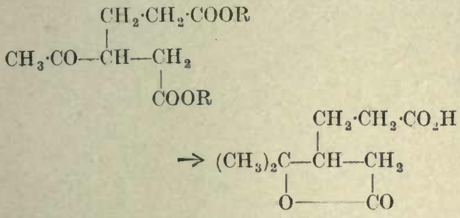
Terpenylic acid.



$$\underset{\underset{\displaystyle O}{|}}{(CH_3)_2C}\text{—}CH(COOH)\text{—}\underset{\underset{\displaystyle CO}{|}}{CH_2}$$

Terebic acid.

Homoterpenylic acid is, as a matter of fact, converted into terpenylic acid and some terebic acid by oxidation with nitric acid. Homoterpenylic acid has been synthesised by Simonsen (Chem. Soc. Trans. 1907, 91, 184) by treating ethyl β-acetoadipate with magnesium methyl iodide and hydrolysing the product.



$$CH_3\cdot CO\text{—}\overset{\overset{\displaystyle CH_2\cdot CH_2\cdot COOR}{|}}{CH}\text{—}\underset{\underset{\displaystyle COOR}{|}}{CH_2}$$

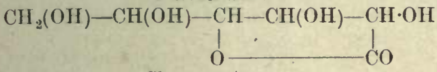
$$\rightarrow \underset{\underset{\displaystyle O}{|}}{(CH_3)_2C}\text{—}\overset{\overset{\displaystyle CH_2\cdot CH_2\cdot CO_2H}{|}}{CH}\text{—}\underset{\underset{\displaystyle CO}{|}}{CH_2}$$

The acid crystallises from water as glistening prisms which melt at 100°–102°.

The formation of γ-lactones from polyhydroxycarboxylic acids. Those polyhydroxy derivatives of the carboxylic acids which have a hydroxyl group in the γ-position yield γ-lactones (Fittig, Annalen, 1892, 268, 4, 34, 40, 62, 68). When hydroxyl groups are present in both the γ- and δ- positions, the γ-lactone is formed, since the five-membered γ-lactone ring is more easily closed than the six-membered δ-lactone ring, thus :

$CH_2(OH)\text{-}CH(OH)\text{-}CH(OH)\text{-}CH(OH)\text{-}CH(OH)\text{-}COOH$

Gluconic acid.



$$CH_2(OH)\text{—}CH(OH)\text{—}\underset{\underset{\displaystyle O}{|}}{CH}\text{—}CH(OH)\text{—}\underset{\underset{\displaystyle CO}{|}}{CH\cdot OH}$$

Gluconolactone.

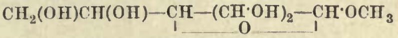
The hydroxylactones, which are derived from the acids of the sugar group and which therefore contain several hydroxyl complexes, are characterised by showing a greater tendency to crystallise than the hydroxy acids themselves; their formation has therefore been of considerable service in elucidating the structure of the sugars. The remarkable property possessed by the acids of the sugar group of passing into the aldehyde, that is, the sugar itself, when reduced by nascent hydrogen, thus :

$$\underset{\text{Gluconic acid.}}{CH_2(OH)\text{—}(CH\cdot OH)_4\text{—}COOH} \rightarrow \underset{\text{Glucose.}}{CH_2(OH)(CH\cdot OH)_4CHO}$$

is entirely dependent on the formation of the lactone. That is to say, the acid itself is not reducible but only the lactone (E. Fischer, Ber. 1889, 22, 2204 ; 1890, 23, 930).

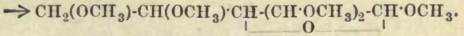
The following lactones are derived from the pentahydroxycarboxylic acids: *d-Mannonolactone* $C_6H_{10}O_6$ melts at 149°–153°, and has $[\alpha]_D = +53{\cdot}8°$; *l-Mannonolactone* melts at 140°–150°, and has $[\alpha]_D = -54{\cdot}8°$: *(d+l)-Mannonolactone* melts at 149°–155°. *d-Gluconolactone* $C_6H_{10}O_6$ melts at 130°–135° and yields grape sugar when reduced by sodium amalgam. *l-Gluconolactone* melts at 185° and gives *l*-xylose when oxidised by hydrogen peroxide. *d-Galactonolactone* melts at 91° in the anhydrous state, but with water yields a hydrate, containing one molecule of water of crystallisation, which melts at 64°. The *(d+l)-lactone* melts at 122°–125°. *α-Rhamnoselactone* melts at 162°–168° ; *β-Rhamnoselactone* melts at 134°–138°. The following lactones are derived from the hexahydroxycarboxylic acids: *d-Mannoselactone* (m.p. 149°); *l-Mannoselactone* (m.p. 154°); *α-d-Glucoselactone* (m.p. 140°–145°) ; *β-d-Glucoselactone* (m.p. 151°) ; *α-d-Galactoselactone* (m.p. 150°) ; *d-Fructoselactone* (m.p. 130°). These lactones are reduced by sodium amalgam to the corresponding heptoses.

The formation of γ-lactones from the acids of the sugar series has been used by Purdie and Irvine (Chem. Soc. Trans. 1903, 83, 1021) to supply direct evidence of the γ- linkage in glucosides. Thus α-methylglucoside when alkylated by the aid of silver oxide yields tetramethyl-α-methylglucoside which, on hydrolysis, is converted into tetramethylglucose (m.p. 81°–83°). When this substance is oxidised by bromine water it is converted into tetramethylgluconolactone



$$CH_2(OH)CH(OH)\text{—}\underbrace{CH\text{—}(CH\cdot OH)_2\text{—}CH}_{O}\cdot OCH_3$$

α-Methylglucoside.



$$\rightarrow CH_2(OCH_3)\text{-}CH(OCH_3)\cdot\underbrace{CH\text{-}(CH\cdot OCH_3)_2\text{-}CH}_{O}\cdot OCH_3.$$

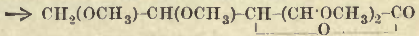
Tetramethyl-α-methylglucoside.

$\rightarrow CH_2(OCH_3)\text{-}CH(OCH_3)\text{-}CH(OH)\text{-}(CH\cdot OCH_3)_2CHO$

Tetramethylglucose (m.p. 81°–83°).

$CH_2(OCH_3)\text{-}CH(OCH_3)\text{-}CH(OH)\text{-}(CH\cdot OCH_3)_2\text{-}COOH$

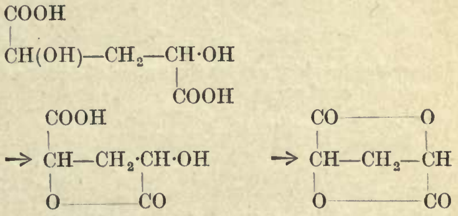
Tetramethylgluconic acid.



$$\rightarrow CH_2(OCH_3)\text{-}CH(OCH_3)\text{-}\underbrace{CH\text{-}(CH\cdot OCH_3)_2\text{-}CO}_{O}$$

Tetramethylgluconolactone.

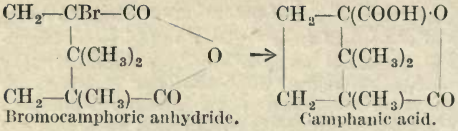
Polyhydroxy derivatives of the dicarboxylic acids yield γγ-dilactones, where possible. Thus αα′-dihydroxyglutaric acid yields in the first instance the hydroxylactonic acid melting at 167°–168°, and finally the dilactone (Fittig, Annalen, 1907, 353, 1)



$$\overset{\overset{\displaystyle COOH}{|}}{CH(OH)}\text{—}CH_2\text{—}\underset{\underset{\displaystyle COOH}{|}}{CH\cdot OH}$$

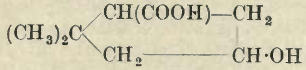
$$\rightarrow \overset{\overset{\displaystyle COOH}{|}}{\underset{\underset{\displaystyle O}{|}}{CH}}\text{—}CH_2\cdot\underset{\underset{\displaystyle CO}{|}}{CH\cdot OH} \quad \rightarrow \overset{\overset{\displaystyle CO}{|}}{\underset{\underset{\displaystyle O}{|}}{CH}}\text{—}CH_2\text{—}\overset{\overset{\displaystyle O}{|}}{\underset{\underset{\displaystyle CO}{|}}{CH}}$$

The formation of lactones from alicyclic compounds appears to proceed in much the same manner as with the open chain substances. In many cases, the formation of the lactone proceeds normally as, for example, when bromocamphoric anhydride is converted into camphanic acid by the action of boiling water (Wreden, Annalen, 1872, 163, 330) :



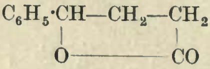
Bromocamphoric anhydride. Camphanic acid.

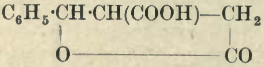
On the other hand, steric hindrance seems, in some cases, to prevent the formation of the lactone. Thus 1-1-dimethyl-4-hydroxy-*cyclo*pentane-2-carboxylic acid

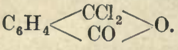


shows no tendency to pass into the inner anhydride (Perkin, Thorpe, and Walker, Trans. 1901, 79, 783). It is, however, possible that in this instance the hydroxy acid may represent the *trans*-configuration of this substance, in which case the formation of the lactone would be prevented (*see* orthocoumaric acid).

The γ-lactones of the aromatic series. The following lactones are important members of this series. (For methods of preparation see above.) *The lactone of o-hydroxyphenylacetic acid* $C_6H_4<\substack{CH_2\\O}>CO$, exists in two modifications, a labile form, melting at 28°, and a stable form, melting at 49°. It boils at 248°–252° and is slowly converted into the hydroxy acid on shaking with water. *Phenylbutyrolactone*

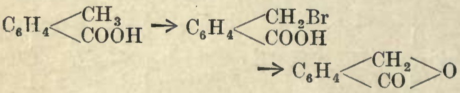


melts at 37°. It is volatile with steam and has a pleasant aromatic odour. *Phenylparaconic acid*  is formed by the condensation of benzaldehyde with sodium succinate in the presence of acetic anhydride. It crystallises with $\frac{1}{4}H_2O$ and melts at 99°. When dried at 90° it melts at 121° and after resolidifying melts at 106°. If the melted specimen is heated at 115° and seeded with a crystal melting at 121°, the modification of higher melting-point is produced (Fittig, Annalen, 1889, 255, 143). It is sparingly soluble in cold water. *Phthalide* $C_6H_4<\substack{CO\\CH_2}>O$ is formed by the reduction of phthalic anhydride and was first obtained by Kolbe and Wischin in 1866 by the reduction of phthalyl chloride



$$C_6H_4<\substack{CCl_2\\CO}>O.$$

It can also be obtained by the action of bromine on *o*-toluic acid at 140° :



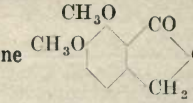
$$C_6H_4<\substack{CH_3\\COOH} \rightarrow C_6H_4<\substack{CH_2Br\\COOH} \rightarrow C_6H_4<\substack{CH_2\\CO}>O$$

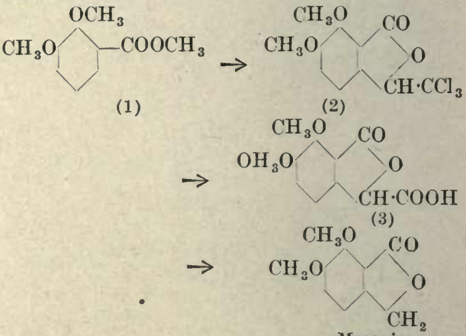
Phthalide.

Phthalide crystallises from hot water as rhombic plates which melt at 73° ; it boils at 290° without decomposition and is sparingly soluble in alcohol, ether and in cold water. The lactone is converted by alkalis into the salt of the corresponding hydroxy acid

$$C_6H_4(CH_2{\cdot}OH)COOH.$$

This acid is stable, but by long standing in aqueous solution, or by melting, is converted into phthalide.

Meconine  This substance, which was formerly named *opianyl*, was discovered independently in 1830 by Couerbe and by Dublanc in opium. It also occurs in the root of the *Hydrastis canadensis* (Linn.), and is, moreover, one of the products which are formed when narcotine is oxidised by nitric acid. It has been prepared synthetically by Fritsch in the following way (Annalen, 1898, 301, 352): Methyl 2:3-dimethoxybenzoate (1) is condensed with chloral, under the influence of concentrated sulphuric acid, to form 5:6-dimethoxytrichloromethylphthalide (2). This compound, when hydrolysed, is converted into the corresponding carboxylic acid (3) which is transformed into carbon dioxide and meconine when heated :



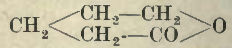
(1) (2) (3)

Meconine.

Meconine forms white crystals which melt at 101°–102°. It sublimes unchanged and dissolves in 700 parts of water at 15·5° and in 22 parts at 100°.

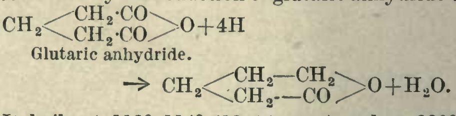
δ-Lactones. The remarks which have already been made respecting the ease of formation of the γ-lactones from the γ-hydroxy acids apply also to the production of the δ-lactones from the corresponding δ-hydroxy acids, excepting that the six-membered δ-lactone ring is not so readily formed as the five-membered ring of the γ-lactones and is consequently more easily broken.

Aliphatic δ-lactones. *δ-Valerolactone*



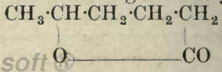
$$CH_2<\substack{CH_2-CH_2\\CH_2-CO}>O$$

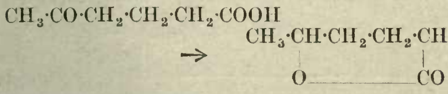
is formed by the reduction of glutaric anhydride :



$$CH_2<\substack{CH_2{\cdot}CO\\CH_2{\cdot}CO}>O+4H \rightarrow CH_2<\substack{CH_2-CH_2\\CH_2-CO}>O+H_2O.$$

Glutaric anhydride.

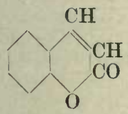
It boils at 113°–114° (13–14 mm.) and at 220° under ordinary atmospheric pressure, is sparingly soluble in water and is characterised by passing, on standing, into a crystalline polymeride melting at 47°–48°. When water is added to the lactone an acid reaction is at once obtained, showing that the lactone ring is readily broken. *δ-Caprolactone,*  was the first δ-lactone of the aliphatic series to be prepared and was obtained by Fittig and Wolff (Annalen, 1883, 216, 127) by the reduction of γ-acetobutyric acid:

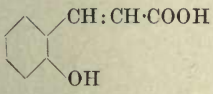


$$CH_3{\cdot}CO{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}COOH \rightarrow \begin{array}{l}CH_3{\cdot}CH{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2\\ \quad O\text{———————}CO\end{array}$$

It boils at 230°–231° and forms needles melting at 17°–19°. It is miscible with water and absorbs moisture from damp air passing into the hydroxy acid.

Aromatic δ-lactones. Several δ-lactones of the aromatic series are of considerable importance because they either occur free in nature or are obtained as the products of fission of certain natural glucosides. They are largely used industrially for the preparation of perfumes.

Coumarin  which is the δ-lactone of *o*-hydroxycinnamic acid

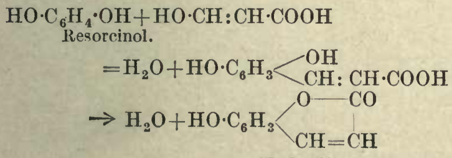


may be regarded as the prototype of this group to which the general name of 'the Coumarins' is applied, chiefly because the other members of the series are derivatives of coumarin in which hydroxyl or methoxyl groups are present in the benzene nucleus.

The coumarins may be prepared either by applying the Perkin method for the synthesis of coumarin (see below) to the necessary derivatives of salicylaldehyde, or by the v. Pechmann method, which is carried out by heating phenols with malic acid in the presence of concentrated sulphuric acid (v. Pechmann, Ber. 1884, 17, 929; v. Pechmann and Welsch, *ibid.* 1646). This reaction is explained by assuming that the strong sulphuric acid first decomposes malic acid into carbon monoxide, water, and hydroxyacrylic acid, thus:

$$\underset{\text{Malic acid.}}{COOH{\cdot}CH(OH)CH_2{\cdot}COOH} \rightarrow CO+H_2O+CH(OH){:}CH{\cdot}COOH$$

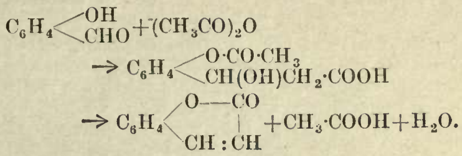
and that the hydroxyacrylic acid then condenses with the phenol to form the coumarin, thus:



$$\underset{\text{Resorcinol.}}{HO{\cdot}C_6H_4{\cdot}OH}+HO{\cdot}CH{:}CH{\cdot}COOH$$
$$=H_2O+HO{\cdot}C_6H_3{<}\begin{array}{l}OH\\ CH{:}\ CH{\cdot}COOH\end{array}$$
$$\rightarrow H_2O+HO{\cdot}C_6H_3{<}\begin{array}{l}O\text{——}CO\\ \quad|\\ CH{=}CH\end{array}$$

Umbelliferone.

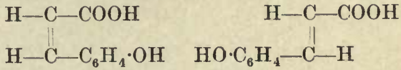
This reaction yields the best results with the *m*-substitutes phenols. *Coumarin* was first isolated in 1820 from Tonka beans, the seed of the *Dipteryx odorata* (Willd.), and was subsequently characterised by Guibort. It was first prepared synthetically by Perkin from salicylaldehyde by heating with sodium acetate and acetic anhydride:



$$C_6H_4{<}\begin{array}{l}OH\\ CHO\end{array}+(CH_3CO)_2O$$
$$\rightarrow C_6H_4{<}\begin{array}{l}O{\cdot}CO{\cdot}CH_3\\ CH(OH)CH_2{\cdot}COOH\end{array}$$
$$\rightarrow C_6H_4{<}\begin{array}{l}O\text{——}CO\\ \quad|\\ CH:CH\end{array}+CH_3{\cdot}COOH+H_2O.$$

This synthesis may, moreover, be applied to the formation of other coumarins since, by the method of Gattermann (Ber. 1899, 32, 278, 287), many hydroxyaromatic aldehydes can now be prepared from phenols by the action of hydrocyanic and hydrochloric acids in the presence of aluminium chloride.

Coumarin forms prismatic crystals which melt at 67° and boil at 290°–290·5°. It is sparingly soluble in cold water but readily dissolves on warming. The corresponding hydroxy acid, coumarinic acid, cannot be isolated in the free state, but when coumarin is boiled for some time with a solution of potassium hydroxide, an acid separates on acidification which decomposes above 200° with evolution of carbon dioxide but does not yield coumarin (Zwenger, Annalen Suppl. 1872, 8, 23). This acid, which is called orthocoumaric acid, is stereoisomeric with the unstable coumarinic acid (Clayton, Chem. Soc. Trans. 1910, 2102) the two acids being represented by the formulæ:

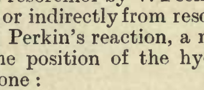


$$\begin{array}{l}H\text{—}C\text{—}COOH\\ \quad\ \|\\ H\text{—}C\text{—}C_6H_4{\cdot}OH\end{array}\qquad\begin{array}{r}H\text{—}C\text{—}COOH\\ \|\quad\quad\ \ \\ HO{\cdot}C_6H_4\text{—}C\text{—}H\end{array}$$

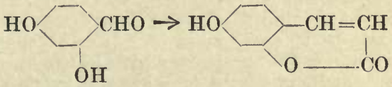
Coumarinic acid (cis-form) *o*-Coumaric acid (trans-form).

The ease of formation of coumarin from coumarinic acid is explained by the proximity of the hydroxyl and carboxyl groups in the cis-configuration (*cf.* Borsche, Ber. 1904, 37, 346).

Umbelliferone, Hydroxycoumarin

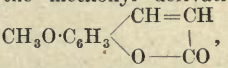


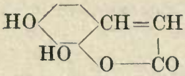
This substance, which is the δ-lactone of 2:4-dihydroxycinnamic acid, is found in the bark of the *Daphne Mesereum* (Linn.) and is also obtained by distilling various resins such as galbanum and asafœtida. Its synthesis may be effected directly from resorcinol by v. Pechmann's malic acid method, or indirectly from resorcylaldehyde by the aid of Perkin's reaction, a method which establishes the position of the hydroxyl group in umbelliferone:

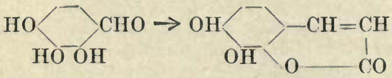


Resorcylaldehyde. Umbelliferone.

Umbelliferone crystallises from hot water in slender needles melting at 225°. It dissolves very sparingly in water, yielding a solution which shows a marked blue fluorescence.

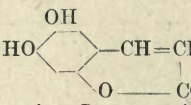
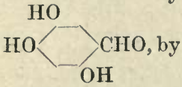
Herniarin is the methoxyl derivative of umbelliferone  $CH_3O{\cdot}C_6H_3{<}\begin{array}{l}CH{=}CH\\ \quad|\\ O\text{——}CO\end{array}$, and occurs in *Herniaria hirsuta* (Linn.) (Barth and Herzig, Monatsh, 1889, 10, 161). It melts at 117°–118°.

Daphnetin  is obtained by the fission of the glucoside daphnin, either by acids or by ferments. It can be prepared synthetically either from pyrogallol by the malic acid method or from pyrogallolaldehyde by Perkin's reaction; the second method of preparation determines the positions of the hydroxyl groups in daphnetin:

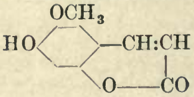


Pyrogallolaldehyde. Daphnetin.

Daphnetin crystallises as needles or prisms, melts at 256°, and develops a pleasant coumarin-like smell when heated. It dissolves in alkali, forming a reddish-yellow solution and gives in aqueous solution a green colouration with ferric chloride.

Æsculatin  is isomeric with daphnetin. It occurs in the bark of the horse chestnut, partly free and partly as the glucoside æsculin. It also occurs in the seed of the *Euphorbia Lathyris* (Linn.), and can be prepared synthetically from hydroxyhydroquinone by converting this substance into hydroxyhydroquinonealdehyde  by means of hydrocyanic and hydrochloric acids in the presence of zinc chloride (Gattermann's reaction), and then by subjecting the aldehyde to the Perkin reaction. Æsculetin crystallises from water as leaflets or needles, melts at 268° with decomposition, and is sparingly soluble in cold water, but readily dissolves in hot water and in alcohol. The aqueous solution, which has a faint blue fluorescence gives a green colouration with ferric chloride. The lactone dissolves in alkali, forming a yellowish-red solution.

Scopoletin (*Chrysatropic acid*)

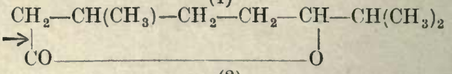


which is the methoxyl derivative of æsculetin, was isolated by Eykman (Rec. trav. chim. 1884, 3, 171) from the rhizome of *Scopolia japonica* (Maxim.). It also occurs in *Atropa belladonna* (Linn.), in *Gelsemium*, in the bark of the *Prunus serotina*, and in jalap. The lactone crystallises from ethyl acetate as needles which melt at 204°, and exhibits a fine blue fluorescence in aqueous solution, which is enhanced by the addition of alkali. The constitution of this substance as 4-hydroxy-5-methoxy-coumarin has been determined by Moore (Chem. Soc. Trans. 1911, 99, 1043).

ε-Lactones. The existence of ε-lactones has been shown to be possible by the researches of v. Baeyer and his collaborators. Thus when the hydroxy acid (1) is distilled, it is partially decomposed into water and the ε-lactone; β-methyl-ε-*iso*propyl-ε-caprolactone (2) (Baeyer and Öhler, Ber. 1896, 29, 29; Baeyer and Seuffert, *ibid.* 1899, 32, 3619):

$$COOH{\cdot}CH_2{\cdot}CH(CH_3)CH_2{\cdot}CH_2{\cdot}CH(OH)CH(CH_3)_2$$

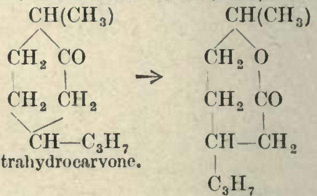
(1)



(2)

The hydroxy acid (1), which is derived from menthone by oxidation and subsequent reduction, exists in two forms, one of which is liquid, the other solid. There are, therefore, two lactones (both of which are feebly lævorotatory), one melting at 47° derived from the solid acid, and the other, a liquid boiling at 135° (12 mm.) derived from the liquid acid. Both modifications of the lactone are insoluble in cold alkali but dissolve on warming. The solid ε-lactone (m.p. 47°) is also formed when menthone is oxidised by Caro's acid (Baeyer and Villiger, Ber. 1899, 32, 3628; 1900, 33, 860).

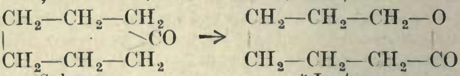
β-*iso*-**Propyl-ε-methyl-ε-caprolactone** is formed when tetrahydrocarvone is treated with Caro's acid (Baeyer and Villiger, Ber. 1899, 32, 3629; Wallach, Annalen, 1902, 323, 331):



Tetrahydrocarvone. ε-Lactone.

The lactone boils at 155·5°–156° (21 mm.).

ζ-Lactones. An unstable lactone of this series is formed when suberone is treated with Caro's acid (Baeyer and Villiger, Ber. 1900, 33, 862; v. Braun, *ibid.* 1906, 39, 4362):



Suberone. ζ-Lactone.

The lactone was not isolated but its existence in the crude product of oxidation was inferred from the fact that when treated with alcohol and sulphuric acid it was converted into the ethyl salt of ζ-hydroxyœnanthylic acid

$$OH(CH_2)_6COOR.$$

J. F. T.

LACTOPHENIN *v.* Synthetic drugs.

LACTOPICRIN *v.* Lactucarium.

LACTOSE *v.* Carbohydrates.

LACTUCARIUM. *Lettuce opium.* The inspissated juice of *Lactuca virosa* (Linn.) and other species of *Lactuca* (*v.* Woodville, Med. Bot. 1, 31,; Bentl. a. Trim. 160, 161). Lactucarium is sometimes employed in medicine as a substitute for opium, and has often been examined chemically. A list of the earlier investigations, with a summary of the results, is given by Pereira (Mat. Med. 1853. 2, 1569).

Nearly half the weight of lactucarium consists of the tasteless inodorous compound *lactucerin* or *lactucon*, first obtained in a crystalline form by Lenoir (Annalen, 59, 83).

It was further studied by Franchimont and Wigman (Ber. 12, 10); Hesse (Annalen, 234, 243; 244, 268); Kassner (*ibid.* 238, 220), and others. Lactucarium is first washed with benzene and then extracted with hot alcohol. From the alcoholic solution crude lactucerin separates in crystals. These are purified by solution in ether, agitation of the ethereal solution with aqueous potash, the addition of alcohol until a precipitate begins to form, filtration, and finally the addition of water, when the lactucerin comes down in microscopic needles (Kassner). Franchimont and Wigman prepared a lactucerin or lactucon from lactucarium derived from *Lactuca altissima* (Bieb.), which gave the formula $C_{14}H_{22}O$. It melts at 296°, is insoluble in water, sparingly soluble in benzene and carbon disulphide, but dissolves in ether, light petroleum, and in fixed and volatile oils. By the action of phosphorus pentasulphide a *hydrocarbon* $C_{14}H_{22}$ was obtained, which boils at 247°–252°.

According to Hesse, lactucerin consists of a mixture of the acetates of two isomeric alcohols. Alcoholic potash decomposes the esters, and, on the addition of water, a precipitate of the two alcohols falls, which may be separated by taking advantage of their different solubility in alcohol. *α-Lactucerol* $C_{18}H_{30}O,H_2O$, the least soluble in alcohol, consists of silky needles which melt at 173°–181°. It is soluble in chloroform, ether, light petroleum, or hot alcohol. The *acetate* $C_{20}H_{32}O_2$ or $CH_3{\cdot}CO{\cdot}OC_{18}H_{29}$ which exists in lactucerin, may also be prepared from the alcohol. It is crystalline and melts at 202°–207°. It is slightly soluble in cold alcohol and glacial acetic acid, and easily in chloroform, ether, and light petroleum. The *diacetate* melts at 198°–200°, the *propionate* at 152°, and the *benzoate* at 156°. *β-Lactucerol* $C_{18}H_{30}O,H_2O$ may be obtained in long needles from ether or chloroform. It is more soluble in alcohol than α-lactucerol, and forms an *acetate* $C_{20}H_{32}O_2$ or $CH_3{\cdot}CO{\cdot}OC_{18}H_{29}$, the constituent of lactucerin, which is obtained in crystals from alcohol and melts at 230°. It is less soluble in alcohol and light petroleum than the α-acetate. Crude lactucerin, examined by Flückiger and Hanbury, melted at 232° (Flück. a. Hanb. 398).

After purifying crude lactucerin by sublimation in a current of carbon dioxide, Kassner found it to melt at 210°, and on analysis to give numbers agreeing better with the formula of Franchimont and Wigman, $C_{14}H_{22}O$ or $C_{28}H_{44}O_2$, than with that proposed by Hesse. Fusing lactucerin with potash, Kassner obtained a new compound, *lactucol* $C_{13}H_{20}O$ or $C_{13}H_{19}{\cdot}OH$, together with acetic acid and hydrogen. Lactucol consists of needles melting at 160°–162°. It forms an *acetate* which melts at 198°–200°.

Lactucin, lactucic acid, lactopicrin, and lactucerin, as constituents of the Canadian lettuce *Lactuca canadensis* (Linn.), have been investigated by Flowers (Pharm. J. [iii.] 10, 44).

From German lactucarium Sperling (Chem. Zentr. 1904, i. 1162) obtained *lactucon*, m.p. 184°, to which he gives the formula $C_{23}H_{36}O_2$. On hydrolysis it yields acetic acid and lactucol $C_{21}H_{33}OH$, the latter melting at 154°–155°.

The bitter taste, and probably the medicinal value of lactucarium, depends upon three other constituents, which occur in relatively minute quantities. The first of these, *lactucin* $C_{11}H_{12}O_3,H_2O$, was studied by Walz (Annalen, 32, 85; J. Pharm. 14, 25; Neu. J. Pharm. 15, 118); Aubergier (Compt. rend. 19, 923); Ludwig (Arch. Pharm. [ii.] 50, 1 and 129); Kromayer (*ibid.* [ii.] 105, 3); Ludwig and Kromayer (*ibid.* [ii.] 111. 1); and Buchner (Rep. Phar. 43, 1). It has a decidedly bitter taste and crystallises in white pearly scales. It is soluble in water, sparingly soluble in alcohol or acetic acid, and insoluble in ether. It reduces Fehling's solution. Of the remaining two constituents, *lactucic acid* is a light yellow mass, becoming crystalline on standing (Ludwig and Walz), and *lactopicrin*, an amorphous bitter mass, soluble in water and alcohol (Kromayer, Die Bitterstoffe, Erlangen, 1861, 79).

Lactucarium also contains a trace of volatile oil, sugar, gum, albumen, caoutchouc, resin, asparagin, oxalic, citric, and malic acids, and yields 8–10 p.c. of *ash* (*cf.* Kremel, Pharm. Zentralh. 1888, 512). A. S.

LACTUCERIN, LACTUCEROL, LACTUCIC ACID, LACTUCIN, LACTUCOL, and **LACTUCON** *v.* Lactucarium.

LAC VARNISH *v.* Varnish.

LÆVOBORNEOL *v.* Camphors.

LÆVOCAMPHOR *v.* Camphors.

LÆVULIC ACID *v.* Ketones

LÆVULOSE *v.* Carbohydrates.

LAKE ORE *v.* Limonite; Iron.

LAKES. The origin of their manufacture, as well as of the term 'lake' itself, is seen from the following brief historical sketch:—

According to Pliny, the dried scum collected by the dyers of Tyrian purple from their dye-liquors furnished a costly purple-coloured pigment employed by painters. The *indicum* of the Roman artists was probably obtained in the same manner from a woad or indigo vat. Caneparius, a Venetian writer on dyeing, in 1619, states that it was the custom of dyers to evaporate the waste lac dye-liquors in order to obtain an artificial lac used by artists.

Similar pigments were afterwards prepared or collected from the waste dye-liquors of kermes, brazilwood, &c. Such pigments were called by the Italians *laccæ*, and these were distinguished from each other by adding the name of the substance whence the colour was derived—*e.g. lacca di verzino* (Brazilwood), *lacca di grana* (kermes), *lacca di cremise*, &c.

As to the word 'lake' itself, the Indian 'lac' or 'lakh' means a hundred thousand, and refers to the immense numbers in which the lac insects (*Coccus laccæ*) appear at certain seasons on the branches of the trees infested with them.

At the present time true lakes are like those of the early days—namely, insoluble pigments obtained by precipitating solutions of organic colouring matters with metallic salts, &c. They are, indeed, the same coloured precipitates which it is the object of the dyer to produce and fix directly on the fibre, but they are no longer the waste products of the dye-bath, but are specially prepared for the use of artists and others.

The precipitating agent employed in their preparation varies according to the nature of the colouring matter; if the latter is of an acid or phenolic character the active constituent of the former is of a basic character, and *vice versâ*. The essential part of all such lakes consists of colouring matter chemically combined with the active constituent of the precipitating agent.

In some cases, no doubt, there may be colouring matter or precipitating agent mechanically mixed with the true lake, the amount varying according to the proportions and the method of preparation adopted; but these must be regarded as more or less adventitious and not essential to the composition of a lake.

Most of the vegetable colouring matters are of a phenolic character, and the metallic compounds of some are so insoluble that, to produce lakes from them, it suffices to add to a filtered solution of the colouring matter the solution of the metallic salt, for example, alum. In most cases, however, the acid character of the colouring matter is not sufficiently pronounced to enable it to displace the acid of the metallic salt; hence the further addition of an alkali (*e.g.* sodium carbonate) is necessary, in order to neutralise the strong acid of the salt and to liberate the base, with which the colouring matter then combines to form the lake.

If it is possible to employ an alkaline solution of the colouring matter, a lake may be at once obtained on adding to it a metallic salt solution.

Freshly precipitated metallic hydroxides are also capable, in many cases, of attracting and combining with phenolic colouring matters when agitated or heated with their solutions.

It is well to bear in mind that not unfrequently the normal compounds of a colouring matter with a single metallic hydroxide are comparatively soluble, and in these cases the addition of a second metallic salt (*e.g.* calcium salts) may be found necessary to bring about the formation of the lake, which then bears the character of a double salt. All the older lakes, derived from vegetable or animal colouring matters, were produced by one or other of the foregoing methods; and these same methods may be employed with all phenolic colouring matters produced from coal tar. A variety of pigments are now obtained by precipitating certain basic and acid coal tar colours from their solutions by making suitable additions, and although they are not always veritable lakes, they usually bear the name 'aniline lakes,' and are, therefore, most conveniently considered here.

In some cases, no doubt, certain elements of the precipitant combine with the colouring matter, and produce an insoluble pigment to which the term 'lake' may be legitimately extended. In those instances, however, where their production depends upon the property, possessed by many insoluble bodies, of attracting the colouring matters from their aqueous solutions by mere absorption, or in virtue of molecular surface attraction, &c., they cannot be regarded as true lakes. The same remarks apply to the modern pigments from insoluble azo colours (pigment colouring matters) and the developed or ice colours.

Such insoluble substances as are here referred to act as a base or substratum for the colouring matter; they are termed 'carriers,' and consist of kaolin, aluminium hydroxide, barytes, &c.

It is quite usual, however, to find such insoluble bodies mixed with all lakes, not as precipitants, but for the purpose of increasing the body or covering power of the pigment, or as diluents in order to obtain pale shades.

Good lakes should never dissolve in the vehicles by means of which they are applied as pigments, otherwise all their covering power will be lost, and what should be a paint becomes in this case merely a coloured varnish.

LAKES DERIVED FROM PHENOLIC COLOURING MATTERS.

Reds.

Madder-lake. In the preparation of madder-lake extraction of the madder with *boiling* water is avoided, in order not to dissolve those impurities which would cause the production of a less brilliant lake. It is well, first of all, to decompose the glucoside of the madder, and thus increase the actual colouring matter, by steeping in slightly tepid water and allowing the mixture to ferment for 24 hours, then wash with cold water and extract with alum solution at 60°–70°, employing about equal weights of madder and alum. The hot filtered alum solution of the colouring matter is precipitated as an alumina lake by adding sodium carbonate, and the precipitate is washed.

Another method is to precipitate impurities from a hot filtered decoction of madder by adding a small quantity of lead acetate, then filter, add a solution of alum, and precipitate with sodium carbonate.

Matters may be so arranged as to precipitate basic aluminium sulphate instead of aluminium hydroxide, namely, by adding an insufficiency of sodium carbonate to the cooled solution of alum and colouring matter, and then boiling the mixture.

Garancine is preferable to madder for preparing madder-lake, since it does not contain any of the colouring matter in the form of glucoside (ruberythric acid), and the soluble impurities have also been for the most part removed. Extract 1 kilo. garancine repeatedly for several hours with 20 litres of boiling water containing 0·25–0·5 kilo. alum, and filter hot through flannel. On cooling, the colouring matter separates from the filtrate as a flocculent precipitate. This is collected and dissolved in ammonia, and the filtered solution is precipitated with alum, or stannous chloride, or a mixture of both. The colour intensity of the lake varies with the proportions of ammonia and precipitant employed. A method similar to that described for madder may also be employed in preparing madder-lake from garancine.

Bright carmine-red lakes are obtained if, in the preparation of madder-lake, an ammoniacal solution of cochineal-carmine is employed for precipitating the alum solution, instead of the sodium carbonate. This method can be adopted to render the lower qualities of madder-lakes more attractive. Cheap qualities of madder-lakes are also prepared sometimes by extracting mixtures of madder and Brazilwood with sodium carbonate, and precipitating with alum or a solution of tin.

So-called 'crystallised-madder-lakes' are such as contain a certain quantity of potassium or sodium sulphate, &c., and are not to be recommended.

'Madder-pink-lake' is simply madder-lake diluted with about 7 parts of 'blanc fixe' (precipitated barium sulphate).

Madder-lake is entirely, or for the most part, soluble in caustic potash and soda. If chalk or other diluent is present, this may remain undissolved. Boiled with dilute sulphuric or hydrochloric acid, the lake is decomposed, alizarin being liberated in the form of a flocculent or crystalline precipitate. In dilute ammonia pure well-made madder-lake is not soluble (distinguishing test from cochineal-carmine).

References.—Colomb, Bull. Mülh. 12, 307; Dingl. poly. J. 73, 47; Persoz, Traité de l'Impression des Tissus, 1, 507; Merimé, *ibid.* 1, 505; Robiquet and Colin, *ibid.* 1, 505; Khittel, Polyt. Centr. 1859, 81.

Alizarin-red lake is the modern representative of the old madder-lake. It is made either with alizarin (20 p.c.) only, or with mixtures of alizarin and purpurin. Generally the alizarin-red lake contains, in addition to alizarin and aluminium hydroxide, calcium salts, sulphated oil (Turkey-red oil), and sodium phosphate; the exact function of these latter in the formation of the lake is not properly understood, but they exercise great influence on the brightness of the final product as well as in rendering it less sensitive to the action of dilute acids and alkalis.

The Turkey-red oil may be assumed to influence the brilliancy of the shade as in the production of Turkey red by the dyer; the part played by the sodium phosphate is more obscure, but it is always present in the finished lake, and without it there is a loss in brightness.

The absence of calcium salts is also detrimental; in most cases no satisfactory lake can then be obtained.

The general procedure is to dissolve the alizarin in a cold solution of soda, adding in succession the sodium phosphate and Turkey-red oil with thorough stirring to ensure complete admixture. The solution of aluminium sulphate is then run in at such a rate that the evolution of carbon dioxide never becomes very vigorous. When no more gas is given off the requisite amount of lime-water is included and the whole mass stirred for many hours; heat is applied very gradually, so that the boiling-point is reached in 4 or 5 hours, always stirring. After boiling for several hours the lake is allowed to cool, well washed by decantation, filtered, and dried at the temperature of the air.

A method given by Meister, Lucius, and Brüning for their brands of alizarin RR and 1B extra, is as follows:—

2 kilos. aluminium sulphate 18 p.c. are dissolved in 13 litres of water and precipitated hot by the addition of a solution of sodium carbonate (1 kilo. calcined soda in 7 litres of water), stirring continuously. The precipitated alumina is boiled for half an hour to remove the last traces of carbon dioxide, and after standing overnight, the supernatant liquor is decanted off.

To this cold substratum the solution of sodium phosphate (0·16 kilo. in 1·8 litres water) is next added, and subsequently calcium chloride (1·266 kilos. liquor, 24°Bé., diluted with 2 litres of water) in the same manner, stirring well during the additions, and taking care that the former has been thoroughly incorporated before proceeding with the latter.

2 kilos. of the colouring matter mixed with 2 litres of water and 0·6 kilo. of Turkey-red oil (50 p.c.) diluted with 0·8 litre of water are further run in with the same precautions and the whole heated gradually to boiling within 1 hour and boiled for 2½ hours, stirring throughout the whole time as before.

Modern improvements in the methods of manufacturing alizarin-red lakes have furnished results showing a much higher degree of intensity and brightness than was formerly possible. After-treatment of the lake by boiling (steaming) under pressure is said to yield brilliant shades and of great intensity.

Slight additions of tin salts are also added on occasion to brighten the shade.

In making alizarin-red lake it is very essential that the aluminium sulphate employed be free from iron if brilliant lakes are desired. Further, the solutions should be as dilute as possible, as this ensures fineness of structure and softness in the finished article.

Maroon and **claret-red lakes** are produced from alizarin with chromium salts, and **purple lakes** may be obtained by the aid of iron salts.

In connection with the production of alizarin-red lake, the following observations of Liechti and Suida (Mittheil. Gewerb. Museum, Wien, May, 1885) are of interest.

Pure aluminium hydroxide is incapable of directly forming a lake with alizarin—*e.g.* when boiled with an aqueous solution of the latter. The addition, however, of calcium salts at once effects the formation of a lake.

Aluminium-alizarin lakes of definite composition are best prepared by mixing solutions of aluminium salts with an alkaline solution of alizarin. Lakes are also produced if a solution of aluminium acetate mixed with alizarin is heated; or if aluminium hydroxide is heated with alizarin and ammonia, and the mixture is carefully neutralised with acetic acid; or if a mixture of aluminium hydroxide, alizarin, and concentrated sodium acetate solution is heated.

Normal aluminium alizarate $Al_2(C_{14}H_6O_4)_3$, produced by the double decomposition of solutions of aluminium sulphate and ammoniacal alizarin (1 mol. Al_2O_3 to 3 mols. alizarin), forms a purplish-red precipitate, which changes to purplish-black on drying. It is soluble in distilled water and alcohol with a red colour, and in alkalis, especially ammonia, with a fine purplish-red tint. Basic aluminium alizarates of definite composition are prepared by proportionately decreasing the amount of alizarin employed in the above-mentioned decomposition. $Al_4(C_{14}H_6O_4)_3(OH)_6$ is a bright-red precipitate changing to brownish-red on drying. It is soluble in ammonia with a bright-red colour. $Al_2(C_{14}H_6O_4)(OH)_4$ is also a bright-red precipitate, which gives a red powder on drying. In ammonia it is much less soluble than the foregoing. $Al_4(C_{14}H_6O_4)(OH)_6$ is a bright-red precipitate, which still remains a fiery-red powder on drying and is very sparingly soluble in ammonia. All the above basic aluminium alizarates are insoluble in water and in alcohol.

Alkaline solutions of normal aluminium alizarate and of the basic compound

$$Al_4(C_{14}H_6O_4)_3(OH)_6$$

may be mixed with solutions of sodium phosphate, sulphated oil, soap, &c., without undergoing decomposition, but, on neutralising these mixed solutions with acids, very brilliant red lakes are precipitated. Normal aluminium phosphate $Al_2(PO_4)_2$ obtained by precipitation and well washed, cannot be dyed with alizarin, The formation of a lake only occurs when a calcium salt, *e.g.* calcium acetate, is also added. Aluminium-calcium-alizarin lakes of varied composition may be prepared by boiling together definite proportions of pure aluminium hydroxide, calcium acetate solution, and alizarin. They form either dark or bright brownish-red precipitates. All are insoluble in water, and some are insoluble in ammonia. The amount of calcium entering into the composition of the lakes produced in this manner depends upon the amount of alizarin employed and *vice versâ*.

The probable formula of normal alizarin-red lake is given as $Al_2Ca(C_{14}H_6O_4)_3(OH)_2$ by the above-mentioned authors.

Cochineal-carmine. In the preparation of this brilliant scarlet lake, cochineal is extracted in tin-lined vessels with a large quantity of boiling water. Certain additions are made to the filtered decoction, and it is then allowed to stand for several weeks, or even months, in shallow vessels of tin or porcelain, during which period the carmine gradually separates in the form of a fine red powder. The additions referred to vary with different makers, and include the following: potassium binoxalate, acid potassium tartrate (cream of tartar), alum with or without cream of tartar, hydrochloric acid, &c. In all cases the presence of iron must be strictly avoided. The necessary ingredients may also be added to the water with which the cochineal is boiled, in which case the decoction must be filtered hot, since it rapidly becomes turbid on cooling. The addition of gypsum, calcium carbonate, zinc oxide, &c., so usual in other cases, must be avoided, since these would produce violet-coloured lakes.

The manufacture of cochineal-carmine is now very restricted, and the methods employed for producing the finest product have always been kept secret.

According to Alyon and Langlois 500 grams cochineal are boiled for 1½ hours in 30 litres water containing 25 grams sodium carbonate. The decanted solution is well stirred up with 25–35 grams powdered alum, and then allowed to settle about 20 minutes; the clear liquid is poured off, a dilute solution of isinglass or albumen is added, and the whole is heated until the carmine collects together in the form of a coagulum. After cooling and allowing to settle, the supernatant liquid is decanted off, the carmine is collected on a filter, washed, and dried at a low temperature. The deeply coloured filtrate serves for the production of carmine-lake.

Even alum alone could apparently be used as the precipitating agent, according to an old recipe, but it seems likely that in this case water possessing an alkaline reaction must of necessity have been employed. Boil 16 parts ground cochineal for 10 minutes with about 600 parts of water, then add 1 part ground alum, boil a few minutes longer, filter the hot solution and allow the filtrate to stand in shallow porcelain basins. In the course of a few days the carmine is said to separate in the form of a red slimy precipitate, which is collected and dried. The decanted liquor on standing yields a further quantity of carmine of a lower quality; its precipitation is facilitated by the addition of a small quantity of stannous chloride.

The residual cochineal which has thus been only partially exhausted serves for the preparation of carmine-lake.

In other similar recipes a mixture of alum and cream of tartar is used instead of alum only, but in that of Madame Cenette, at one time a celebrated maker of carmine, the statement that the effective precipitating agents are potassium nitrate and potassium binoxalate is difficult to understand.

Chinese carmine is said to be prepared by extracting cochineal with a boiling solution of alum, heating the filtered decoction with the addition of a solution of tin in nitric and hydrochloric acid (*aqua regia*), and finally leaving the liquid to stand till the carmine separates.

Cochineal-carmine is insoluble in water but soluble in alcohol. In ammonia solution it dissolves readily with a purplish crimson colour; from this solution tartaric acid precipitates the original carmine, for although when dried the precipitate has a brownish-red colour it becomes bright red when powdered. The following analysis of cochineal-carmine is given by C. Liebermann (Ber. 18, 1969):

Moisture	17 p.c.
Nitrogenous matter . .	20 ,,
Ash	7 ,,
Colouring matter . . .	56 ,,
Wax	traces

The ash consists of SnO_2 0·67 p.c., Al_2O_3 43·09, CaO 44·85, MgO 1·02, Na_2O 3·23, K_2O 3·56, P_2O_5 3·20. From these analyses Liebermann considers cochineal-carmine to be a peculiar aluminium-calcium-protein compound of the carmine colouring matter, somewhat analogous to the Turkey-red lake, in which alizarin is combined with aluminium and calcium. According to the experiments of the late J. Bedford of Leeds, cochineal-carmine can only be prepared if a calcareous water is employed, or calcium salts are not added during the reaction. Cochineal carmine can, indeed, be readily produced by adding to a cold extract of the dye prepared with a hard water potassium carbonate, alum, and subsequently cream of tartar (or potassium binoxalate) in definite proportion. The carmine precipitate separates very gradually during some days, and has an extremely brilliant character. If a small quantity of stannic chloride is also added to the mixture the precipitation is hastened and the product possesses a more scarlet tint (private communication).

Carmine-lake is simply an ordinary aluminium or tin lake of the colouring matter of cochineal, produced by adding sodium carbonate to a cochineal decoction containing alum or stannous chloride, or both. The latter may also be added to an alkaline solution of the colouring matter.

Florentine-lake is merely a special quality of carmine-lake, containing usually an excess of alumina, and sold in the form of 'drops'; and the so-called Venetian-lake, Hamburg-, Chinese-, Roman-, and scarlet-lakes, are all varieties of Florentine-lake.

Brazil Indian-lake or **lac-lake** is a dark purplish-red lake analogous to carmine-lake, and prepared in a similar manner from the Indian product 'lac.'

Brazilwood lake can be prepared by extracting Brazilwood or peachwood with boiling water, adding alum and tin solution to the filtered decoction, and finally precipitating with sodium carbonate, avoiding excess. Another method is to add precipitated and washed aluminium hydroxide to a filtered decoction of Brazilwood. Freshly prepared decoctions are never suitable for the manufacture of these lakes; they should always be oxidised, by exposure to air or otherwise, in order to change the principle brazilin into the necessary colouring matter brazileïn.

Vienna-lake is a species of Brazilwood lake, prepared in the following manner. A mixture of ground starch (30 kilos.), chalk (10 kilos.), and a little gypsum, is stirred up with a decoction of Brazilwood; then ground alum (1 kilo.) is added and the whole is well stirred for 12 hours and finally allowed to settle. After decanting the clear liquor, Brazilwood decoction is again added to the residual precipitate, together with a further quantity of alum (1 kilo.), and the stirring is continued as before. This process is repeated until the precipitate has taken up sufficient colouring matter and acquired the character of a lake. The decanted liquors are agitated with fresh starch, chalk, &c., in order to yield further quantities of lake.

In the foregoing process the alum is decomposed by the chalk, and the alumina precipitate thus produced combines with the colouring matter. At first the lakes appear violet through the presence of excess of chalk, but with the continued addition of alum they gradually acquire a crimson colour.

Fine dark carmine-red lakes are obtained by adding stannous chloride and cream-of-tartar to a concentrated old decoction of Brazilwood.

Yellows.

Persian-berry lake is prepared by extracting Persian-berries two or three times with boiling water, dissolving alum in the combined and filtered liquors, and then precipitating with sodium carbonate, taking care to avoid excess. The precipitate is collected on a filter, washed, and sold in the form of paste. This lake, containing much starch, and sold in the dry form, is said to be employed in the colouring of sweetmeats.

Persian-berry carmine is produced if stannous chloride is employed instead of alum in the above process. It is a bright orange lake employed by calico-printers.

Persian-berry lakes may also be made after the manner of Vienna-lake, *i.e.* with the use of chalk, alum, and starch.

It is essential to employ only freshly prepared decoctions if bright-coloured lakes are desired.

Quercitron-yellow lake, Flavin-lake, or **Dutch-pink** is made according to the method adopted in the case of Venetian-lake, by precipitating a decoction of quercitron-bark containing alum with chalk. The methods employed in making yellow lakes from Persian-berries may also be used. To ensure bright colours the decoction of quercitron bark is clarified by adding a little gelatin solution, thereby removing the tannic acid. Sometimes milk of lime is used instead, taking care to avoid excess.

It is said that these quercitron colours retain their intensity by gaslight better than all other vegetable yellows, and are hence useful for theatre decorations, &c.

The yellow natural colouring matters, especially flavine and Persian-berries, are still in some demand for the production of green lakes by combination with basic green artificial colouring matters.

The yellow lake is first prepared and a solution of the coal-tar colour precipitated upon it by tannin and tartar emetic. A partial precipitation of the basic colour is effected by the tannic acid in the vegetable colour, but must be completed by a further addition. These lakes are used for wall papers and for colouring toys.

Stil de grain is a low quality of Dutch-pink.

English- and **Italian-pinks** are other qualities of quercitron-bark yellow lakes.

The above lakes are sold in the dry condition in the form of pyramidal-shaped 'drops.' They never possess the brilliancy of those obtained from Persian-berries.

LAKES DERIVED FROM ARTIFICIAL COLOURING MATTERS.

The great increase in the number and variety of coal-tar colouring matters has given rise to a corresponding increase in the colour lakes made from them. Moreover, many of the lakes so formed are at least as fast as any obtainable from natural colouring matters. In consequence the latter have lost much of their former importance.

In the preparation of these lakes the 'base' or 'carrier' upon which the colouring matter is precipitated in a more or less insoluble form is a most important element, since it determines in great measure their brilliancy, covering power, and general qualities.

On the other hand, upon the character of the colouring principle depend other properties of the lake, *e.g.* fastness to light, to spirit, to alkalis and acids.

'Carriers' for lakes are usually very finely divided, insoluble, white (more rarely coloured) materials, such as starch, kaolin (China clay), gypsum, heavy spar (barytes), artificial barytes (blanc-fixe), lithopone, precipitated chalk, kieselguhr, zinc white, red lead, &c. They are intimately mixed with the colour solution, and attract the colouring matter either directly or when suitable precipitating agents are added to the mixture. More often, however, they are formed and precipitated along with the colouring matter, and may then consist of aluminium hydroxide, phosphate, or arsenate, or the first named along with barium sulphate.

The precipitating agent to be employed in any particular case varies according to the nature of the colouring matter—whether acid or basic, for example—and the purpose for which the lake is intended. For lakes employed in decorative painting finely ground barytes is considered to be the most serviceable 'carrier.' Gypsum and kaolin are also used. The chief base for lakes employed in printing wall-papers is blanc-fixe, since it excels all others in giving body and covering power; usually some quantity of alumina, starch, or China clay is admixed with it to render the resulting lake lighter and easier to work. Higher-class papers contain a proportionately greater amount of alumina.

For paper-staining, lithographic, and printing inks the lakes must possess fineness and covering power to a very high degree, and for these aluminium hydroxide, precipitated apart from the colouring matter, is highly esteemed. It is particularly valuable in producing lakes of a transparent nature for use in the three-colour process; some blanc-fixe is often precipitated together with the alumina. Starch, China clay, zinc white, and lithopone are also employed where transparency in the pigment is not of primary importance.

China clay is most largely used with the basic coal tar colours, since for these its attractive power is very marked. Barium sulphate and aluminium hydroxide precipitated during the process of forming the lake, are chiefly used with the azo colours and the acid colouring matters generally. Lead sulphate and red lead are important bases for the eosin lakes.

The proportions of the various materials employed in making the lakes vary considerably according to the desired intensity of the final product.

All lakes should be washed with water, preferably by decantation, till neutral and free from soluble salts. They are sold as pastes or powders, the latter being sometimes in the form of light porous blocks or 'drops' of suitable size.

In all cases the 'extra' brands of all colouring matters should be purchased. They contain the dyestuff in a more highly concentrated form, for ordinary brands are standardised for the use of the dyer by the addition of starch, common salt, or sodium sulphate, and these are useless, or even harmful, from the point of view of the lake manufacturer.

A. *From Basic Colouring Matters.*

The chief methods of precipitating basic colouring matters are—

(*a*) With tannic acid; (*b*) with soap or sulphonated oil; (*c*) with sodium phosphate or arsenate; (*d*) with resin soap; (*e*) with casein or albumen.

(*a*) Tannic acid is the most generally used of all precipitating agents for basic colouring matters, combining with them to form tannates insoluble in water. It is but rarely used alone, since the resulting lakes are dull and extremely fugitive; an addition of half the equivalent quantity of tartar emetic causes the complete fixation of the lake, and improves its properties as regards brightness, fastness to light, spirit, &c. Sodium acetate, or occasionally sodium carbonate, is employed to reduce the acidity of the solution.

The 'carrier' is well mixed with water, the solution of the colour added together with sufficient sodium acetate to combine with the mineral acid liberated by the colour base. The solution of tannic acid is next poured in whilst stirring well, and the precipitation completed with tartar emetic.

This method is most suitable for green and red colours, such as malachite green, brilliant green, magenta, rhodamine, and safranine.

(*b*) A method especially suitable for violet and blue basic colours is based on the precipitation of their colour bases as salts of oleic, palmitic, and stearic acids. A pure soap, containing no free alkali, or a sulphonated olive oil (*e.g.* Turkey-red oil) is employed. Aluminium sulphate, tannic acid, zinc or tin salts are also added on occasion.

(*c*) For basic colours of the methyl violet class a further method consists in the precipitation of aluminium phosphate, together with the added colour by means of aluminium sulphate and sodium phosphate to which sufficient sodium carbonate has been added to produce a perfectly neutral solution.

$$\mathrm{Al_2(SO_4)_3+2Na_2HPO_4+Na_2CO_3}$$
$$\mathrm{=Al_2(PO_4)_2+3Na_2(SO_4)+H_2O+CO_2}.$$

Similarly sodium arsenate, freshly prepared from white arsenic and sodium carbonate, is used in place of sodium phosphate—no addition of soda is then necessary, but care must be taken that the solution is neither strongly acid nor alkaline. As a rule, the precipitation is made in a very slightly acid solution obtained by using a slight excess of aluminium sulphate with addition of sodium acetate.

(*d*) All basic colouring matters form lakes of great brilliancy with resin soap, *i.e.* a solution of colophony in caustic or carbonated alkali. They are precipitated on the carrier along with a metallic salt of the resinate, usually zinc or aluminium.

Auramine, magenta, rhodamine, and patent blue furnish the most satisfactory lakes, and are much used for wall papers. They are of no value for oil or lithographic work, being very fugitive and readily soluble in alcohol and benzene.

It has been found possible to use the benzene solution of these 'resinate' colours for dyeing silk without injuring its finish, lustre, and general appearance. They are also used for preparing coloured varnishes employed in ornamenting metallic surfaces, wood, leather, glass, &c.

(*e*) According to Weber albumen can be employed as a precipitating agent for basic colouring matters with production of lakes of excellent brilliancy, notably fast to water and light. A cold aqueous solution of the dyestuff is mixed with the albumen (also in aqueous solution), stirred into the carrier, and the whole precipitated by raising the temperature to 90° with or without the final addition of a little acetic acid.

Casein may also be applied in a somewhat similar manner.

It is stated that this method is also applicable to the acid colouring matters, and is of special importance for producing non-poisonous eosin and rhodamine lakes.

Blue and violet lakes of great brilliancy may be obtained by mixing certain blue and red colour solutions with precipitated and washed Prussian-blue, which thus becomes dyed.

Potassium dichromate along with starch, &c., has been used as a precipitant with safranine, with which it produces a brownish-red lake changing to carmine-red on drying.

Basic colouring matters are especially remarkable for their ready absorption by inert materials, such as kaolin, starch, diatomaceous earth, green earth, &c., without the aid of any precipitating agent. A solution of the dyestuff is well mixed with the finely divided and well-washed base, and allowed to stand for some time with occasional stirring. A certain amount of colouring matter is attracted from the solution and the carrier becomes, as it were, dyed. Other carriers, *e.g.* gypsum, blanc-fixe, zinc oxide, &c., may be used, but their attractive power for the colouring matter is very small, and they serve chiefly as diluents. The lakes from the silicious earths are the more firmly fixed, and withstand the action even of strong alkalis. For this reason they find application in the manufacture of cheap lime washes.

Coloured powders, prepared according to these latter methods, can scarcely be regarded as true lakes, as they mostly give up their colouring matter on repeated washing.

B. *From Acid Colouring Matters.*

The great majority of the acid colouring matters referred to here are the sulphonic acid derivatives of certain colour bases and azo colouring matters derived from benzene, naphthalene, &c. With these barium chloride is almost exclusively employed as the precipitating agent; a further addition of aluminium sulphate is also often made, especially if the colouring matter exhibits mordant dyeing properties according to the law of Liebermann and Kostanecki.

More rarely, lead salts replace barium chloride.

Some of the phenolic colouring matters which possess special features may be included under this head, notably the eosins. Lead acetate or nitrate is especially suitable as a precipitating agent for colours of this class.

Other suitable materials are alum, aluminium acetate, calcium, magnesium, zinc, or stannic salts; as a rule, they are used in conjunction with caustic or carbonated alkali.

As in the case of the basic colour lakes, so here, the 'base' or 'carrier' upon which the lakes are precipitated is of great importance, and the reader is referred to what has been said already upon this point.

The standard method for the formation of lakes from acid colouring matters containing the sulphonic acid group is that with aluminium sulphate and barium chloride. The aluminium sulphate is precipitated as hydroxide in the first instance by soda, the colouring matter stirred in and then precipitated by the addition of barium chloride. In this way part of the 'carrier' is also produced, in the form of artificial barytes, at the moment of precipitation through the interaction of the barium chloride and the sodium sulphate resulting from the decomposition of the aluminium sulphate, and not only is the precipitation rendered more complete thereby, but also a very intimate admixture of the 'carrier' and precipitated colour is secured.

A proportion of inert 'carrier,' *e.g.* heavy spar, kaolin, lithopone, may also be added to the solution of aluminium sulphate before precipitation when lakes of greater opacity or less tinctorial power are desired; an extra addition of Glauber's salt before the final precipitation, will bring about the same result by increasing the amount of artificial barytes produced. Replacing the aluminium sulphate by alum yields lakes of a higher quality and valuable for printing purposes. They are, of course, more costly to manufacture.

A typical example of this method, published by the Farbwerke vormals Meister Lucius and Brüning, Hoechst am Main, is the following:—

30	parts	aluminium sulphate	1/100 solution
12	,,	calcined soda .	1/100 ,,
12	,,	colouring matter .	1/50 ,,
42	,,	barium chloride .	1/100 ,,

Precipitate at 50°–60°C. This method is stated to be suitable for the various brands of azo scarlets.

Reds. These are chiefly derived from the azo colouring matters. A great variety are now on the market, furnishing shades from a very bright scarlet to a dark bluish-red. Such are Ponceau 2G, G, GR, R, 2R, 3R, &c., Fast red, Bordeaux red, Crocein scarlet, &c.

Red lakes, in nearly all cases, are shaded by admixture with other colours, especially the various brands of oranges (*see* below under *Combined Lakes*). In such cases it is of considerable importance whether the colours are dissolved separately or together, the latter method often producing brighter lakes than the former.

Generally speaking, complete precipitation is obtained by the use of barium chloride upon a 'base' of alumina with or without the admixture of an inert diluent, blanc-fixe being produced simultaneously with the precipitation; certain colours are more difficult to throw down completely, but this may be obviated by suitable variations of quantities, temperature, dilution, &c. The addition of a little Turkey-red oil frequently has a favourable influence.

Another method in the case of some red azo colouring matters consists in treating a solution of aluminium sulphate with milk of lime, forming a 'base' of alumina and calcium sulphate. The colour is thrown down upon this by the addition of barium chloride, and at the same time the calcium sulphate is replaced more or less completely by blanc-fixe. The resulting lakes are said to be very soft and light.

The milk of lime may be replaced by levigated chalk with advantage.

Eosins. These colouring matters give scarlet and crimson lakes of great brilliancy, some of which (the so-called 'vermilionettes') are employed as substitutes for vermilion. They are mostly very fugitive. For yellowish-reds a yellow shade of eosin is employed; for reds, gradually increasing in blueness, erythrosine, phloxine, cyanosine, and rose bengal may be used. The usual precipitants are lead salts, 1 part pure eosin being precipitated by 1 part lead acetate, or 0·75 lead nitrate. Aluminium, tin, and zinc salts are also used.

The nature of the precipitating agent influences the shade of the resulting lake; thus lead acetate gives more yellowish products than lead nitrate from the same colouring matter. Lead salts give blue, tin and aluminium salts yellow shades.

For 'vermilionettes' red lead is a suitable base, with or without the addition of small quantities of lead sulphate or barytes. Better class varieties are made with chromate-of-lead-orange and alumina, in order to lessen their high specific gravity. Due allowance must be made for the variation in shade caused by the presence of a coloured 'carrier.' Their production is very simple; the solution of colouring matter is mixed with the base, complete precipitation being obtained on the addition of a lead salt.

Printing and lithographic colours (known as *geranium* lakes) are largely produced from the eosin colouring matters. They may be transparent or opaque, according to the special use for which they are intended; they all possess great covering power. Alumina and blanc-fixe—either alone or in conjunction—and lead sulphate are chiefly used as the 'carriers'; or, occasionally, starch, kaolin, or red lead. The colour is precipitated upon them by a lead salt. Aluminium (as alum, &c.) does not produce so complete a precipitation.

If desired the lake may be shaded up by the addition of rhodamine B, which unites with, and is precipitated along with the eosin.

Combined lake pigments are also made with the various brands of azo scarlets and orange II.

Oranges. The methods applicable to the red colouring matters are also suitable for making orange lakes.

Orange II. furnishes a bright lake of good fastness to light, and is in considerable demand on account of its cheapness. Other brands are orange R, O, and fast orange O. For better-class lakes used in printing and lithography brilliant orange G and R are employed.

As stated above, orange colouring matters find frequent application in shading the scarlet azo colours.

Yellows. The number of yellow lakes is comparatively small owing to the superior properties of the various chrome yellows (*see* PIGMENTS). They are employed, however, to shade green lakes in a manner similar to that of the oranges for azo scarlets.

The most important colours used are naphthol yellow S, quinoline yellow S, Victoria yellow, &c.

Greens. The colouring matters mostly employed for these lakes are sulphonic acids of the triphenylmethane series, *e.g.* the various acid greens, but are among the most difficult of all the acid colouring matters to precipitate.

Naphthol green belongs to a different class.

They are only partially precipitated by barium chloride, employing the usual aluminium sulphate and soda method, and special modifications must be resorted to, such as after-precipitation with further quantities of aluminium sulphate or barium chloride, or both at once, reversing the order of precipitation and so on.

The lakes from acid greens (the so-called viridine greens) possess a bluish-green shade. Lakes from naphthol green are particularly fast to light. Better results and a greater range of shades are obtained by admixture with naphthol yellow or quinoline yellow. Combination apparently takes place with the basic amino groups of the acid green with the formation of a less soluble combined colour.

Blues. With the exception of the red acid colouring matters the blues furnish the greatest number of colours for lake-making. A large number of shades are obtainable, but, unlike the scarlets, a separate brand is used for each particular shade, and mixtures are rarely found necessary. Alkali blues (opal blue, water blue, &c.), patent blue, and erioglaucine are chiefly in demand. They are readily precipitated by barium chloride upon a mixed alumina and blanc-fixe or other suitable base. The patent blues and erioglaucines are exceptions; for the former the addition of a little barium hydroxide has been found effective, for the latter some zinc sulphate is added, and this is precipitated by sodium carbonate as mixed hydroxide and carbonate.

For printing purposes alkali blue can be precipitated by Turkey-red oil or soap, and subsequent addition of a lead or aluminium salt, with a suitable carrier. The latter, again, may be dispensed with, and in such cases the lakes often exhibit a magnificent lustre.

Violets. Very few violet lakes are manufactured from acid violet dyestuffs, although they are very much faster than the corresponding lakes from basic colours. Fast acid violet is principally employed. They are all expensive to make, and only find application for special purposes.

A very blue violet is formyl violet S4B; it furnishes lakes suitable for the manufacture of printing inks.

All these colours are precipitated by barium chloride upon a suitable 'carrier.'

C. *From Mordant Colouring Matters.*

Besides the very important alizarin-red lakes already described, a certain number of other adjective colouring matters are used for lake making. They are mostly closely related to alizarin itself, *e.g.* alizarin orange, brown, bordeaux, yellow, green, black, blue; acid alizarin blue, and galloflavin, cœrulein, and gallein are also employed. They furnish lakes very fast to light, although they cannot compare in brilliancy of shade with other, but much more fugitive lakes from basic and acid colours.

Lake formation is brought about in the same manner as with alizarin red, the general principle involved being the precipitation of an alkaline solution of the colour by aluminium hydroxide.

Colours which do not dissolve in soda require a modification or reversal of the usual method; they are stirred up with the solution of aluminium sulphate (or alum), and combination is effected by addition of soda, sodium phosphate, and Turkey-red oil.

The Badische Anilin und Soda Fabrik publish a special method for cœrulein:

22 lbs. colouring matter in 27½ gallons of water with 44 lbs. sodium bisulphite (40°Bé.) are well mixed and allowed to stand for 12 hours; then heated to 70°C. with a further 27½ gallons of water, filtered, and the filtrate diluted with 110 gallons water. The whole is then raised to boiling, and 44 lbs. potassium alum added. After half an hour's boiling a final addition of 33 lbs. sodium bisulphite is made, the boiling again continued for half an hour, and the lake filtered, washed, and dried at the ordinary temperature.

D. *From Insoluble Colouring Matters.*

A series of azo colours insoluble in water are now made by the principal German colour-works and sold in paste form for working up into lakes, according to specially adapted methods. The range of shades varies from yellow to bluish-red. The series of 'pigment' colours (Meister Lucius and Brüning) may be mentioned, *e.g.* pigment chlorine GG, pigment orange R, pigment red G and B, pigment purple A, and lake red C and D.

Also the autol orange and red and lithol red of the Badische Co., together with the helio purpurin and helio fast red of Bayer & Co. and the 'red for lakes' of the Berlin Aniline Co.

They are mixed with suitable 'carriers' such as heavy spar, lithopone, orange lead, magnesium oxide, and chalk. Frequently the mixture is simply ground together in the cold; another method is to heat to boiling and add barium chloride. Salts of magnesium, copper sulphate, and ferrous sulphate with Turkey-red oil are also used. The dry lakes are subjected to prolonged grinding with zinc white, orange lead, &c., this process greatly increasing their intensity. They are employed for lithographic and printing inks, as well as for oil and varnish colours and possess good brilliancy, whereas many of them are exceptionally fast to light as well as to alkalis and spirit.

E. *From Developed Azo Colours.*

The application of the 'ice colours' to carriers for the production of lake pigments was a natural outcome of their successful use upon textile fibres.

At the present time the method is in very general use as the lakes made after this manner are distinguished by their fastness to light and other valuable properties. Practically all shades are obtainable except a green.

The pigments are all produced by the diazotisation of an amino followed by coupling with a phenol or another amine in a solution which contains the 'base' or 'carrier' in suspension.

The chief amines used in diazotising are: *m*- and *p*-nitraniline, the nitro-toluidines, anisidine, nitrophenetidine, benzidine, tolidine, α- and β-naphthylamines. Bluer shades, but less fast to light, are obtained from aminoazobenzene and -toluene.

The diazo compounds are coupled with various phenols and amines, especially β-naphthol which produces very bright lakes fast to water (the *insoluble azo-colours*). Other phenols used are phenol itself, resorcinol, α-naphthol, and its disulphonic acid, and β-naphtholdisulphonic acid.

The principal amines are diphenylamine and *m*-phenylenediamine.

Certain precautions are necessary to produce lakes of maximum brightness, *e.g.* care must be taken to regulate the proportions of acid and alkali so that a neutral liquor is present when the formation of the lake is complete. In practice a little sodium acetate is added, acetic acid having a less harmful action than free hydrochloric acid. An alkaline liquor renders the lake dull and dirty in shade.

The following recipes (published by Chem. Fabrik Griesheim-Elektron) will best illustrate the manufacture of these lakes.

A base (A) is prepared from solutions of
1330 grams aluminium sulphate
650 ,, calcined soda,
490 ,, barium chloride.

The precipitate is washed thoroughly and well mixed with the alkaline solution of β-naphthol (B) prepared from
300 grams β-naphthol dissolved in
300 c.c. caustic lye (34°Bé.) and 2 litres boiling water.

Add 300 grams calcined soda in 3 litres cold water,
180 grams Turkey-red oil,
300 grams sodium acetate, making the whole up to 10 litres.

Into this is run the diazo solution (C) from
280 grams *p*-nitraniline dissolved in
600 c.c. hydrochloric acid (21°Bé.) and 2 litres boiling water.

The temperature of this liquid is then reduced to 10°C. by addition of 2 litres cold water and ice and then diazotised with a solution of 144 grams of sodium nitrite.

The precipitated lake is washed thoroughly and dried. The above recipe is said to yield a deep-red shade.

The azophor reds of M.L.B. may be used in place of the diazotised bases.

F. *From Sulphide Colouring Matters and Indigo.*

Within recent years a number of processes have been patented for the manufacture of lake-pigments from the vat dyestuffs, especially the sulphide colours. They are brought into solution as in dyeing cloth and precipitated upon a base by various means.

According to one such patent, taken out by Cassella & Co., the dyestuff (25 p.c. paste) is dissolved in 1 p.c. sodium sulphide and precipitated upon barytes or other suitable 'carrier' by the addition of sodium carbonate and barium chloride.

In another method, patented by the Berlin Aniline Co., the dyestuff is dissolved in sodium sulphide, a solution of barium chloride added, and oxidation brought about by blowing air through or adding manganese dioxide.

For instance, 20 parts sulphur black T extra are dissolved in a solution of 15 parts sodium sulphide, a solution of 25 parts barium chloride run in and air blown through the mixture.

Lakes may also be obtained from indigo. They are said to be exceptionally fast and especially suitable for producing very bright combined lakes.

COMBINED LAKE PIGMENTS.

As already mentioned a lake is frequently produced by the precipitation of more than one colouring matter, either separately or in conjunction, upon the 'carrier.' The colours may be of similar chemical nature, but varying shade, or they may differ absolutely in both these respects. To the first class belong, for example, the numerous scarlet lakes obtained by combining orange and scarlet colouring matters of various shades.

Lakes belonging to the second class differ materially both in shade and properties from any member of the combination used to produce the pigment, *e.g.* the maroon lakes made from scarlets combined with magenta or safranine.

For the latter lakes and others of the same class the initial colour is always either red, orange, or yellow, and from these all possible shades from bluish-red to yellowish-green are obtained by the addition of other colours such as magenta, safranine, methylene blue, malachite green, acid green, and even diamond black.

The methods available for manufacturing these combined lakes are obviously too numerous for detailing here, but a few general outlines and precautions may be indicated. Thus due consideration must always be given to the acid or basic character of the colours used and suitable means of precipitation arranged. Acid and basic colours should never be dissolved together, since combination takes place often with the production of a dark resinous precipitate. The same applies to colours such as the acid greens, which contain groups capable of combining with the acid or basic groups of the second colour.

The first colour may be made into a pigment (termed the 'initial lake'), upon which a second colour is then precipitated by suitable reagents. When, as most frequently happens, the initial lake is prepared from a soluble azo colour by means of barium chloride, and a basic colour is thrown down upon it, care must be taken that the precipitating agent used in the latter case does not affect the pigment first formed. For this reason materials such as Turkey-red oil and resin soap must be excluded, and the tannic acid and tartar emetic method is the only one really suitable for this purpose.

Analysis of Lake Pigments.

The analysis of the colouring matters in a lake is often a matter of great difficulty, and the subject remains largely in an empirical state. The composition of the 'base' or 'carrier,' on the other hand, presents no serious difficulties; a portion of the lake is incinerated and the residue examined by the usual processes of qualitative analysis. In this way the presence of mineral pigments to which coal-tar colours have been added may also be detected. Valuable indications may often be given by the presence of the precipitating agent in the mineral residue, *e.g.* a red lake which is found to contain lead is most likely to have been produced from a colouring matter of the eosin series, &c.

Other properties, chemical and physical, also furnish important evidence, the colour, fastness to light, to acids, alkalis, spirit, &c. Further, the selling price of a lake will often be a deciding factor where two colours are under consideration, of similar shade but different in price.

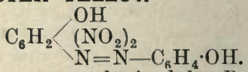
The class of colouring matter from which any given sample of a lake may have been derived can generally be settled with considerable precision by employing the schemes drawn up by various authors for the analysis of dyestuffs, both on the fibre and in the solid state, making allowance for the alterations in properties brought about by the presence of the carrier and precipitating agent. The identification may be carried further by noting the behaviour of the sample towards such reagents as sulphuric acid, caustic soda, hydrochloric acid, alcohol, &c.; but where more than one colouring matter is present the only satisfactory method of determining the shading colours is by trials in the laboratory or by comparison with a series of standards. Modern pigments, as previously stated, are mostly examples of 'combined' lakes, and in such cases, though the principal constituent may be identified, it is frequently all but impossible to detect the small quantity of the secondary colours present by any process of direct analysis. In this case it is best to ascertain their nature indirectly by a comparison with lakes specially prepared for the purpose.

Literature.—Lehrbuch der Farbenfabrikation, J. G. Gentele; Die Erd-Mineral-und-Lack-Farben, &c., S. Mierzinski; Die Chemie des Steinkohlentheers (2nd ed.), 2, 22, G. Schultz; The Manufacture of Lake Pigments from Artificial Colours, F. H. Jennison; A Treatise on Colour Manufacture, Zerr and Rübencamp, translated by Ch. Mayer; The Manufacture of Mineral and Lake Pigments, Bersch, translated by A. C. Wright; Painters' Colours, Oils, and Varnishes, G. H. Hurst; Journ. Soc. Dyers and Colourists (1890, 6, 32); Instructions issued by several Coal-tar Colour Manufacturers; Weber (J. Soc. Chem. Ind. 1891, 10, 896; 1893, 12, 650; 1894, 13, 1151).

For the analysis of lake pigments.—Tests for Coal-tar Colours in Aniline Lakes, Geo. Zerr, translated by Mayer. A. G. P.

LAMPBLACK is the soot or finely divided carbon produced by the imperfect combustion of various substances of a fatty or resinous nature, such as vegetable and animal oils, pinewood, and dead oil; and it may be taken that whatever the combustible material which, on full exposure to the oxygen of the air, produces the best illumination, that material will, if partially deprived of air, produce the greatest amount of sooty deposit. The German mode of manufacturing lampblack consists in collecting it on a woollen cloth exposed to the smoke emitted from resinous woods burning in a close furnace. The cloth being shaken from time to time, the particles are detached and collected. Lampblack is employed in the manufacture of printing-inks and pigments (*v.* Indian ink; Carbon).

LANCASTER YELLOW



$$C_6H_2\left<\begin{array}{l}OH\\(NO_2)_2\\N=N-C_6H_4\cdot OH.\end{array}\right.$$

A colouring matter obtained by P. Greiss, in 1875, by the action of picramic (*iso*purpuric) acid on phenol. Sparingly soluble in water; soluble in sulphuric acid, with reddish-yellow colour. Dyes silk and wool in an acid bath brownish-yellow. No longer used.

LANOLIN *v.* Cholesterol.

LANTHANUM. Sym. La. At.wt. 139·0. Crude lanthana was obtained from the cerite earths in 1839 by Mosander, who afterwards separated this material by fractional crystallisation of the sulphates into lanthana and 'didymia' (neo- and praseo-dymia).

Sources.—The minerals containing the cerite metals, *e.g.* cerite, orthite, monazite, and lanthanite (native lanthanum carbonate containing didymium).

Separation. If the material employed as the source of lanthanum contains considerable quantities of yttrium earths a preliminary separation of the two main groups may be effected with sodium sulphate.

Methods of Isolation depending on Differences in Basic Strength.

The separation of lanthana from 'didymia' is quickly effected, although with some loss of material, by adding magnesia to a boiling solution of the mixed salts until the liquid ceases to give the characteristic absorption bands of neodymium and praseodymium, the less basic oxides of these elements being precipitated, whilst the more basic lanthana remains dissolved (Muthmann and Rölig, Ber. 1898, 31, 1718; R. J. Meyer and Marckwald, *ibid.* 1900, 33, 3009). Fractional precipitation with ammonia or caustic soda is hardly to be recommended for experiments on a large scale, because of the difficulty of collecting and washing the hydroxides. Moreover, ammonium salts are decomposed by lanthana and 'didymia' so that these bases are not effectively removed from solution by ammonia.

An interesting modification of the basic method consists in utilising the ignited mixed oxides of the rare earth metals to precipitate fractionally an equivalent proportion of these metals from the neutral solution of their nitrates. A solution of the neutral nitrates is divided into two parts, one portion precipitated with oxalic acid, the oxalates ignited, and the resulting oxides added to the remaining portion of the nitrates in 12 p.c. aqueous solution. A vigorous action occurs, the mixture is diluted, heated on the water-bath, and the clear liquid decanted from the precipitate. The fractionation is repeated on both the soluble and insoluble portions. By this process the lanthanum accumulates in the solutions, whilst the praseodymium and neodymium are concentrated in the precipitates (Hermann, J. pr. Chem. 1861, 82, 385; Auer von Welsbach, Monatsh. 1883, 4, 630; *ibid.* 1884, 5, 508; Schottländer, Ber. 1892, 25, 378).

Boiling the rare earth oxides with ammonium salts leads to a fractionation, since the more basic constituents displace ammonia and pass into solution (Drossbach, Ber. 1902, 35, 2826).

The fractional decomposition of the nitrates is another method depending on differences in basic strength (Bettendorff, Annalen, 1890, 256, 159; Urbain, Ann. Chim. Phys. 1900, [vii.] 19, 184).

The mixed nitrates of lanthanum, praseodymium, neodymium, and samarium melt at about 400°–500° to a clear liquid, in which are gradually formed small crystals of basic nitrate. The solution obtained by boiling the product of fusion with 10 parts of water deposits the basic salt. The fusion is then repeated on the normal nitrates from both the insoluble and soluble portions. The lanthanum accumulates in the undecomposed nitrate, while praseodymium, neodymium, samarium, together with terbium and yttrium metals are found in the basic nitrate fractions.

Methods of Isolation by Crystallisation.

By a systematic fractional crystallisation of the double ammonium nitrates

$$R(NO_3)_3,2NH_4NO_3,4H_2O$$

in nitric acid solution, Auer von Welsbach succeeded in separating lanthanum from the other cerite metals, and also in dividing 'didymium' into its components, praseodymium, and neodymium. In this fractionation lanthanum accumulates in the least soluble portions, and is followed successively by praseodymium and neodymium, whilst the most soluble fractions contain samarium and the terbium and yttrium metals (Monatsh. 1885, 6, 477). In operating on large quantities of cerite earths it is more convenient to work in neutral solutions rather than in nitric acid, but in the absence of acid the number of fractions is considerably increased (Wien Sitzungsber. 1903, 11A, 112).

Other modifications of von Welsbach's method have been devised, having for their object the more rapid separation of praseodymium and neodymium (*cf.* Schéele, Ber. 1899, 32, 409; Dennis and Chamot, J. Amer. Chem. Soc. 1897, 19, 799; Demarçay, Compt. rend. 1900, 139, 1019, 1185; Drossbach, Ber. 1902, 38, 2826; Lacombe, Bull. Soc. chim. 1904, [iii.] 31, 570).

By each of these processes lanthanum can be readily separated in a highly purified condition, because it yields the least soluble double nitrates. Last traces of praseodymium are removed by fractional crystallisation of the double carbonates $K_2R_2(CO_3)_4$, $12H_2O$, where R=La, Ce, Pr or Nd, the metals being arranged in ascending order of solubility (R. J. Meyer, Zeitsch. anorg. Chem. 1904, 41, 94).

The classical 'sulphate' method may also be employed in separating lanthanum from the other cerite metals (Holtzmann, J. pr. Chem. 1858, 75, 321).

Metallic lanthanum, m.p. 810°, sp.gr. 6·1545–6·193, sp. heat 0·04637, is best prepared by the electrolysis of the fused chloride, a current of 50 amperes and 10–15 volts being required; it is the most active of the rare earth metals, tarnishing in dry air, and in presence of moisture becoming coated with white hydroxide (Muthmann, Kraft and Weiss, Annalen, 1903, 325, 261; 1904, 331, 1).

When heated in air lanthanum furnishes a mixture of oxide and nitride, and in hydrogen it yields the hydride. With aluminium, lanthanum forms the alloy $LaAl_4$, a crystalline white substance (sp.gr. 3·923), stable in air, and insoluble in nitric acid (*cf.* Muthmann and Beck, Annalen, 1904, 331, 46).

Lanthana (*Lanthanum oxide*) is a snow-white powder produced by heating the hydroxide or oxalate; its sp.gr. is 5·94, or 6·53 after raising to white heat. The amorphous oxide readily absorbs water or carbon dioxide, but the crystalline modification (sp.gr. 5·296) obtained in rhombic prisms by heating lanthanum carbonate in fused borax can no longer be directly hydrated.

The oxide has been reduced to the metal by magnesium but not by aluminium.

Lanthanum hydroxide $La(OH)_3$, a white amorphous precipitate produced by adding excess of ammonia or caustic alkali to the solution of a lanthanum salt, is the strongest base of the rare earth series; it turns red litmus blue, absorbs carbon dioxide from the atmosphere, and displaces ammonia from ammonium salts. In the presence of hydrogen peroxide, the hydroxide gives a hydrated lanthanum peroxide.

Lanthanum hydride LaH_3 or LaH_2 (Winkler, Ber. 1891, 24, 873; Muthmann and Kraft, Annalen, 1903, 325, 279), formed by direct union of its components at 240°, is a black substance more stable in air than the corresponding cerium compound

Lanthanum carbide LaC_2, sp.gr. 5·02, is prepared by heating in a carbon tube, with an electric current of 350 amperes and 500 volts, 100 parts of lanthana and 80 parts of sugar carbon. When decomposed with water the carbide yields 70–71 p.c. of acetylene, 27–28 p.c. of methane, and 2·0 p.c. of ethylene (Moissan, Compt. rend. 1896, 123, 148).

Lanthanum nitride LaN, a black powder prepared from lanthanum and nitrogen at red heat, is decomposed by moisture yielding ammonia and lanthanum hydroxide (Annalen, 1903, 325, 261). A basic lanthanum azide $La(N_3)_2{\cdot}OH,1\frac{1}{2}H_2O$ having explosive properties, is obtained by dissolving lanthana in aqueous hydrazoic acid, and precipitating with ether-alcohol (J. pr. Chem. 1900, [ii.] 61, 408).

Lanthanum sulphide La_2S_3. A yellow powder, sp.gr. 4·9108, obtained by heating the anhydrous sulphate in hydrogen sulphide, is stable in air but decomposed by boiling water. A higher sulphide La_2S_4 has been produced by the further action of hydrogen sulphide on the sesquisulphide at 600° (Biltz, Ber. 1908, 41, 3341).

Lanthanum nitrate $La(NO_3)_3,6H_2O$ crystallises from water in transparent colourless prisms; it loses $5H_2O$ over strong sulphuric acid, and is readily soluble in alcohol. A strong solution of the commercial nitrate is used as a stamping fluid for marking the maker's name or brand on incandescent mantles, so that when these are burnt the design appears in brown on the white thoria skeleton.

Lanthanum ammonium nitrate

$$La(NO_3)_3,2NH_4NO_3,4H_2O$$

monoclinic crystals, is isomorphous with the corresponding double salts of the other cerite metals (Kraus, Zeitsch. Krist. 1901, 34, 307).

Lanthanum magnesium nitrate

$$2La(NO_3)_3,3Mg(NO_3)_2,24H_2O$$

separates in lustrous colourless rhombohedral prisms belonging to the hexagonal system. Lanthanum also forms well-defined double nitrates with pyridine, quinoline, and other organic bases.

Lanthanum sulphate $La_2(SO_4)_3,9H_2O$ is the most stable of three hydrates, and the least soluble sulphate of the rare earth series, its solubility diminishing with rise of temperature; it separates in hexagonal prisms, isomorphous with the cerous salt $Ce_2(SO_4)_3,9H_2O$. The anhydrous sulphate is produced by heating the hydrate with strong sulphuric acid, when the acid sulphate $La(SO_4H)_3$ first produced is afterwards decomposed above 280°. The double sulphates $La_2(SO_4)_3,3K_2SO_4$ and

$$La_2(SO_4)_3,Na_2SO_4,2H_2O$$

are sparingly soluble, particularly in the presence of excess of alkali sulphate.

Lanthanum fluoride LaF_3 prepared in the anhydrous state by burning lanthanum carbide in fluorine (*cf.* Moissan, *l.c.*) and as a gelatinous precipitate $2LaF_3,H_2O$ by the interaction of hydrofluoric acid and lanthanum acetate; the sulphate yields the acid fluoride $2LaF_3,3HF$.

Lanthanum chloride $LaCl_3$, m.p. 907°, sp.gr. 3·947, is prepared by the general methods for preparing anhydrous chlorides (*cf.* CERIUM; and Matignon and Bourrion, Compt. rend. 1904, 138, 627; 1905, 140, 1181; Ann. Chim. Phys. [viii.] 5, 127); it is a colourless compound dissolving in water or alcohol with considerable generation of heat. In aqueous solution this salt shows very little hydrolytic dissociation; its hydrate $2LaCl_3,15H_2O$ or $LaCl_3,7H_2O$ forms triclinic crystals, the alcoholate is $LaCl_3.2C_2H_5{\cdot}OH$ (Zschiesche, J. pr. Chem. 1868, 104, 174; Cleve. Bull. Soc. chim. 1874, [ii.] 21, 196). The following double chlorides $2LaCl,3PtCl_4,24H_2O$; $LaCl_3,PtCl_4,13H_2O$; and $LaCl_3,AuCl_3,10H_2O$ have been described.

Lanthanum platinocyanide

$$2La(CN)_3,3Pt(CN)_2,18H_2O$$

forms yellow fluorescent prisms with a blue reflex.

Lanthanum acetate $La(C_2H_3O_2)_3,1\frac{1}{2}H_2O$, thin prisms, furnishes in the cold with ammonia a gelatinous precipitate of basic acetate, which, when mixed with solid iodine, becomes blue like starch iodide. This reaction, which does not occur with the nitrate or with the precipitate from boiling solutions of the normal acetate, depends on the colloidal nature of the basic salt, the colour being due to an adsorption compound. Although this colouration is used as a test for lanthanum it is uncertain so long as other elements are present (Biltz, Ber. 1904, 37, 719).

Lanthanum oxalate $La_2(C_2O_4)_3$, 9, 10, or $11H_2O$, a white curdy precipitate becoming crystalline, is more soluble in acid or in aqueous ammonium oxalate than the oxalates of other rare earth metals (*cf.* Cleve, Bull. Soc. chim. 1874, [ii.] 21, 196; Power and Sheddon, J. Soc. Chem. Ind. 1900, 19, 636; Brauner and Pavlíček, Chem. Soc. Trans. 1902, 81, 1243).

Lanthanum acetylacetonate $La(C_5H_7O_2)_3$, colourless needles, m.p. 185°, crystallises from water with $3H_2O$ (Annalen, 1902, 323, 26; 1904, 331, 334).

Spectra of lanthanum.—Spark and Arc Spectra, *v.* Exner and Haschek, Die Wellenlängen der Bogenspektra, I. and II. 1904; Rowland, A Preliminary Table of Solar Spectrum Wave Lengths, 1896.

Unless rendered impure by the presence of traces of other rare earths, lanthana and lanthanum salts do not become luminiscent *in vacuô* under the influence of cathode rays.

G. T. M.

LAPIS-LAZULI (Ger. *Lasurstein*; Fr. *Outremer*). An opaque precious stone valued for its rich deep blue colour. It takes a good polish, and is much used for small ornaments and for inlaying. Formerly it was the only source of the then valuable pigment ultramarine, which is now manufactured on a considerable scale.

Rather than being a simple mineral, it is a mixture of minerals, amongst which the members of the sodalite group predominate, together with calcite, pyroxene, amphibole, mica, scapolite, felspar, iron-pyrites, &c. The material is really an impregnation of various secondary minerals in a crystalline limestone, and has been formed by the contact-metamorphism of calcareous rocks at their junction with granite. The minerals of the sodalite group have been investigated by Brögger and Bäckström, and for the predominant blue constituent of lapis-lazuli they proposed the name *lazurite* (Zeitsch. Kryst. Min. 1890, 16, 231). This is a sodium aluminium silicate and sulphide, and is essentially the same in composition as artificial ultramine. The formulæ they give for the members of the sodalite group are:

Sodalite $Na_4(AlCl)Al_2(SiO_4)_3$
Haüynite $(Na_2,Ca)_2(NaSO_4{\cdot}Al)Al_2(SiO_4)_3$
Noselite $Na_4(NaSO_4{\cdot}Al)Al_2(SiO_4)_3$
Lazurite $Na_4(NaS_3{\cdot}Al)Al_2(SiO_4)_3$.

An analysis by Brögger and Bäckström of lapis-lazuli from Central Asia gave:

SiO_2	Al_2O_3	CaO	Na_2O	K_2O	SO_3	S	Cl	Total.
32·52	27·61	6·47	19·45	0·28	10·46	2·71	0·47	99·97

Here, as in all other analyses, sulphate and chloride are present in addition to sulphide, and, in fact, the haüynite molecule actually predominates in this case.

Lazurite is decomposed and decolorised by hydrochloric acid, with the separation of gelatinous silica and evolution of hydrogen sulphide. It is occasionally found as deep-blue crystals with the form of the rhombic-dodecahedron; sp.gr. 2·38–2·42; hardness 5½.

The best quality of lapis-lazuli comes from Badakshan in Afghanistan; the mines here were visited by Marco Polo in the year 1271. Another occurrence of importance is at the western end of Lake Baikal in Siberia; here the material varies in colour from deep-blue to light-blue, violet, and green. Large blocks of pale-blue lapis-lazuli are also found in the Chilean Andes, and small crystals in the ejected limestone blocks of Monte Somma, Vesuvius.

L. J. S.

LARCH TURPENTINE *v.* OLEO-RESINS.

LARD. The term 'lard' was originally used to denote the fat rendered from the leaf of the pig, *i.e.* the fat from the kidneys and the bowels. The increased consumption of lard during the latter half of the last century (which has seen the rise of large American packing houses manufacturing lard on an enormous scale) has chiefly contributed to the extension of the above definition of lard, so that at present 'lard' denotes the fat from any and every part of the hog.

Leaf lard is still being sold on a small scale as 'butcher's lard' and 'home-rendered lard,' but the amount is insignificant in comparison with the enormous quantities produced in the slaughter-houses of the United States and Canada. The term 'bladder lard,' so named from the package, used to be leaf lard rendered in small establishments. At present this term is still used to denote the best quality of home rendered, as also of American lard of the quality (*c*) (*v. infra*). The commercial quality 'keg lard' contains, besides leaf lard, the fat taken from other parts of the animal. This extension of the term 'lard,' viz. that it denotes the fat taken from any and every part of the hog, has been implicitly acknowledged by the Adulteration Laws of the United States, according to which lard is defined as the 'rendered fat from slaughtered, healthy hogs, free from rancidity and containing no more than 1 p.c. of substances other than hog fat.'

The production of, and trade in, lard at present may be considered as being completely dominated by the processes and trade usages in vogue in the United States, especially in the large packing houses of Chicago.

The rules of the Chicago Board of Trade define the following brands of edible lard: (*a*) Neutral lard No. 1; (*b*) Neutral lard No. 2 ('Imitation neutral lard'); (*c*) Leaf lard; (*d*) Choice lard, choice kettle-rendered lard; (*e*) Prime steam lard. These brands will be described here in the order in which they are produced in the factory, so as to give, at the same time, a concise account of the manufacturing processes involved in the production of edible lard.

(*a*) **Neutral lard** is prepared from the leaf, which is taken out of the animal immediately after it has been slaughtered, freed from the flesh and skin, and chopped up in a fat-cutting machine into small lumps, which are thoroughly washed with iced water. The comminuted mass is then delivered into jacketed rendering vessels, in which it is heated up to a temperature of 40°–50°. The lard so obtained is practically neutral, and is used almost exclusively in the manufacture of margarine (termed in America 'oleomargarine').

(*b*) **Neutral lard No. 2** ('Imitation neutral lard') is the fat taken from the back, and rendered in a similar manner.

As the Neutral lard No. 1 and Neutral lard No. 2 are not 'cooked' (*i.e.* not rendered at a higher temperature than 50°), these lards do not keep well, and cannot, therefore, be used, like 'leaf lard' and 'steam lard,' for domestic purposes.

(*c*) **Leaf lard ('Flare lard,' 'Flair lard').** When the residue from (*a*) is subjected to steam heat under pressure in a digester, the leaf lard of commerce is obtained. Formerly this was the only kind of lard recognised by the Chicago Board of Trade, and was prepared from the whole leaf, and thus embraced the three qualities described under (*a*), (*b*), and (*c*). This lard is not exported, but is consumed at home. The Adulteration Laws of the United States now define leaf lard as 'the lard made from the internal fat of the abdomen, excluding that adhering to the intestines, and having the iodine number 60.'

The portions of the leaf remaining after the rendering of Neutral lard No. 1, are put together with the residues obtained in the preparation of Neutral lard, and 'rendered' by steam heat in open steam-jacketed kettles or in autoclaves (digesters).

Thus (*d*) '**Choice lard**' or '**Choice kettle-rendered lard**' is obtained. The latter term is due to this fat being rendered in steam-jacketed kettles, which represent the survival of the old-fashioned open kettles, in which butchers used to render the lard over free fire. Such lard has the peculiar, pleasant flavour of fried fat, and therefore the name 'Kettle-rendered lard' has been retained, even after the rendering over free fire had given way to heating by means of steam. In large establishments the rendering is carried out under pressure in digesters. The regulations of the Chicago Board of Trade define 'Choice lard' as lard made from leaf and trimmings only, either steam or kettle rendered. The manner of rendering is branded on each tierce. Its flavour is much superior to that of 'Prime steam lard.'

(*e*) **Prime steam lard,** also termed 'Standard prime steam lard,' is obtained from any trimmings not used up in the production of lard (*d*), and all other parts of the hog that will yield lard, with the exception of the liver, lungs, the intestines proper, and that part of the heart which is free from fat. This quality is rendered in digesters in a similar manner to lard (*d*). Such lard is passed solely on inspection, and as the inspector has no authority which enables him to supervise rendering establishments, in order to secure a proper control, we may take it that prime steam lard consists of the fat from any part of the hog, either from the whole animal, or from portions of it (head, foot, &c.).

The foregoing qualities represent the commercial qualities of *edible* fat.

All those parts of the hog which have not been used for the production of the above qualities are worked up in autoclaves, in order to obtain the last portion of the fat they contain. The fat so recovered is termed 'Yellow grease.' With this yellow grease are mixed all the refuse fats resulting in the course of rendering the edible qualities. 'Yellow grease' is also obtained from the fat rendered from all the animals that have died in the 'stock-yards.' If in the working up of animals which have died in transit, the intestines, &c., have been removed, a whiter quality of fat is obtained. This is sold as 'white grease' for manufacturing purposes. A lower kind of grease than the 'Yellow grease' is 'Pig's foot grease,' a by-product obtained in the glue department of the rendering houses. This 'Pig's foot grease' finds an outlet in the manufacture of low class lard oil and of soap.

The two qualities of 'Neutral lard' hardly require refining. After the clear melted lard has settled in the jacketed vessel, it is run off into a receiving tank, in which the last traces of water and any fibres are precipitated by sprinkling salt over the fat. In fact, this part of the manufacture simulates exactly the processes employed in the preparation of 'Premier Jus.' The settled lard is then immediately ready for use in the manufacture of margarine—which is mostly produced in the same works,—or is run into tierces for shipment.

The next qualities of edible lard usually undergo a somewhat more complicated process of refining, consisting in treating the melted fat in a refining vessel with fuller's earth, and blowing it at the same time with air. The fat is thereby also deodorised. It is next pumped through a filter press, from which the clear, bleached lard is run over horizontal cylinders cooled by brine. The warm lard is thus quickly chilled on the cooled surface of the lard cooler, and forms a continuous sheet of solidified fat. Before the cylinder dips again into the warm lard on the other side, the solidified mass is removed by a scraper ('doctor'), and falls into a trough. In this trough a rotating screw conveyer breaks up the sheet of fat and carries it forward into a mixer, in which the lard is agitated by a mechanical arrangement. Here 'lard stearine' is added to 'stiffen' the lard, in case it be too soft.

The lard stearin is obtained by subjecting cooled lard in hydraulic presses to a moderate pressure, when the softer portion—lard oil—exudes. The lard stearin either serves in the manufacture of butter substitutes (margarine, 'oleomargarine'), or is used, as described above, for 'stiffening' soft lard. In this country, where the addition of beef fat for 'stiffening' lard is now forbidden, considerable quantities of lard stearin are used.

Leaf lard is the hardest; the lards from the back, &c., are softer. The consistence of the lard is not only conditioned by the part of the animal from which it has been taken, but depends also, and chiefly, on the food which has been given to the animal. Hogs fed exclusively on acorns or on 'tankage' yield a harder lard than hogs fed on maize.

Leaf lard has a granular texture and a salve-like consistence, and should be of pure white colour. The lards which represent mixtures from all parts of the body, especially those manufactured in large slaughter-houses, have no longer a crystalline texture, as the object of the last operation in the manufacture is to destroy such texture and give to the product a smooth appearance.

The lard rendered from the leaf, as also from the back, has an agreeable taste. The lower qualities have an insipid taste; this disappears, however, on standing. Some of the steam lards have an 'animal flavour,' which may be judged by an inexperienced person to indicate admixture with tallow or 'beef stearine.' This flavour also disappears on standing or on warming.

Lard consists of the glycerides of lauric, myristic, palmitic, stearic, and oleic acids, and small quantities of linolic acid (and perhaps also of linolenic acid). The proportion of stearic acid determined in a number of commercial lards, varied from 6 to 24·91 p.c.

The analytical differences between lards from different parts of the hog are best expressed by their iodine values. Since important differences exist between North American and European lards, chiefly and almost solely owing to the mode of fattening, it is important to note that American lards have considerably higher iodine values than lards obtained in Europe. The iodine values of the latter range, as a rule, between 46 and 60. The iodine value of American lard reaches, however, higher figures than 60, and may even exceed 70.

Lard (like butter and olive oil) used to be adulterated on the largest scale. Beef fat, beef stearin, cotton seed oil, cotton seed stearin, and other vegetable oils, amongst which during the last few years cocoanut oil and palm kernel oil predominate, are the adulterants most frequently employed. Such admixtures had been for a long time an openly acknowledged practice in the United States of America, and such expressions as 'refined lard,' 'compound lard,' and 'lard compound' were used to designate a mixture of lard with vegetable oil, chiefly cotton seed oil, and cotton seed stearin. At present, however, the restrictions imposed by law have become much more stringent, and lard exported from the United States under official supervision, may be accepted as guaranteed pure, that is, free from admixture with another animal or with a vegetable fat.

The detection of adulterants in lard plays a most important part in the practice of the public analyst. It is impossible here to follow the various practices of the adulterators of lard and follow up such adulterations through their several stages. The reader must, therefore, be referred to Lewkowitsch, Chemical Technology, ii. 577–615. It may, however, be pointed out that the chief characteristics which the analyst must determine are: specific gravity, melting-point, iodine value of the fat, iodine value of the liquid fatty acids, and amount of unsaponifiable matter. The proportion of the latter is important, inasmuch as admixture of paraffin wax with lard (which had been practised to a considerable extent in former years, and had then been abandoned) appears to have been resumed during the last few years. Modern methods of chemical analysis have rendered the detection of vegetable oils and fats added fraudulently to lard, a somewhat easy process, as the phytosteryl acetate test permits the detection of even as little as 1 p.c. of admixed vegetable oil or fat, and the endeavours of the adulterator to circumvent this test by the addition of a very small quantity of soft paraffin wax have been frustrated by more refined methods of chemical analysis. The detection of cocoanut oil and palm kernel oil is rendered (in addition to the phytosteryl acetate test) somewhat easy by the determination of the volatile fatty acids. In this connection, however, a note or warning must be sounded, as it has been shown recently that hogs fed on copra (as is done in the Philippine Islands) furnish a lard which exhibits the characteristics of lard adulterated with cocoanut or palm nut oil (the cocoanut oil having been pushed forward into the body fat, much as feeding cows with oil cake leads to the pushing forward of the vegetable oil into the milk fat). Detection of added beef fat or beef stearin to lard is more difficult, and the (formerly relied upon) Belfield test, which was supposed to rest on the detection of (beef) stearin, has been shown to be entirely nugatory. The so-called Stock-Belfield test, which aimed at a quantitative determination of added 'beef stearin,' has been shown to be utterly fallacious, inasmuch as the crystals, on the isolation of which reliance was placed, are given by the lard stearin itself. A method proposed by Polenske, viz. to determine the so-called 'difference' between solidifying- and melting-points has been shown to be unreliable.

A considerable amount of lard is consumed in the manufacture of lard substitutes.

J. L.

LARDERELLITE (*Ammonium borate*). A mineral found in the lagoons of Tuscany. It occurs in small crystalline rhomboidal plates.

B_2O_3	72·06
$(NH_4)_2O$	9·83
H_2O	18·11
	100·00

(D'Achiardi, Chem. Soc. Abstr. 1900, ii. 600).

LARD SUBSTITUTES consist chiefly of a mixture of lard, or lard stearin with 'beef stearin' ('oleostearin'), cotton seed stearin, cotton seed oil, maize oil, arachis oil, sesame oil, cocoanut oil, and palm kernel oil. In the infancy of this industry these artificial products were sold under such names as 'refined lard,' 'commercial lard.' Other products (*e.g.* 'lard compound') contained no lard whatever, being judiciously prepared mixtures of beef stearin and cotton seed oil. At present, however, all lard substitutes proper contain some lard, or at least 'lard stearin,' as a basis. The manufacture consists simply in mixing the various fats, in the melted state, and oils in a mixing machine, and cooling the mixture rapidly by running it over cooling cylinders, so as to destroy any tendency to crystallisation.

In order to impart to the finished mixture a pure white colour, it is usual to stir air into the fat until it acquires a salve-like consistence. The stirring with air must not, however, be carried too far, as otherwise the lard substitute not only becomes more liable to rancidity, but easily acquires a foamy consistence. J. L.

LASERPITINE $C_{15}H_{22}O_4$. An alkaloid obtained by Kütz (Arch. Pharm. 1883, 221, 161) by extraction with light petroleum of the roots of the white *Laserpitium latifolium* (Linn.). Forms large colourless well-formed crystals belonging to the monoclinic system. Melts at 118°; is insoluble in water and dilute acids. Easily soluble in chloroform and ether, slightly soluble in alcohol and light petroleum.

LASURSTEIN *v.* LAPIS-LAZULI and PIGMENTS.

LAUDANUM. Laudanum is understood in this country at the present day to be the simplest liquid preparation of opium available for medical purposes. The word is an old one, and has undergone considerable change of meaning, but its precise origin has never been ascertained with certainty.

According to some authorities, the term is borrowed from *labdanum* or *ladanum*, an oleoresin of Greek origin, which is collected from various species of *Cistus* (*v.* OLEO-RESINS); while others derive the word from the Latin *laus*, praise, which is supposed to indicate the high esteem in which the medicine has always been held. In a discussion of this question (Pharm. J. [iii.] 17, 404, 424, 503, 584, 644), it is pointed out by Eagle that according to Mathiolus (Comment. Dioscoridis Mat. Med. Lugduni, 1563) certain Italians applied the term laudanum to labdanum, and thus Littré and Robin (Dict. Méd. Paris, 1877) and others give the Italian equivalents of the two words as synonymous. This statement of Mathiolus would appear to have been the source of the view that laudanum is derived from labdanum which has been adopted by several lexicographers and writers on materia medica. Hooper (Lex. Med. London, 1848) and Dunglison (Dict. Med. Sc. Philadelphia, 1868) are, however, on the side of the *laus* derivation, and the remarks of such writers as Crollius (Basilica Chymica, Francofurti, 1611), Bruno (Lex. Castello-Brun. Norimbergæ, 1688), Lemery (Pharm. Universelle, 1716), and others are so decidedly in its favour that the weight of evidence at present appears to be with this hypothesis.

But be this as it may, the term laudanum was applied in the 17th century to indicate solid or semi-solid mixtures which generally, though not always, contained opium (*cf.* Lond. Dispensatory, 1678). These were gradually replaced by liquid preparations, of which the most celebrated was that of the physician Sydenham, 1644–1689, whose life was written by Dr. Johnson. This was the *Laudanum liquidum Sydenhami* of the London Pharmacopœia of 1720, and is represented by the *vinum opii* of recent medicine. A *tinctura opii* of simpler composition has, however, long taken the lead among galenical preparations of opium. This is a liquid extract made with proof spirit, and represents in all important respects the physiological activity of the crude drug. To this tincture the term 'laudanum' is now applied, both in this country and in the United States, not only by writers such as Pereira (Mat. Med. 1853, 2135) and Stillé and Maisch (Nat. Dispensatory, 1886, 1537), but more especially in the practice of pharmacy. The editors of the British Pharmacopœia for 1898 have also added the term laudanum as a synonym for tincture of opium (*cf.* OPIUM). A. S.

LAUREL CAMPHOR *v.* CAMPHOR.

LAUREL OIL, Bayberry oil, is obtained from the berries of the laurel tree, *Laurus nobilis* (Linn.), either by pressing the pounded berries or by boiling them with water. The berries contain from 24 to 30 p.c. of fat. Laurel oil has a green colour; at the ordinary temperature it has a buttery consistence; its taste and aromatic odour are characteristic.

Laurel oil is completely soluble in boiling alcohol; on cooling, crystals of trilaurin separate. Judging from its high iodine value, viz. 66 to 96, laurel oil must contain considerable quantities of olein and perhaps also of less saturated glycerides. From the characteristic numbers which laurel oil gives in analysis, the conclusion must be drawn that the proportion of laurin cannot be very high. The presence of laurin is, however, definitively proved by the fact that on distilling laurel oil *in vacuô*, trilaurin is obtained in the distillate. In the unsaponifiable matter of laurel oil, Matthes and Sander identified melissyl alcohol (myricyl alcohol), phytosterol, and laurane, $C_{20}H_{42}$.

Laurel oil is only used in veterinary practice. It is stated to be adulterated with other fats (lard), coloured green with copper salts. J. L.

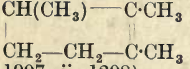
LAUREL WAX. *Myrtle berry wax* (*v.* WAXES).

LAURIC ACID *v.* DODECATOIC ACIDS; and OILS, FIXED, AND FATS.

LAURIN *v.* LAURUS NOBILIS (Linn.).

LAUROLENE and *iso*-**LAUROLENE,** hydrocarbons of the formula C_8H_{14}, first obtained by the distillation of various camphor acids or their salts. (*See* Wreden, Annalen, 1877, 187, 171; Reyher, Inaug-Dissert. Leipzig, 1891, 51; Aschan, Annalen, 1896, 290, 185; Noyes, Amer. Chem. J. 1895, 17, 432; Koenigs and Meyer, Ber. 1894, 27, 3470; Damsky, Ber. 1887, 20, 2959; Moitessier, J. 1866; Walker and Henderson, Chem. Soc. Trans. 1896, 753.)

Laurolene, Δ'-1 : 2 : 3-*trimethyl-cyclo-pentene,*

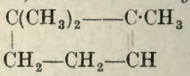


(Eijkmann, Chem. Zentr. 1907, ii. 1208).

Preparation.—(1) By slowly distilling camphanic acid in an atmosphere of CO_2 (Aschan, *l.c.*); (2) by heating sulphocamphylic acid at 170°–180° with aqueous H_3PO_4 (Koenigs and Meyer, *l.c.*); (3) by treating amino-lauronic acid with HNO_3 (K. and M.). Synthesised from αδ-dimethyladipic acid *via* 1 : 2 : 3-trimethyl-*cyclo*-pentanol (Noyes and Kyriakides, J. Amer. Chem. Soc. 1910, 32, 1064).

Properties.—Colourless liquid; b.p. 120°–122°; sp.gr. 0·8097 at 4°/4°, 0·8048 at 10°/10°, 0·8010 at 15°/15°, 0·7974 at 20°/20°, 0·7939 at 25°/25°; mol. mag. rot. 8·987; mol. refraction 61·114 (Crossley and Renouf, Chem. Soc. Trans. 1906, 26); has a sweet odour resembling camphor and turpentine. Rotation very irregular, varies from 0° to +23° and −29°. Combines with 2 mols. Br in chloroform solution; oxidised by HNO_3 to oxalic acid (Crossley and Renouf); oxidised by dilute alkaline $KMnO_4$ to a diketone, b.p. 204° at 750 mm. (corr.), which yields a disemicarbazone, m.p. 194° (corr.) (Noyes and Derick, J. Amer. Chem. Soc. 1910, 32, 1061). With fuming HI on the water-bath yields *laurolene hydriodide*, a greenish-brown, unstable liquid which, heated with zinc dust in 90 p.c. alcohol, yields *dihydrolaurolene*, 1 : 2 : 3-trimethyl-*cyclo* pentane, as a colourless liquid, b.p. 111·5°–114° at 760 mm.; unacted on by Br or $KMnO_4$. It has sp.gr. 0·7718 at 4°/4°; 0·7670 at 10°/10°; 0·7633 at 15°/15°; 0·7596 at 20°/20°; 0·7567 at 25°/25°; mol. mag. rot. 8·332; mol. refraction 61·138.

iso-**Laurolene,** Δ^2-1:1:2-*trimethyl-cyclo-pentene*



(Blanc, Bull. Soc. chim. 1898, 19, 699; Compt. rend. 1906, 142, 1084). Formed by dry distillation of campholytic acid, sulphocamphylic acid, *iso*-campholytic acid, &c. (Walker and Henderson, Chem. Soc. Trans. 1896, 753). Prepared from *iso*-lauranolic acid by heating in sealed tubes for 4 hours at 300° (Blanc, Bull. Soc. chim. 1898, 19, 699); or by distilling with 1½ times its weight of pure anthracene (Crossley and Renouf, Chem. Soc. Trans. 1906, 41). Blanc synthesised it from αα-dimethyladipic acid *via* dimethyl-*cyclo*-pentanone (Compt. rend. 142, 1084).

It is a colourless, mobile liquid, with sweet camphoraceous odour; b.p. 108°–108·2° at 742 mm.; sp.gr. 0·7953 at 4°/4°; 0·7907 at 10°/10°; 0·7867 at 15°/15°; 0·7830 at 20°/20; 0·7795 at 25°/25°; mol. mag. rot. 8·749; mol. refraction 60·565 (Crossley and Renouf). Oxidised by HNO_3 to oxalic acid; oxidised by dilute $KMnO_4$ to dimethyl hexanonoic acid

$$CO(CH_3)C(CH_3)_2CH_2{\cdot}CH_2{\cdot}COOH,$$

with $HgCl_2$ solution gives a sticky amorphous precipitate. Combines with 2 atoms Br, forming 2 : 3-dibromo-1 : 1 : 3-trimethyl-*cyclo*-pentane, m.p. 80°–85°. Heated at 125° with fuming HI yields the *hydriodide*, which, on reduction with zinc-dust in 90 p.c. alcohol, yields *dihydro-iso-laurolene* (1 : 1 : 2-trimethyl-*cyclo*-pentane).

Dihydro-*iso*-laurolene can also be obtained by heating *iso*-laurolene with HI at 200° or with conc. H_2SO_4 (Zelinsky and Lepeschkin, J. Russ. Phys. Chem. Soc. 1901, 33, 549; also 1899, 31, 407). It is a colourless liquid, having a sweet camphoraceous odour, b.p. 113°–113·5° at 750 mm.; sp.gr. 0·7847 at 4°/4°; 0·7800 at 10°/10°; 0·7762 at 15°/15°; 0·7727 at 20°/20°; 0·7694 at 25°/25°; mol. mag. rot. 8·249; mol. refraction 61·078 (Crossley and Renouf).

LAURUS NOBILIS (Linn.). *Bay, Sweet Bay* (*Laurier commun*, Fr.; *Lorbeer*, Ger.).

The classic or noble laurel or bay tree is indigenous to the Levant and is found all along the shores of the Mediterranean. The leaves are used as a flavouring agent, and both the leaves and fruit were formerly employed in medicine.

The fruit, or so-called bay berries, was analysed by Bonastre (J. Pharm. Chim. [ii.] 10, 30) and by Grosourdi (J. 1851, 562). Besides water, a large proportion of starch, lignin, sugar, and small quantities of resin, pectin, albumen, and colouring matter, bay berries contain *solid and liquid fat, volatile oil*, and a *peculiar camphor.*

From the fat, Marsson (Annalen, 41, 330) isolated *lauric acid* $C_{12}H_{24}O_2$, being one of the twelfth members of the $C_nH_{2n}O_2$ or formic acid series of fatty acids. It was subsequently found in numerous other fats (*cf.* Heintz, J. pr. Chem. [i.] 66, 1). Glycerin trilaurate or *trilaurin*

$$C_3H_5(C_{12}H_{23}O_2)_3$$

is associated in the fat with the glycerides of oleic, linoleic, palmitic, myristic, and stearic acids (Staub, Nat. Disp. 1886, 874).

The analytical constants of the expressed oil after being freed from the volatile oil are given by Matthes and Sander (Arch. Pharm. 246, 165), who have also investigated the resinous unsaponifiable matter which is present in the fatty oil. This was found to contain myricyl alcohol; a *phytosterol*, $C_{27}H_{44}O,H_2O$, colourless needles, m.p. 132°–133°; a hydrocarbon, *laurane* $C_{20}H_{42}$, which crystallises from alcohol in slender needles, melting at 69°; and an aromatic unsaturated oily substance.

Bonastre (J. Pharm. Chim. [ii.] 10, 36; 11, 3) was the first to distil a volatile oil from bay berries. It has been studied by Forcke (Arch. Pharm. [ii.] 17, 177); Brandes (*ibid.* [ii.] 22, 160); Bley (Rep. Pharm. 48, 96); Gladstone (Chem. Soc. Trans. 17, 3; 25, 1); Blas (Annalen, 134, 1); Wallach (*ibid.* 252, 94); and Brühl and Müller (Ber. 25, 547). The specimen examined by the last-mentioned investigators distilled between 175° and 275° under ordinary pressure and left a viscid residue. The distillate contained lauric acid, and after treatment with potash and digestion with sodium, yielded a liquid, b.p. 167°–171°. This liquid was found to consist of cineol, pinene, and other hydrocarbons, and is probably the substance described as laurene by the earlier observers. The crude oil also contains large proportions of alcoholic or ketonic compounds which, like menthol or camphor, combine with sodium, the salts so formed being decomposed by water.

Bay camphor or *laurin* $C_{22}H_{30}O_3$ was isolated by Bonastre (J. Pharm. Chim. [ii.] 10, 32) and further investigated by Delffs (J. pr. Chem. [i.] 58, 434) and Marsson (Annalen, 41, 329). The yield is about 1 p.c. It consists of prismatic crystals without taste or smell. It is insoluble in water, but soluble in alcohol and ether, and is chemically neutral and indifferent.

The leaves of *Laurus nobilis* also contain a volatile oil. Examined by Thoms and Molle (Arch. Pharm. 242, 161), free acetic, *iso*butyric, and (*iso* ?) valeric acids were found to be present, also about 1·7 p.c. of free eugenol and about 0·4 p.c. of eugenolic esters. The acid obtained by hydrolysing the oil by alcoholic potassium hydroxide consisted mainly of acetic acid; the other volatile acids present were probably valeric and hexoic. A monobasic acid $C_{10}H_{14}O_2$, m.p. 146°–147°, was also obtained. On fractionating the oil, after the removal of the free acids, phenols, and esters, cineol was obtained. The yield of cineol was equal to 50 p.c. of the original oil. From fractions between 212° and 230°, geraniol was isolated. The fractions of a still higher boiling-point contain oxygenated compounds, probably a sesquiterpene alcohol associated with a sesquiterpene. These fractions, and also the original oil, give an intense blue colouration when dissolved in glacial acetic acid and bromine vapour is blown over the surface of the solution.

The volatile oil of the leaves of the allied Californian laurel, *Umbellularia Californica* (Nutt.), contains the following substances in approximately the percentages given: eugenol, 1·7; *l*-pinene, 6·0; cineol, 20·0; umbellulone, 60·0; safrole, a very small proportion; eugenol methyl ether, 10·0; and traces of fatty acids. *Umbellulone* $C_{10}H_{14}O$ is a colourless oil, boiling at 219°–220° (749 mm.), $[\alpha]_D - 37°$, and has an odour somewhat resembling mint. It is a ketone, and forms compounds with semicarbazide and hydroxylamine (Power and Lees, Chem. Soc. Trans. 85, 629).

The volatile oils obtained from *Laurus nobilis* must not be confused with others bearing similar names, such as commercial bay oil or bayberry leaf oil, distilled from the leaves of the West Indian tree *Pimenta acris* (Kostel.), and which is the flavouring agent in the toilet preparation known as bay rum (Markoe, Pharm. J. [iii.] 8, 1005; Ruse, *ibid.* [iii.] 13, 39); laurel oil of Guiana, natural oil of laurel, or ocotea oil, derived from a tree of Spanish Guiana (Stenhouse, Chem. Soc. Mem. 1, 43; 2, 121); or oil of common or cherry laurel, *Prunus Lauro cerasus* (Linn.) which is similar to volatile oil of bitter almonds. A. S.

LAUTH'S VIOLET *v.* AMINES; METHYLENE BLUE.

LAVA. The term lava is properly applied to those products which issue from volcanic orifices in an incandescent and often in a molten condition, presenting, when cooled, the appearance of slag or clinker, and consisting of rock more or less perfectly fused. It differs from other volcanic substances such as the ashes, sand, and scoriæ, not in chemical composition but in the conditions under which it is ejected from the crater. Thus the analyses by Silvestri of lava, scoriæ, sand, and ashes thrown out by Etna in the eruption of 1865 showed the practical identity of constituents in each form of product:

——	Ashes	Sand	Scoriæ	Compact lava
Silica	50·00	49·80	50·00	49·95
Alumina	19·08	18·20	19·00	18·75
Ferrous oxide	12·16	12·42	11·70	11·21
Manganous oxide	0·40	0·45	0·50	0·49
Lime	9·98	11·00	10·28	11·10
Magnesia	4·12	4·00	4·20	4·05
Soda	3·72	3·60	3·40	3·71
Potash	0·60	0·49	0·69	0·70
Water	0·36	0·29	0·33	0·23
Phosphoric acid Titanic acid Vanadic acid Ferric oxide	traces	traces	traces	traces

Of the whole number of chemical elements, ten, viz. oxygen, silicon, aluminium, iron, magnesium, calcium, sodium, potassium, hydrogen, and titanium, are of common occurrence in lavas; although traces of practically all other elements are found somewhere or other amongst volcanic products.

Among the ten elements commonly existing in lava, oxygen makes up nearly one-half of the weight, silicon one-fourth, and aluminium one-tenth. The other seven elements vary in their proportions relatively to each other. Silica is present in proportions of from one-half to four-fifths of all lava, and, with the bases, viz. oxides of aluminium, calcium, iron, magnesium, potassium, and sodium, forms the silicates. In proportion as the acid constituent silica exists in greater or smaller relative quantity, lavas have been distinguished as 'acid lavas' and 'basic lavas': to this classification Judd (Volcanoes, 1888, 48) suggests the additional term of 'intermediate lavas.' Under this arrangement, 'acid lavas are those which contain from 66 to 80 p.c. of silica; they are poor in lime, magnesia, and oxide of iron, but rich in potash and soda. The basic lavas contain from 45 to 55 p.c. of silica; they are rich in lime, magnesia, and oxide of iron, but poor in soda and potash. In the intermediate lavas the proportion of silica varies from 55 to 66 p.c.' It may be taken, further, that these three distinctive names correspond with the nomenclature of former writers, viz. trachytes, greystones, and basalt. Since basic or basaltic lavas contain a larger proportion of heavy oxides than the acid or trachytic lavas, it follows that the former possess a higher sp.gr. and may usually be classified according to their weight.

In colour fresh lava ranges from nearly white in the acid to nearly black in the basic. After a time, all lavas become reddened on account of the iron present in them being affected by exposure to the weather.

A fourth but much smaller class of lava is one resembling the stony portion of meteorites. Judd suggests for this class the name of ultra-basic lava. This lava contains a very low percentage of silica and a high proportion of iron and magnesia. It has a sp.gr. usually exceeding 3; and it is interesting as being composed of those minerals which occur in meteorites, viz. olivine, enstatite, augite, anorthite, magnetite, and chromite.

Under the microscope, thin slices of lava exhibit two kinds of materials, a glassy base and crystals of various minerals distributed through it in irregular order and proportion; apparently this variation is to be explained by the rate of cooling to which various portions of the molten mass have been subjected. This, however, does not affect the ultimate chemical composition.

Geologists adopt the following names of lavas, in five main classes, Rhyolites, Trachytes, Andesites, Phonolites, and Basalts; and the glassy and the perfectly crystalline forms are distinguished as follows:

Crystalline forms.	*Lavas.*	*Glassy forms.*
Granite	Rhyolite	Obsidian
Syenite	Trachyte	
Diorite	Andesite	
Miascite	Phonolite	
Gabbro	Basalt	Tachylyte

As examples of the extremes in composition of lavas, the following analyses may be quoted: I. rhyolite from Co. Antrim (J. H. Player); II. limburgite from Haddingtonshire (J. H. Player):

	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	FeO	CaO	MgO	Na_2O	K_2O	H_2O
I.	76·4	—	14·2	1·6	—	0·6	—	1·8	4·2	1·5
II.	40·2	2·9	12·8	4·0	10·4	10·4	11·9	2·7	0·8	3·4

Confining this article to the chemical aspects of lava, it may be said generally that the material ejected from the same volcano at wide intervals of time displays a similar chemical composition. Thus analyses of Vesuvius lava of (*a*) 1631, (*b*) 1767, and (*c*) 1868, show practical identity:—

——	(*a*) Eruption of 1631	(*b*) Eruption of 1767	(*c*) Eruption of 1868
SiO_2	48·12	48·20	46·58
TiO_2	0·22	0·27	0·27
Al_2O_3	17·16	17·92	20·00
Fe_2O_3	5·69	5·48	3·20
FeO	5·13	4·75	5·69
MnO	1·20	1·33	1·07
CaO	9·84	8·97	9·09
MgO	3·99	3·51	3·16
Na_2O	2·77	2·61	2·74
K_2O	7·24	7·70	7·35
H_2O	0·08	0·16	0·32

When we come to study the internal structure of ancient volcanos, however, we are impressed by the fact that lavas of very different chemical composition must have issued from the same vent at successive periods. As a general rule, to which there are not wanting notable exceptions, the first lavas to make their appearance have been of intermediate type; while acid and basic lavas have been ejected at a later period in the history of the volcano. Occasionally we find evidence that lavas of very different chemical composition have flowed from the same vent in frequent alternations.

Lavas are at times used as building stones and for paving; whilst those of Niedermendig on the Rhine (here a leucite-nepheline-tephrite) and of Hungary are used for millstones. Pumice (*q.v.*) is a lava full of steam-cavities. Puzzolana is a volcanic dust or ash extensively used for making concrete.

Much detailed petrographical study and numerous chemical analyses have been made of lavas and other rocks of igneous origin, and many names have been introduced for special varieties. See the German treatises on petrography by H. Rosenbusch and by F. Zirkel, and the text-books in English by A. Harker, F. H. Hatch, and J. P. Iddings (Igneous Rocks, 1909). For tabulated chemical analyses, see H. S. Washington, Prof. Papers, United States Geol. Survey, Nos. 14 and 28, 1903, 1904.

L. J. S.

LAVENDER, OIL OF, *v.* OILS, ESSENTIAL.

LAZULITE. A comparatively rare mineral occurring as sky-blue monoclinic crystals of pyramidal habit. It is a basic phosphate of aluminium, magnesium, and ferrous iron, $Al_2(Fe,Mg)(OH)_2P_2O_8$. This name is easily confused with the name lazurite (*v.* LAPIS-LAZULI).

L. J. S.

LAZURITE *v.* LAPIS-LAZULI.

LEAD. Syns. *Blei*; *Plomb*; *Plumbum*. Sym. Pb. At.wt. 207·1.

Occurrence.—Native lead is said to have been found at Grassington and Alston Moor, in certain mines in the province of Guanaxuato in Mexico; and according to Koksharow (J. Min. 1875, 873) in the Kirghis Steppe, where it occurs in hornstone associated with heavy spar and cerussite; also in the gold washings of Katharinenburg, in which it occurs in grains together with gold, magnetic and specular iron ores; also in India (Geol. Survey, India, List of Minerals). Some instances of the occurrence of native lead are given by Liversedge, in his Minerals of New South Wales.

A large number of lead compounds are found in nature, but only a comparatively small number can be considered as ores.

The principal ores of lead in the order of their importance are *galena, cerussite, anglesite.* Other less important naturally occurring compounds of lead are *pyromorphite, mimetisite, matlockite, mendipite, phosgenite, lead ochre, minium.* These are dealt with under their special titles.

Distribution of Lead Ores.

Lead ores are abundantly distributed through the rocks of the different geological formations, from the granite to the triassic formation; but most abundantly in rocks of the Silurian age and in those of the mountain limestone. Whilst many of these deposits are in the form of true veins, some there are which cannot be regarded as true veins. Veins of lead ore which are rich in one formation become suddenly impoverished in passing into another and different rocky stratum. In England three different kinds of deposits of lead ores are distinguished by the miners—viz. (1) rake veins, which are true veins in the geological sense of the word; (2) pipe veins, which are narrow masses, frequently oblong in shape and lying parallel to the rocky strata; (3) flat veins, which are small beds of ore lying in the middle of these strata. Galena generally contains some silver; but lead ores are not always argentiferous, those, however, which occur in crystalline metamorphic rocks are usually so. Further, the lead ores of the older rocks are generally argentiferous, but are not so productive of lead as those of the limestone districts, yet are more persistent in depth.

In England, lead ores are worked in veins and ‘flats’ in the mountain or carboniferous limestone in the neighbourhood of Alston Moor, where the counties of Northumberland, Cumberland, and Durham meet, and elsewhere in those counties. The lead-yielding districts of Derbyshire, Yorkshire, and the Mendip Hills are in the same formation. The Cornish and Devonshire mines are workings in true veins occurring in the Devonian formation—‘Killas’ of Cornwall and Devonshire. The lead workings of the Shelve district in Shropshire, of Cardiganshire, of Montgomeryshire, of Leadhills and Wanlockhead in Scotland, and those of the Isle of Man, are in rocks of the Silurian formation; whilst in Ireland, in Wicklow, and Newtownards in the County Down, lead ores are found in granite.

In Germany lead mines are worked in the valleys of the Lahn and Sieg, and these lead-bearing veins occur in Devonian strata. Those of the Hartz district are also in Devonian slates; they yield a highly argentiferous galena and silver ores proper. In the Hartz district there are three centres—viz. (1) that in the neighbourhood of Clausthal; (2) the mines in the vicinity of Andreasberg; and (3) those at Rammelsberg, near Goslar. The Freiberg mines are in gneiss and yield a highly argentiferous galena. The Silesian lead ores are found in irregular deposits in the muschelkalk, and are associated with ores of zinc and iron. A remarkable stratified deposit of lead ore of triassic age is that of Mechernich in the Eifel, where a bed of sandstone is filled in places with nodules formed of sand grains cemented together by galena.

The mines of Bleiberg and Raibel in Carinthia are among the most important lead mines in Austria. Here the ore is a very pure galena associated with molybdate of lead, and is found in limestones of the triassic formation. At Pzibram, in Bohemia, the veins are in Silurian strata, and yield a galena very rich in silver. The mines are from three to four thousand feet deep.

Whilst lead is found in almost every province in Spain, the chief workings are those of the provinces Jaen, Murcia, and Almeria. In the province of Jaen in the neighbourhood of Linares, two distinct systems of veins occur traversing the triassic sandstone and the granite upon which the former reposes. In the district round Carthagena in Murcia, the lead ores occur in veins in stratified and irregular deposits in Silurian rocks and trachytes. In the province of Almeria lead is found in veins in the mica schists and clay slates of the Sierra Almagrera. Some of the ore of this district is highly argentiferous.

The chief Italian sources of lead are the mines of Sardinia, which may be divided into three types—(1) Ore masses interstratified in Silurian rocks, as in the mine of Monteponi; (2) veins traversing Silurian clay slates, as in the Montevecchio mine, one of the most important lead mines in Europe; and (3) lodes traversing Silurian limestones, *e.g.* Malacalzetta. The ore of the Montevecchio mine consists of galena mixed with blende, iron pyrites, heavy spar, siderite, and copper pyrites. It is poor in silver, whilst that at Malacalzetta carries about 40 oz. of silver to the ton. In Sardinia, the ore is, in all cases, galena. There are numerous deposits of lead ore (galena) on the mainland. In the Brusmipiano mine, in the district of Milan, galena is found associated with cerussite, iron pyrites, jamesonite, copper pyrites, and malachite. At the Morso Alto mine and at the Boltino mine in the mining district of Florence, the galena worked is rich in silver, and at the latter mine is associated with fahlerz, bournonite, and native antimony ore.

The deposits of lead ores of Portugal are very similar to those of Spain. The most important district is that of Mutola, near the Guadiana. The galena contains about 24 oz. of silver to the ton, whereas the cerussite and anglesite associated with it are frequently much richer.

In Greece, ores of lead, silver, and zinc occur constantly associated with one another. They occur in mica schists, limestones, granites, and trachytes, sometimes in irregular masses and sometimes in the form of lodes. The chief mining district is that of Laurium, at the southern extremity of Attica.

In Sweden argentiferous lead ores occur in veins in granular limestones belonging to the crystalline slates. The chief mines are those of Sala, of Lofas in Dalacarlia, and of Guldmenshytta in Westmanland.

In France galena containing silver and associated with blende and iron pyrites occurs at Poullaouen in lodes traversing clay slates of Silurian age. The lodes at Huelgoët yield, in addition to argentiferous galena, cerussite, pyromorphite, and also native silver and horn silver. Whilst galena is found and worked in several localities in France, the most important mines are those of Pontgibaud in the Puy-de-Dôme, where lead lodes are worked which traverse rocks consisting of granite, gneiss, and schists, broken through by dykes of porphyry, and covered by sheets of basalt, beds of cinder, or by flows of lava. The galena is always argentiferous, and is accompanied by blende or iron pyrites, and occasionally by patches of fahlerz.

In Belgium, galena is found in numerous places, but the deposits are seldom of sufficient importance to pay the expenses of working. It is frequently associated with cerussite and pyromorphite. A productive lead mine exists at Bleiberg, near Moresnet, where a vein is worked which traverses the carboniferous limestone and the coal measures.

Lead ores are found in various parts of Russia; galena and several other lead minerals occur in a lode at Ekaterinenburg in the Urals. In the Caucasus deposits of galena exist. In Poland are deposits of galena in the dolomites of the muschelkalk, which have been worked for centuries. The most remarkable mines are those near Olkusk and Boleslaw. Lodes of lead ores occur near Chasing and Kielcé in rocks of Devonian age. Galena associated with fahlerz, molybdenite, iron pyrites, copper pyrites, and blende occurs in deposits in the mining district of Nertschinsk in Eastern Siberia.

Lead ores are found in various provinces of the Indian empire; they occur in beds or pockets, but seldom in veins. Many of these deposits have been worked by natives, but only on a small scale; there are practically no workings carried on at the present time.

Rich ores of silver and lead occur in the northern Shan States of Burma, which were formerly worked by the Chinese for the sake of the silver, and interest in this source of lead and silver has been revived.

Galena is found in many provinces in Japan, but the deposits of this mineral are not particularly valuable. In addition to this mineral, several lead antimony ores are found in Japan.

Australasia.—In Victoria, galena occurs in several localities; that at St. Arnaud is argentiferous. In New South Wales this ore is widely distributed over the colony, but no lead mines are known to be working. In South Australia, the mines of argentiferous galena are situated in the southern part of the colony, near Cape Jervis. In the Champion Bay district of Western Australia both lead and copper ores have been found in gneissic rocks, associated with granite and greenstone. In Tasmania argentiferous galena has been found; at the Penguin, and in the neighbourhood of Mounts Roland and Claude. Galena containing silver is occasionally found in the gold-bearing reefs of Coromandel and Thames, New Zealand.

Africa.—Argentiferous lead and copper ores are found in some mines in Algeria, and lead ores are known to exist in different parts of South Africa; these ores are found chiefly in the limestone formation extending from the junction of the Vaal with the Orange River in a northerly and then in an easterly direction to Rustenburg, in the north-west of the Transvaal. There is evidence of these ores having at one time been worked by the natives.

America.—In the United States of America, argentiferous galena, associated with blende, iron, and copper pyrites, occurs in the Atlantic States in the form of true veins; in the Azoic slates of New York and in the New England States in veins running parallel to the formation; in the State of New York it occurs in irregular deposits in the unaltered Lower Silurian rocks. The chief lead districts are, however, those of the Upper Mississippi Valley and the Missouri. The Upper Mississippi lead district is comprised within the States of Wisconsin, Illinois, and Iowa, the chief lead-producing district being that of the first-named State. The deposits of lead ore are found in the 'galena' or magnesian limestone of the Trenton period of the Lower Silurian formation, and cover an area of about 140 geographical square miles. These deposits assume a variety of forms, *e.g.* the *sheet*, a solid mass of ore filling a vertical fissure; this is the most characteristic mode of occurrence, in addition to which other forms are distinguished, such as an *opening, a crevice with pocket openings, cave openings, flat sheets,* and *vertical openings,* in all of which masses of lead ore occur in variously formed fissures in the limestone. The principal ore is a very pure galena, poor in silver, crystallising in cubes; it is accompanied by blende and zinc carbonate and a brown iron ore. The chief deposits of the Missouri district are situated in the counties of Washington, Franklin, and Jefferson. The ore occurs as 'float mineral,' a term applied to describe the mode in which galena is found imbedded in the superficial soil overlying the limestones of Lower Silurian age, in which the ore is found in deposits very similar to those in which it occurs in the Mississippi district. The galena is usually associated with iron and copper pyrites, and at the famous Lamotte mine, nickel and cobalt ores are found with it. In Utah and the Western States, large and irregular deposits of highly argentiferous lead ore occur.

In Canada galena is found in several localities around Lake Superior, a remarkable vein occurring at Silver Lake, some six miles northward from Thunder Bay, and at 500 feet above Lake Superior. A finely crystallised variety of galena has been found on the East Main coast of Hudson's Bay, in strata similar to those in which it occurs in the Mississippi district.

In Mexico lead ores are found in the mines at Guanaxuato and La Concepcion mine, and lodes containing argentiferous galena, quartz and calc spar occur in the mining district of Tatatila and Zomelahuacan.

For methods of assaying lead ores, *v.* art. ASSAYING.

SMELTING IN REVERBERATORY FURNACES.

The smelting of lead ores, of which galena is the principal one, is carried out either in reverberatory furnaces, blast furnaces, or shallow hearths. The ore is received from the mines dressed and freed as far as possible by mechanical means from the various minerals and gangue material with which it is found associated.

The following are the methods by which the extraction of lead is effected :—

I. *Method of Double Decomposition*, or method by reactions or roast reactions process (Röst reactions Arbeit), or air-reduction process. As the last name implies air aids in the reduction, and it does so in the following manner.

When galena is roasted at a moderate heat, it is partially converted into the oxide, and a portion is also oxidised to the sulphate ; if, after this roasting the temperature be raised, the unaltered galena reacts on the lead oxide and sulphate formed in the previous stage, and metallic lead is produced, sulphur dioxide being evolved.

These reactions are represented by the following equations :

$$(a)\left\{\begin{array}{l}2PbS+3O_2=2PbO+2SO_2.\\PbS+2O_2=PbSO_4.\end{array}\right.$$

$$(b)\left\{\begin{array}{l}PbS+2PbO=3Pb+SO_2.\\PbS+PbSO_4=2Pb+2SO_2.\end{array}\right.$$

II. Method of roasting and subsequent reduction of the oxidised compounds by means of carbonaceous matter (Röstreductions Arbeit).

III. The precipitation process (Niederschlags Arbeit) or method of affinity, in which iron is used to effect the removal of sulphur.

The treatment of a lead ore frequently requires the use of two if not all the above processes.

Smelting in reverberatory furnaces.—The Flintshire process is an example of the method by double decomposition carried out in reverberatory furnaces, which vary somewhat in construction and dimensions.

The following is a description given by Phillips of a *Flintshire furnace*.

The length of the hearth is usually about 11 feet, and its width 9 feet, and under this is an arched vault, extending the whole length of the bed to the fire-bridge. The hearth is made of slag, moulded into the proper form when in a plastic and semi-fluid state. Towards the centre of the hearth is a depression in which the fused metal accumulates, and at the bottom of this is situated the tap-hole. The fireplace is at one end, and before reaching the cavity of the furnace the flame has to pass over a fire-bridge about 2 feet in width, and from 12 to 14 inches below the arch. At the opposite extremity of the hearth are openings communicating with the flue in connection with a lofty chimney. The fuel is supplied through a door at one end of the fireplace, in addition to which the furnace is furnished with six working doors, about 9 inches by 12, protected by heavy cast-iron frames built into the brickwork and closed by iron plates, which can be easily removed when required. The bottom of this furnace is made nearly level with the doors on one of the sides, but is inclined towards the other in such a way as to be from 18 to 20 inches below the middle door, where it communicates with the tap-hole, beneath which a cast-iron tapping pot is set in the ground. In the top of the furnace is a hopper, from which a fresh charge of ore is let down as soon as that which is being worked is withdrawn.

In working this process, the charge (consisting of 21 cwt. in N. Wales, and from 12-14 cwt. in the north of England) is let down into the furnace, which is still hot from a previous working, and is spread evenly over the surface of the bed of the furnace, care being taken to prevent it dropping into the depression in the furnace-bed or well. During the first hour and a half, the charge is frequently stirred, and the supply of air carefully regulated by opening the various doors, the temperature being kept sufficiently high to ensure the oxidation of a portion of the galena, but at the same time not high enough to cause the charge to melt. It is during this period of calcination that the lead sulphide is in part converted into lead oxide and lead sulphate. At the end of this period the doors are closed, the fire is made up, then the temperature is raised to bright redness, and maintained at this point for about 25 minutes. This rise in temperature causes the charge to become plastic, and a reaction takes place between the unaltered galena and the oxy compounds of lead, by which lead is produced, and the metal runs down into the well in the bed of the furnace. At the end of this period, the doors are opened to cool the furnace and the charge, which, when it has become as pasty as ordinary mortar, is pushed back from the well and spread over the higher part of the bed. The doors are again closed and the temperature raised by addition of fresh fuel ; in this way the charge is rapidly run down into the depression in the furnace, and when this is accomplished, some slaked lime is thrown on to the surface and, by means of a rake, thoroughly mixed up with the charge. Thus the slags and unreduced ore are cooled and rendered sufficiently pasty to allow of their again being removed and spread over the higher portions of the furnace bed, where they are again calcined as in the first operation. This calcination lasts about half an hour. At the end of this stage, the temperature is again raised, and the whole charge is melted down into the well. During this stage it is not infrequent to throw a little coal slack on to the charge. When the charge has in this way collected in the well, some slaked lime is thrown on to it, and the slags pushed back on to the sloping side of the furnace and allowed to drain. The lead which has collected in the well is now tapped, and the slags, technically known as *grey* slags, are withdrawn in pasty lumps through the doors at the back of the furnace. The surface of the metal in the tapping pot is covered by slags and mattes, which retain mechanically a considerable proportion of metallic lead, the separation of which is effected by stirring with a paddle and throwing on to the surface some coal slack, which is well worked up with the molten metal. A considerable evolution of gas takes place ; this is ignited, and the heat produced suffices to melt and liberate the metal confined in the slag. The slag is then skimmed off, thrown into the furnace, and the lead ladled out into cast-iron moulds.

Before introducing another charge, the tap-hole is opened to allow the lead produced from the slag and skimmings to run into the metal pot, where it remains until the next charge is run off. The tap-hole is again closed, and another charge of ore dropped into the furnace from the hopper.

This process may, therefore, be summarised as follows:—

(1) Calcination of the ore at a low heat, whereby a certain amount of lead sulphide is converted into lead oxide and lead sulphate.

(2) Melting down of the charge, during which the unaltered lead sulphide reacts upon the oxidised products and a separation of lead occurs.

(3) The admixture of lime with the molten charge and the 'setting up' of the slags, a further separation of lead from the interaction of the sulphide and the oxy compounds of lead, and the production of an excess of lead oxide and lead sulphate over the lead sulphide present.

(4) The tapping of the metal which has accumulated during the operation, and the drawing of the slags in a pasty condition.

In Flintshire, the ores smelted by this method yield 75–80 p.c. of lead by the dry assay, and of this, 90 p.c. is obtained by smelting in reverberatory furnaces, the remaining 10 p.c. being obtained by subsequent treatment of the slags (of which about 4 cwt. per charge is produced) and fume. The time required for the working of the charge is from 5 to 6 hours.

In some cases, in Flintshire, another process of extraction is used, similar to that employed at one time in Cornwall. The mode of treatment consists of two operations:

(1) Calcination of the ore,
(2) Melting down of the calcined ore.

Each operation is effected in a distinct furnace. The method is a combination of all the different processes for the extraction of lead, utilising

(1) The air-reduction process,
(2) The desulphurisation of galena by iron,
(3) The reduction of oxidised lead compounds by carbonaceous fuel.

The ore treated in Cornwall consisted principally of galena associated with blende and sulphurised copper ores, and also a silicious gangue. Furthermore, it contained a considerable amount of silver. These ores yielded on an average 60 to 70 p.c. of lead containing about 35 ounces of silver to the ton.

The first operation, or calcination, was performed in a reverberatory furnace having three working doors, one on either side of the furnace, and the third on the side opposite the fire-bridge, and smaller than the others. Below the bed of the furnace was an arched chamber, into which the calcined ore was raked through holes in the bed opposite each of the lateral working doors. The furnace was built of ordinary rubble-work, lined internally with 9 inches of fire-brick. The doors were hung in a cast-iron framework, or had the sides protected by slabs of granite. The charge was introduced through a hole in the roof merely closed by a slab. The charge varied from 25 cwt. to 3 tons, but usually consisted of about 1 ton 18 cwt. to 2 tons, and was spread over the furnace bed and calcined at a high temperature, regulated so as to prevent clotting. The operation lasted from 15 to 18 hours, the charge being raked over every hour, and at the end was raked through the holes in the furnace bed into the vault below, whence it is conveyed into the flowing or melting furnace, which is very similar to the Flintshire furnace.

This furnace had five working doors, a pair on either side, and the fifth on the side opposite the fire-bridge, as in the calcining process. Near one of the lateral working doors, the hearth sloped to the one near the bridge, where the tap-hole was situated, from which the metal, &c., ran into an iron pot placed outside the furnace, near to which was a small pit to receive the regulus or slurry. The metal pot was also provided with a channel to convey away the slag.

The charge for such a furnace consisted of two tons of calcined ore, and was brought into the furnace through the back working doors. The charge was first spread over the sloping hearth, the doors closed, and the temperature raised until the charge was melted down, requiring some 2 or 3 hours.

In some cases, as with pure ores, the lead produced in this stage was tapped off, but more usually the charge was mixed with lime and culm (anthracite coal) and set up on the higher part of the furnace bed.

In some cases fluorspar was used as a flux, and 1 or 2 cwt. of scrap iron was added to assist in the decomposition of the lead sulphide.

The doors were again closed and luted, and the charge melted down. The furnace was then tapped, and the molten metal flowed into the metal pot, followed by the regulus or slurry, consisting chiefly of iron sulphide and containing the principal proportion of the copper. The regulus ran over from the metal pot into the pit below, and after a time the slag began to make its appearance; the lip of the pot was then stopped with ashes, and the flow of the slag directed along the channel by which it was conveyed out of the building.

The whole operation of melting, from the time of introducing the charge to the tapping of the metal, took about 8 hours. The slag was generally sufficiently free from lead not to require subsequent treatment. The regulus was treated for the lead and silver it contained, and then when sufficiently rich in copper sold to the copper smelter.

In calcination, 6 cwt. of coal were required for every ton of ore, the melting down requiring about 8 or 9 cwt. The lead obtained was usually hard, and required softening at a high temperature to remove the antimony which it contained.

A modification of the Flintshire process is used in France, the following description of which, as practised at Couëron, is taken from Phillips's account given in his Elements of Metallurgy:—

The construction of the furnaces at Couëron Loire Inférieure, France, will be readily understood by reference to the accompanying woodcuts.

Fig. 1 is a longitudinal section.

Fig. 2 is a horizontal section on the line CD.

Fig. 3 is a transverse section through the tapping-hole.

The fireplace A is of the usual dimensions, and the hearth B, instead of being on an arch, as is commonly the case in North Wales, is supported on iron bars, on which is laid a course of flat tiles. On these is placed a course of fire-bricks on edge, on which is arranged the usual slag bottom. The furnace has the ordinary number of working doors, *a*, with a fire-door *b*, and a tapping-hole *c*; there is a small fireplace below the pot *d*, to prevent the too rapid chilling of the lead during the process of ladling into moulds.

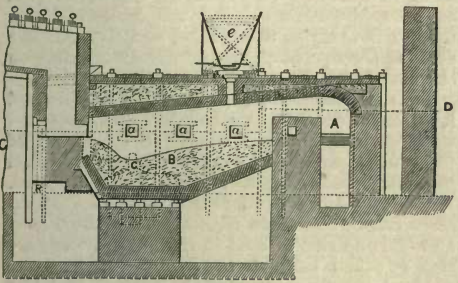


Fig. 1.

Although similar in form and dimensions to the ordinary Welsh furnace, it differs from it in one important particular, namely, in having the tapping-pot placed near the flue end instead of under the middle door.

This arrangement gives a larger surface to the hearth for roasting the charge, and permits of the lead being collected in the coolest part of the furnace, where it is least exposed to loss from volatilisation.

The mode of working varies with the nature and composition of the ores treated. This variation depends principally on the length of time required for roasting the ores before subjecting them to the higher temperature of reactions. Pure ores, especially those containing a notable proportion of lead carbonate or sulphate, require very little previous roasting, whilst those containing blende, pyrites, &c., must be calcined for a considerable time before smelting.

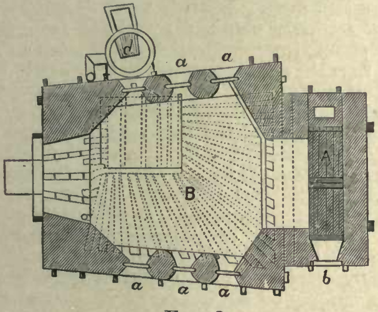


Fig. 2.

In general, the ores treated are derived from Sardinia, and contain on an average about 81 p.c. of lead, and but little silver. They are tolerably free from impurities, being composed of galena associated with lead carbonate and sulphate, and a calcareous gangue, in which are found small quantities of blende, calamine, ferric oxide, and silica. The cobbed ores, before delivery to the furnace, are ground between rollers and passed through sieves of eight holes to the linear inch. A charge of ore weighs 27 cwt.

Two men are employed at each furnace, one of whom, the chief, works on the fore-side and takes the leading part in the work.

In the treatment of rich ores, the ordinary method of working consists in roasting them in such a manner that more than one-half of the lead sulphide present in the ore is converted into a mixture of oxide and sulphate. On raising the heat of the furnace to bright redness the oxide and sulphate formed in roasting react on the undecomposed sulphide in the charge, producing metallic lead, sulphur dioxide, and a residue of slag.

The process is thus divisible into two well-marked and distinct operations:

I. Calcination or oxidation.

II. Smelting or reduction.

I. *Calcination.*—Supposing a charge to have been just worked off and the residual slags withdrawn, the furnace will be empty and at a red heat. The damper having been lowered, the charge of ore in the hopper, *e*, is let down through the opening in the arch, and spread evenly over the furnace bottom by means of rabbles. This done, the working-doors are closed, but the fire-door is left open and the fire damped with cinders, in order so to moderate the heat that the charge may become red-hot without clotting. The charge is thus left undisturbed for some time. During the first hour it is once or twice lightly rabbled; at the expiration of that time, after being well turned with the paddle, it will be found to be red-hot throughout. The damper is then lowered so as to leave just sufficient draught for the free escape of the gaseous products of calcination. The working-doors are now left partially open to admit the air necessary for the oxidation of the galena, and under its oxidising action the charge soon acquires a high temperature. Care must, however, be taken to prevent the heat from increasing so much as to cause softening of the ore. When the heat is properly controlled a white crust, consisting of a mixture of lead oxide and sulphate, in which the former predominates, is rapidly formed on the surface of the charge, and no fumes are visible.

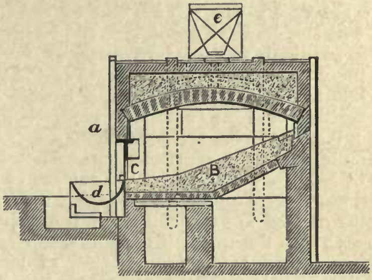


Fig. 3.

The surface is renewed from time to time, about every quarter of an hour, either by rabbling or by paddling. The requisite heat is maintained in the furnace during this process by firing with cinders only, which are preferable to coal for that purpose, not merely on account of their lower value, but also because they give a steadier heat and do not yield gaseous hydrocarbons to interfere with the oxidation.

The alternate raking and paddling of the charge is continued at regular intervals, until on examination, it is thought to be sufficiently desulphurised, which is generally the case at the end of from four to four and a half hours.

The grate is then freed from clinker, coal is thrown on the fire, the damper is opened, and a brisk fire is got up; thus in a few minutes the heat in the furnace is so raised as to lead to a *commencement of the reaction period.*

II. *Smelting.*—As soon as the firing has commenced, the ore lying at the back and extreme end of the furnace is raked towards the bridge. With the increase of temperature which now takes place, the roasted ore soon begins to soften and to give off white fumes, thus showing that the reactions which result in the liberation of metallic lead have commenced. Great care and attention on the part of the smelter are, however, necessary, in order to prevent too great a loss of lead by volatilisation during the heating up of the charge. The ore must on no account be allowed to liquefy, and as often as it shows a tendency to fuse, some slaked lime in powder is thrown on the charge and well worked into it with a rake. By this means, and by carefully regulating the draught, the charge can be heated to the required temperature without fusion. Lime must be frequently added during the process, but in small quantities at a time. The consumption of lime amounts altogether to about 2 p.c. of the ore treated.

Shortly after the reactions commence, globules of lead may be seen on the surface of the charge, and before an hour has elapsed a certain quantity of lead has drained down the slope of the hearth into the well. The charge, having in due time attained the temperature of bright redness, must not be fired too hard, therefore both the draught and the firing are so regulated that the heat is kept at the requisite degree without going beyond it.

The reactions are much aided by frequently rabbling and turning the ore; but as the working doors must remain open for this purpose it follows that a large quantity of air enters the furnace, thus oxidising the sulphide in the ore, and so cooling the charge that the flow of lead becomes interrupted. When the cooling is judged to have been carried sufficiently far, the charge is rabbled, the doors closed, and the fire so urged as to fill the furnace with flame during several minutes; then, on re-opening the doors and paddling, the flow of lead recommences as before.

At the expiration of from two and a half to three hours from the commencement of the reactions, a considerable amount of lead will have accumulated in the well. A first tapping is then made, the lead being received in the tapping-pot, under which a small fire has been previously lighted in order to warm it, and to retain the lead in a molten condition; the tap-hole is stopped with a plug of stiff clay.

The thick dross which rises to the surface of the lead, and which contains a certain quantity of sulphide removed from the charge by the hot lead and again separated on cooling, is skimmed off with a shovel and put back into the furnace. A little fine coal, together with some burning cinders and lime, is now thrown on the lead, which is vigorously agitated with a small paddle and stirred until it is clean. It is then skimmed, the skimmings being put on one side and the clean lead ladled into moulds.

The firing, paddling, and cooling of the charge are repeated several times, until at last the residue becomes dry and gives but little lead. Thereupon the heat in the furnace is considerably increased, but not sufficiently to fuse or flow down the charge, and towards the close of the operation the material remaining on the hearth consist to a great extent of oxides.

The pot skimmings, composed of cinders and lead matte, are now thrown into the furnace and well paddled with the charge, the reaction of the lead sulphide and cinders on the oxide and sulphate producing a further yield of lead. When this has ceased and it is seen that no more can be extracted without a very high heat and the addition of coal to the charge, the grey slag is raked through the middle door at the back of the furnace, and the second and last tapping is made.

The whole period of reactions occupies from 5 to 5½ hours. After the withdrawal of the slags, the bottom is examined, and if it is corroded into holes, or in any way injured, is repaired by putting into the cavities a mixture of grey slag and lime and beating it smooth with the paddle. It is of great importance to maintain the bottom perfectly smooth and with a good slope on all sides towards the tap-hole. A little lime is now spread over the bottom, and a fresh charge is at once let down into the furnace, the damper having previously been lowered to prevent loss of fine ore by the draught. The weight of coal consumed is equal to 40 p.c. of the ore smelted. The produce of lead per charge of 1350 kilos. of ore (at 81 p.c. of lead) is 15 pigs weighing 901 kilos. and 290 kilos. of slags containing 50 p.c. of lead. Hence the total loss of lead in the reverberatory furnace is 3·52 p.c. by volatilisation; out of this a certain proportion is recovered from the fume collected in the condensers and flues. A larger percentage of lead in pigs might be obtained by adding more coal to the charge towards the end of the process and firing hard, to reduce part of the lead left in the slags. It is, however, considered more economical to limit the production in the reverberatory to about 80 p.c. of the lead contained, and to carry the richer slags to the blast furnace. This is especially the case when the blast furnace is connected with good condensers and long flues.

It will be seen from the foregoing description that the process of reverberatory smelting adopted at Couëron differs principally from that generally employed in England in there being (1) no melting or flowing down of the charge; (2) the long preliminary calcination of the ore before commencing the reactions.

The position of the tap-hole near the flue end of the furnace gives a longer slope to the hearth, and allows of heavier charges being worked; at the same time the lead produced is collected in the well at a greater distance from the fire.

Spanish furnace or boliche.

In the south of Spain, the smelting of lead ores has been carried on for many centuries in a form of furnace known as the *boliche*. It consists of two chambers, separated from one another by a fire-bridge. One of these only is used for the reduction of the ore, and the second, which is situated between the first and the chimney, serves apparently to moderate the draught.

The fireplace projects from one side of the hearth, and is without a grate; the fuel, consisting of wood, is supplied through a door at the end of the fireplace.

The smelting hearth inclines towards the working door, situated at the end of the longer axis, immediately within which is a receptacle in the floor for the collection of the metal.

The boliche is constructed of rubble work, cemented together by clay and strengthened by buttresses built at the angles.

The interior is lined with firebrick, the lining for the hearth consisting of a species of clay resulting from the decomposition of talcose schists, known as 'laja' or 'laguena,' or of a mixture of this clay with broken galena.

The English firms smelting lead ores in the Linares district use a boliche constructed of sandstone and without any special lining, the sandstone being bound together by means of iron braces.

The method of smelting is in principle similar to the Flintshire process, and the process is divided into three operations:

1. *Caldeo,* or calcination, occupying from 1 to 1½ hours.
2. *Blandeo,* or sweating, lasting from 4 to 4½ hours.
3. *Corrida,* or running down, occupying the remainder of the shift, *i.e.* from 2 to 3 hours.

The ore thrown into the furnace through the working door is first spread evenly over the surface of the hearth and then calcined. When the calcination is completed, the temperature is raised and the running down of the charge begun. The slags are dried up after the completion of the melting down by throwing into the furnace the ash and breeze from the ashpit. The metal is tapped into a vessel, in which it is stirred with dry leaves, and finally ladled into moulds.

The yield of the boliche is about 80 p.c. of the lead of the ore as given by the dry assay. The grey slags contain from 45 to 50 p.c. of lead and represent 15 to 17 p.c. of the charge. These slags are subsequently treated in a blast furnace. The charge of a boliche consists of 60 arrobas, or 13 cwt. 1 qr. 16 lbs., and requires for its reduction 1550 to 1750 lbs. of brushwood. It is stated that the lead obtained by using the boliche is softer than that produced in the Flintshire furnace, but Phillips states that the difference in quality is not very marked. The difference is supposed to be due to the fact that in the boliche the smelting is effected at a much lower temperature. At Linares boliches have been built so as to burn a mineral fuel, but the result of working has in no way shown this form of furnace to be superior to the English reverberatory furnace.

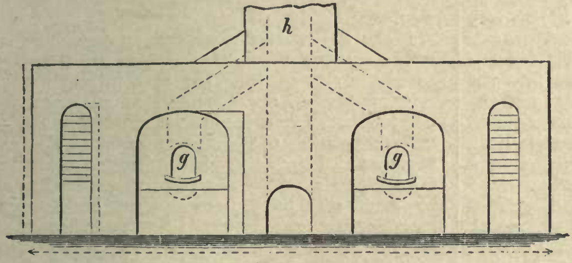


Fig. 4.

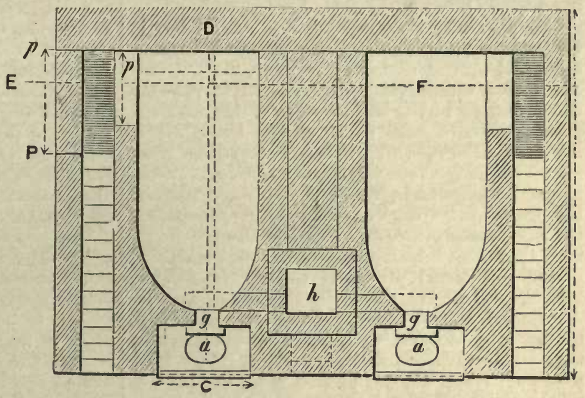


Fig. 5.

Bleiberg process.—At Bleiberg in Carinthia, reverberatory furnaces of a special construction are used, two being usually built side by side and arranged to work into one chimney.

Fig. 4 represents a front elevation, and Fig. 5 a horizontal section. The hearth is about 10 feet long, and at the back near the fire is about 4 feet 10 inches wide. This width is maintained for about half the length of the furnace, when it is gradually reduced, until at the working door it is about a foot wide. The hearth is sloped from the back and also from the two longer sides, thus forming a depression in which the metal may collect and flow into the metal pot, *a*, in front of the working door, *g*.

The hearth is formed of a lower layer of beaten clay and an upper one of fused slags, having a united thickness of about 6 inches. The fireplaces are built parallel to the longer axis of the furnace, and separated from the latter by a fire-bridge. The products of combustion pass into the chimney, *h*, by a flue above the working door. The grate is of stone, having a greater inclination than the hearth, and is traversed by openings for the admission of air.

The fuel employed is wood, but in some cases brown coal is used, and then the stone grate is replaced by one with iron bars.

The galena smelted at Bleiberg is associated with cerussite, anglesite, and lead molybdate, also with zinc blende, calamine, and willemite. The zinc ores are separated mechanically and treated for zinc. The lead ores are delivered to the smelter either in the rough state or in the form of slimes. In the former state on assaying they yield from 65–70 p.c. of lead, in the latter from 60–65 p.c.

In smelting, a charge of 375 lbs. of ore is thrown into the furnace through the working door and spread over the hearth. This is calcined at a temperature low enough to prevent the softening of the charge—the calcination occupying 3 to 4 hours—the charge being raked over at intervals. The temperature is next raised to bring about the usual reaction between the oxy compounds and the unaltered galena, the charge being carefully rabbled to promote a thorough admixture, and thus aid the reactions. This operation lasts from three to four and a half hours, the metal produced constantly flowing into the depression, and thence to the metal pot. At the end of this operation the slags are dried up by the addition of ashes and breeze, and then withdrawn from the furnace. The lead produced from the ore in this way, amounting from 125 to 150 lbs., is supposed to be specially pure, and is known as '*Jungfernblei*,' or 'virgin lead.' After the withdrawal of the slags a second charge of ore is treated, the slags produced being left in the furnace, and to them the slags from the previous smelting are added. These slags are free from sulphide and contain lead in an oxidised state only. The temperature is raised and charcoal added, the whole being intimately mixed with the rabble. The oxidised lead compounds are in this way reduced in from 7 to 8 hours, about 150 lbs. of lead being produced.

The complete working of the two charges will occupy from 21 to 23 hours, the yield of lead being usually about 2½ p.c. below that obtained in the dry assay.

Smelting galena with iron in reverberatory furnaces.—A method depending on the 'process of affinity' was at one time used in France in the reduction of a silicious Spanish galena. The furnace used was constructed with a hearth sloping from the fire-bridge to the working door. In front of the furnace, below the working door, is the tap-hole, in front of which is the metal pot for receiving the metal. Above the working door is a flue communicating with a chimney for the removal of the products of combustion, &c., the fireplace being at the end of the furnace opposite the door. The method of working consisted in introducing a charge of some 800 lbs. of galena, to which was added some 200 lbs. of scrap iron; the mixture was then heated and stirred from time to time, the galena in this way being reduced by the iron, when lead and iron sulphide are produced. The contents of the furnace are, at the end of the operation, run into the tapping-pot, in which the lead collects, and the matte and slag are allowed to flow over on to the floor. Both the matte and slag contain lead, for which they are subsequently treated in a blast furnace.

Galena containing 80 p.c. of lead yielded by this method from 67–70 p.c. of metal, the matte contained from 5–12 p.c. of lead, and from 4–5 p.c. are found in the slag, whilst 4 p.c. would be volatilised. This method of reduction of raw galena with iron in reverberatory furnaces is stated to be wasteful and expensive.

Smelting in Cupolas or Blast Furnaces.

Cupolas or blast furnaces are employed not only for the reduction of slags obtained in the smelting conducted in reverberatory furnaces, and of the various drosses produced in the purification and desilverising of lead, but also for the smelting of ores which by reason of the minerals associated with them and their poverty in lead are unsuited for treatment in reverberatory furnaces. This reduction is effected either by a treatment of the raw ore in the blast furnace, or by submitting the ore to a preliminary roasting and subsequently smelting it in a blast furnace.

In the treatment of raw ores the reducing agent is iron, which is added to the charge either in the form of metallic iron, as was at one time practised at Clausthal; or the iron is replaced by the basic iron silicates, obtained as slags in refining and puddling of iron, or from copper smelting. In some cases the iron required is added in the form of iron ores. The fuel usually employed is coke. This mode of smelting of raw ores is dependent on the decomposition of lead sulphide by metallic iron yielding metallic lead and iron sulphide. When basic iron silicates or other iron compounds are used, the iron required for the reduction is obtained by the reduction of these compounds by the carbon of the fuel or the carbon monoxide produced by its combustion. The iron sulphide formed unites with some lead sulphide and the sulphides of other metals, such as copper and silver, present in the ores, forming a fusible matte or regulus, which being lighter than lead collects above the metal in the hearth of the furnace, and is tapped out with the metal, from which it is easily separated. Some of the copper sulphide in the ore is reduced to metallic copper, and this alloys with the lead, as also does the silver which may have been reduced by iron and lead.

Antimony and arsenic sulphides, if present, are reduced by the metallic iron, the metals combining with the lead, or being in part volatilised and thus occasioning a loss of lead. As will be seen, these sulphides must also lead to an increased consumption of iron, and also a greater yield of matte. In addition to lead and matte, a fusible slag is formed, which consists chiefly of an iron silicate and contains lead, which is recovered from it by re-smelting in the blast furnace with another charge of ore. This is repeated until the amount of lead present is reduced sufficiently to allow of its being thrown away.

From the mattes produced as described, a further amount of lead is obtained by roasting the matte and smelting the roasted matte in a small cupola, an operation which produces, in addition to lead, a second matte and slag. A similar treatment of the second matte may, as at Clausthal and Freiberg, yield a further quantity of lead, and a matte in which, where lead ores associated with copper are smelted, the copper is sufficiently concentrated to serve for the extraction of the copper. The reduction of lead ores in blast furnaces is more usually preceded by a roasting of the ore, conducted as a rule in reverberatory furnaces, and in this manner the whole of the galena is converted into oxide and some sulphate, and finally the roasted ore is heated to a temperature sufficiently high to effect a partial fusion or render the mass of roasted material pasty. In this latter stage, a portion of the lead oxide reacts with the silica associated with the ore, producing a lead silicate. The roasted ore is next passed on to the blast furnace, where it is smelted with coke and suitable fluxes into the composition of which iron, either as metallic iron or as a basic silicate, enters. In some instances, the iron compounds required for the decomposition in the blast furnace are supplied by the iron ores associated in the first instance with the lead ores. This is the case in the smelting as conducted at Freiberg. In the melting down in the blast furnace, the oxy compounds of lead are reduced in part by the carbonaceous fuel, but chiefly by the iron, which in presence of carbonaceous matter is able to decompose the lead silicates. The product of this smelting should consist of lead, containing the greater portion of the silver present in the ore, and a slag consisting essentially of silicates of iron, lime, alumina, and magnesia and not more than 3 p.c. of lead. Highly silicious lead ores are smelted at Pontgibaud in this manner, the roasted ore being treated with a mixture of scrap iron, limestone, and lead slags in a blast furnace. At Couëron, the silicious ores are roasted and smelted in a blast furnace together with the grey slags produced in the smelting richer ores in reverberatory furnaces in the manner already described, to which are added agglomerated fume and iron slags. When the calcination of the ore is complete and the sulphur entirely removed by oxidation, the products of the subsequent smelting in the blast furnace consist of lead and slag only, but otherwise a matte or regulus is formed in addition, as at Freiberg. The mattes produced are treated in a manner similar to that already mentioned, being first roasted and subsequently smelted in a special cupola, or are returned, after roasting, to the blast furnace and smelted with a fresh charge of ore.

Various forms of blast furnaces have been employed in different lead-smelting districts for the reduction of lead ores. The older forms of furnace, such as those used at Clausthal and Freiberg, and the Castilian furnace for the smelting of Spanish slags and introduced into this country for the treatment of slags, have been replaced in late years by furnaces of newer construction; such as the Raschette furnace, the horizontal section of which is rectangular, with two long sides and two shorter. In each of the longer sides are placed three or more twyers, and there is a single twyer in each of the two shorter sides; the hearth is provided with a tap-hole on each of the narrow sides. The hearth bottom slopes downwards toward each narrow end. Water twyers similar to those employed in iron-smelting are also used. Another of the improved forms is the Pilz furnace, which is cylindrical in form, wider at the top than the bottom, with a circular or octagonal section inside and supplied with from 5 to 8 twyers. These furnaces are charged from the top, the gases being drawn off either by a vertical pipe leading to condensing flues, or by a lateral one. These furnaces have been further improved by replacing the brickwork in the hottest part of the furnaces by an annular cylinder of iron, provided with apertures for the twyers and an opening through which the slag flows. The sides of the cylinder are kept cool by a constant stream of water circulating through it. Blast furnaces provided with water-jackets are in use at Freiberg, at Couëron, and Pontgibaud (*v.* Phillips, Elements of Metallurgy), and at Leadville the Raschette furnaces there are provided with this arrangement. Water-jacketed furnaces for smelting lead ores, also for smelting slags, have been erected in this country.

The Raschette type of furnace, built with water-jackets, appears to be most favoured in American and Australian practice; the developments appear to be mainly in the increase in the dimensions of the hearth, and consequently increased number of twyers. Attempts have been made to adapt some of the devices which have proved serviceable in iron-smelting practice, *e.g.* closing the furnace and feeding by a bell and cone arrangement, also increasing the height of the furnace. Experience has shown that such adaptations are altogether unsuited for the working of lead, owing to its volatility. Hixon, in Notes on Lead and Copper Smelting (New York and London Scientific Publishing Co.), relates an experience in the working of a blast furnace at Aquas Calientes, which convincingly shows how little suited to lead smelting are high-shaft furnaces with top feed. The more usual arrangement of feeding the furnace from an open top, the gases being drawn off by a down-take below the feeding floor, is the more satisfactory.

Smelting of lead ores at Clausthal.—As an example of the practice of the 'iron precipitation' process, the treatment adopted at Clausthal may be cited, for a more detailed account of which the reader is referred to a series of papers by J. Clark Jefferson, A.R.S.M., in Engineering, vols. 24 and 25, from which the following account is taken.

The ores smelted at Clausthal consist of an argentiferous galena, associated with copper pyrites, fahlore, bournonite, zinc blende, spathic iron ore, iron pyrites, brown spar, quartz, calc spar, heavy spar, clay-slate, and greywacke. The minerals are first submitted to mechanical treatment and supplied to the smelter in the form of *schlieg*, of which the following may be regarded as representing the average composition:—

Lead	50·7	to 73·6 p.c.[1]
Silver	0·555	,, 0·185 ,,
Copper . . .	0·02	,, 0·6 ,,
Zinc	0·3	,, 4·1 ,,
Antimony . . .	0·02	,, 0·3 ,,
Iron	0·4	,, 3·7 ,,
Sulphur . . .	8·5	,, 14·2 ,,
Alumina . . .	0·07	,, 1·5 ,,
Lime	0·2	,, 1·4 ,,
Insoluble residue . .	5·9	,, 32·4 ,,

The old method of smelting practised at Clausthal consisted in reducing the *schlieg* by fusion with metallic iron and coke in a blast furnace 20 to 25 feet high and 3 feet square in the widest part. The form of furnace has gradually been altered, as also the method of treating the ores; the chief change in this latter has been the replacement of the iron by the iron silicates obtained from the copper works in

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[1] Kerl Grundriss der Metallhüttenkunde, p. 60.

the Lower Harz, and also the use of the iron residues left by the extraction of copper from burnt pyrites by the wet method. In respect to furnace development it will be sufficient to describe the later model of furnace used, which is the third form in use at Clausthal; its construction will be understood from the accompanying diagram.

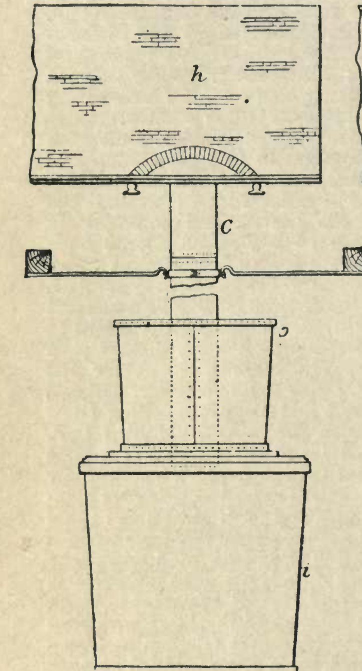


Fig. 6.

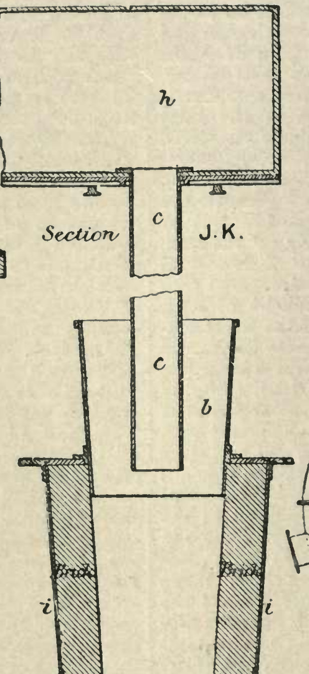
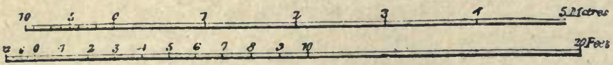


Fig. 7.



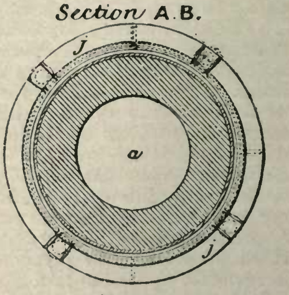


Fig. 8.

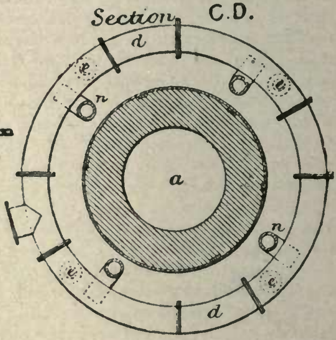


Fig. 9.

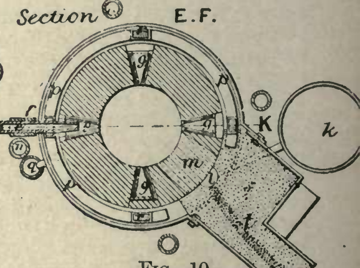


Fig. 10.

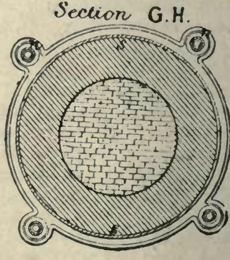


Fig. 11.

Fig. 6 is a front elevation; Fig. 7, sectional elevation; and Figs. 8, 9, 10, and 11, horizontal sections. *a*, is the shaft of the furnace; *b*, iron charging funnel; *c*, waste gas pipe; *d*, blast main; *e*, four vertical blast pipes; *f*, socket blast pipes; *g*, four water twyers; *h*, flue to condensing chamber; *i*, sheet-iron casing; *j*, bearers carrying sheet iron casing; *k*, iron tapping hearth; *l*, fore hearth; *m*, breast stone; *n*, iron column for supporting the bearers; *o*, copper piping to convey water to the twyers; *p*, outlet water pipe from the twyers; *q*, cast-iron cistern for water from the twyers; *r*, perforated sheet boxes to prevent a stopping up of the pipe *p*; *s*, cast-iron foundation cylinder; and *t*, slag gutter.

The furnace is built on a cast-iron foundation plate 1·5 inches thick; on this rests the main wall, which is 4 feet high, 4 feet 2 inches inside, and 7 feet 2 inches outside diameter. The space inside this brick wall is filled to a height of about 2 feet 3 inches with slag bricks, on the top of which is a layer of clay 1 foot in thickness, and this again covered flush with the top of the main wall with brick. In the centre and forming the bottom of the hearth is a slab of fire sandstone 16 inches thick. The shaft of the furnace built on this foundation is for a height of 7 feet built of fire-brick, and the remainder, 10 feet, is built of ordinary brick, the thickness being that of two bricks throughout the whole height. As will be seen, the section of the furnace gradually enlarges; its diameter at the hearth is 3 feet, and 5 feet at the extreme upper end. The height of the furnace is about 25 feet to the charging opening, and 21 feet 6 inches to the top of the boshes. The furnace bottom is made of clay and coal dust, resting on the slab of sandstone, and hollowed out as shown in Fig. 7. The four twyers are symmetrically arranged some 30 inches from centre to centre; the diameter of the circular blast main is 60 inches.

The materials smelted in these furnaces consist of ore in the form of *schlieg*, lime, roasted lead matte, slags obtained in smelting ore, as also a proportion of slags obtained from the smelting of regulus, together with slags obtained in smelting copper pyrites at Oker, known as Oker slags, or the residue left in the wet extraction of these copper ores. These two last-named materials supply the iron required for the reduction of the lead ore, the former in the form of iron silicate, and the latter containing iron in the form of the sesquioxide.

The materials composing the charge are prepared on the charging floor and thrown into the furnace with the fuel, the mineral and flux being disposed in layers alternating with layers of coke. The following is an example of the composition of the charge:

	Cwt.
Ore	100·00
Lead fume	1·01
Lead scrapings from the smelting house .	0·63
Roasted lead regulus	47·51
Schlieg scrapings from the charging floors	1·21
Oker slags	60·00
Slags from the same process	3·70
Regulus slags	42·00
Slags from schlieg smelting . . .	54·00
	310·06

The products obtained are work-lead (*Werkblei*), lead regulus (*Bleistein*), and a slag containing more or less lead. The lead, as is shown by the following analyses, contains many metallic impurities, a portion of which are derived from the minerals associated with the galena and some from the materials used in the reduction:

Lead . .	98·8378	98·9648
Copper . .	0·1862	0·2838
Antimony .	0·5743	0·7685
Arsenic . .	0·0009	0·0074
Bismuth . .	0·0039	0·0082
Iron . .	0·0035	0·0028
Zinc . .	0·0025	0·0028
Nickel . .	0·0023	0·0028
Cobalt . .	0·0016	0·0003
Cadmium . .	trace	trace
	99·6130	100·0414

The lead is refined at Lautenthal, or, if it contains sufficient silver, is desilverised by Parkes' process.

The following analysis gives the composition of the lead regulus:

Sulphur . . .	26·877
Iron	53·112
Lead	10·655
Copper	4·620
Silver	0·030
Antimony . . .	0·267
Arsenic . . .	—
Zinc . . .	2·110
Manganese . . .	0·385
Cobalt and nickel . .	0·306
Lime	0·383
Magnesia . . .	0·054
Silica	0·510
	99·309

The lead regulus is roasted in heaps, wood being employed as fuel, and in some cases coal, the roasting process occupying altogether some two months. The heaps are constructed as follows: first a layer of about 3 inches of powdered slag is spread on the ground, on this is placed a layer of pine wood, 100 cwt. of regulus requiring 110 cub. feet of wood for complete roasting. The regulus to be roasted is spread over the wood in a pyramidal heap, 14–20 feet broad, 20–30 feet long, and 5–6 feet high, and containing some 2000–3000 cwt. of regulus. The ignition is effected by setting fire to shavings placed under the wood. The first firing lasts from 8 to 10 weeks. After the heap has burnt out, it is broken up, and the portion insufficiently roasted separated, to be again submitted to a similar roasting. When by this roasting the sulphur has been sufficiently reduced, but not completely burnt away, the regulus is then smelted in the ore furnace, and this mode of treatment is adopted so long as the copper in the regulus does not amount to more than from 6 to 7 p.c., in which case the roasted regulus is smelted in a low blast furnace with slags from ore smelting and coke. This operation yields a work-lead amounting to 7–9 p.c. of the roasted regulus treated, and a regulus in amount varying from 24 to 42 p.c. of the roasted regulus. The amount of lead obtained is 75 p.c. of that contained in the regulus, the remainder being lost by volatilisation. This lead contains antimony and from 0·4 to 1·5 p.c. of silver. The regulus produced in this operation is again roasted and smelted, and thus a regulus produced which now contains some 20 p.c. of copper and is next treated for copper.

Lead-smelting at Freiberg.—The treatment of the great variety of minerals smelted at Freiberg for lead consists essentially of two sets of operations; first, the roasting of the ore to desulphurise it as completely as possible; secondly, the smelting of the roasted ore in blast furnaces and thus producing a work-lead, a matte or regulus, and a slag. The matte produced is submitted to repeated roasting and smelting operations, pretty much as practised at Clausthal.

The mines of Saxony, from which the ores smelted at Freiberg are chiefly derived, supply a great number of different mineral species which are classified as follows: (1) Lead ores, (2) copper ores, (3) arsenical ores, (4) zinc ores, (5) sulphur ores, (6) silver ores. The first class represent all minerals which contain above 15 p.c. of lead, and these are again subdivided into two groups: (1) '*Bleiische Erze*,' plumbiferous ores, containing from 15–30 p.c. of lead; (2) lead glances, in which the amount of lead in some cases is as much as 80 p.c. The mean lead content of the ores may be stated as 40 p.c., and this is associated with 150 grams of silver per 100 kilograms. The following represents the average composition of the '*bleiische Erze*':

Lead . . .	15–20 p.c.
Sulphur . . .	30 "
Zinc . . .	10 "
Arsenic . . .	7–15 "
Silver . . .	60 grams per 100 kilograms.

The copper minerals known as '*kiesblendige Erze*' are constituted of three species, viz. iron pyrites, copper pyrites, and zinc blende; the copper varies in amount from 1 to 3 p.c. Arsenical minerals are constituted of arsenical pyrites containing about 10 p.c. of arsenic, and the zinc minerals consist essentially of blende containing from 30 to 40 p.c. of zinc. All these various minerals are more or less argentiferous. Those minerals containing above 20 p.c. of sulphur are classed as sulphur minerals.

For the purpose of calcination the ores are divided into two classes; those containing at least 20 p.c. of sulphur and not more than 25 p.c. lead are submitted to a preliminary roasting in kilns so arranged that the sulphur dioxide produced may be utilised in the manufacture of sulphuric acid. In this operation a portion only of the sulphur is removed, the greater portion being reduced by roasting the partially desulphurised ore with raw ores which from their composition are unsuited for roasting in kilns. This second and final calcination is performed in reverberatory furnaces known as the 'Sinter röstöfen,' consisting of two beds, one above the other, the lower bed having the grate at one end, at the opposite end is a passage communicating with the upper part along which the heated gases pass and are finally conveyed from the furnace by a flue which communicates with condensing chambers.

This form of calcining furnace with two beds has been replaced by a furnace with a single bed, and with working doors upon both sides, in which the ore is charged at one end from a hopper placed above, viz. at the end furthest from the fire. The ore is spread in a layer over this portion of the furnace bed, and after remaining in this part for a given time it is moved on to the next portion of the bed, and its position filled by a fresh charge. In this way the charge is gradually moved along the furnace to the fire-bridge, and at this point it is subjected to a heat sufficiently intense to effect a partial fusion or agglomeration and is then withdrawn. In this manner the ore is continually submitted to a gradually increasing temperature, whereby the sulphur of the sulphides is burnt away and oxides produced, which in the final heating react with the silica and produce silicates.

The construction of the 'Fortschaufelungs-röstöfen,' will be understood from the accompanying figures, for the drawings of which as also for much information respecting the present practice of lead smelting, the wirter is indebted to Mr. W. Maynard Hutchings, general manager of the lead works of Messrs. Cookson & Co., Newcastle-on-Tyne.

Fig. 12 is a front elevation of the furnace, which is constructed of brickwork with a lining of fire-brick, and stayed together with iron standards and crossbars. In this is also shown the hopper *a* for charging ore, the ten working doors *b*, the door *c* for the withdrawal of the charge, and the door *d* for charging fuel into fire-grate.

Fig. 13 represents a vertical section, showing the fire-grate *e*, the fire-bridge *f*, and bed of the furnace, constructed of iron plates supported by pillars of brickwork, which are cooled by circulation of air below; upon these plates are built the materials composing the bed of the furnace. *g* is the opening in the roof through which the ore from the hopper is discharged into the furnace bed, *h* the flue leading to a series of condensing chambers.

Fig. 14 is a plan of the furnace, and Figs. 15 and 16 are vertical sections through CD and FG respectively.

The charge of unroasted minerals and roasted minerals is carefully prepared so as to attain as nearly as possible the following conditions.

(1) The amount of lead shall not exceed 20–25 p.c., an amount which experience has shown serves well as vehicle for the silver.

(2) The amount of zinc should not exceed 10 p.c., a greater proportion of zinc rendering the separation of slag and matte unsatisfactory owing to the viscosity of the slags.

(3) Silica should be present to the amount of 20–25 p.c., and thus insure the production of slags consisting essentially of iron protosilicates.

The amounts of lead, silver, copper, zinc, and silica are assayed to ascertain whether the above conditions have been fulfilled. The following are two examples of such assays:

—		Lead p.c.	Copper p.c.	Zinc p.c.
No. 1	Before roasting .	22	2·5	—
	After roasting .	21	2·5	10
No. 2	Before roasting .	25	5·5	8
	After roasting .	22	5·4	10

—		Silica p.c.	Silver grams per 100 kilograms
No. 1	Before roasting .	—	75
	After roasting .	27	67
No. 2	Before roasting .	14	100
	After roasting .	20·7	102

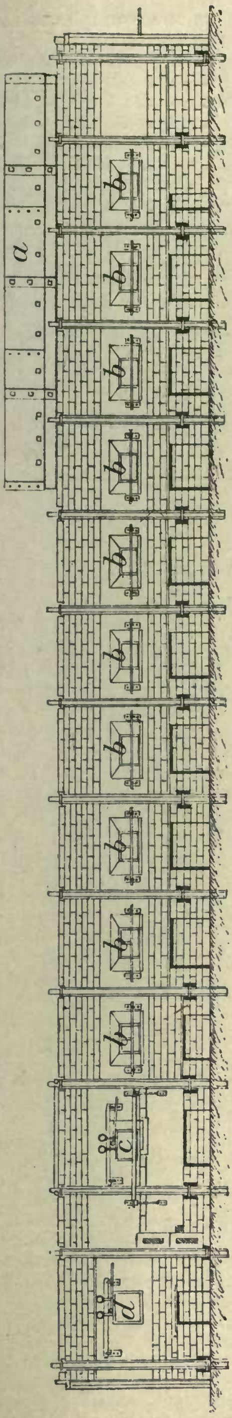


FIG. 12.

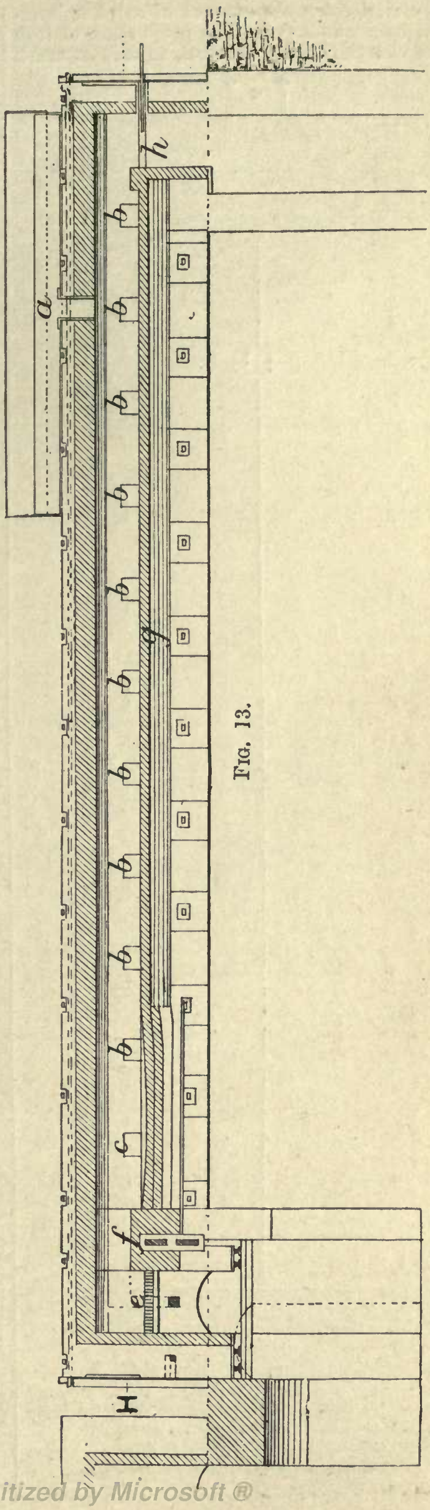


FIG. 13.

By calcination the amount of sulphur is reduced to about 2 p.c. The proportion of iron in the charge is never assayed, in fact as much iron pyrites as possible is added, and in some cases iron ores also.

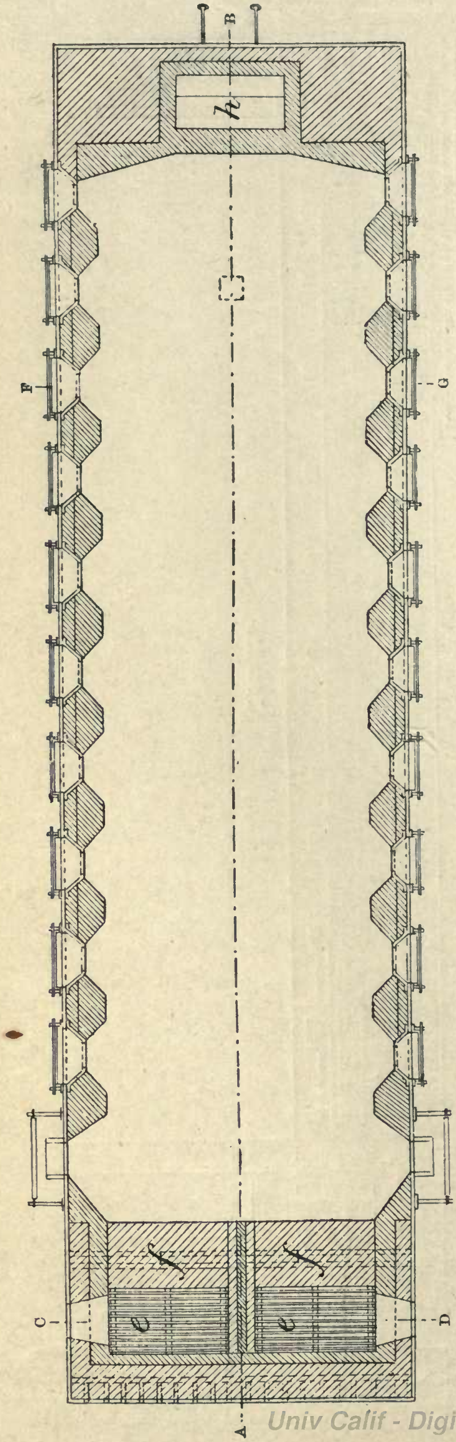


Fig. 14.

The following are two examples of a charge prepared for roasting :

	No. 1	No. 2
Galena . . .	41·00	37·20
Bleiische Erze . .	7·47	11·00
Iron pyrites . .	43·33	40·46
Silicious iron pyrites	4·50	4·81
Silicious minerals .	1·60	6·53
Residues from zinc manufacture . .	2·10	—
	100·00	100·00

The proportions of crude to roasted ore in the above mixture are as follows :—No. 1 : Crude ore 53·88, roasted ore 44·03. No. 2 : Crude ore 60·73, roasted ore 39·27.

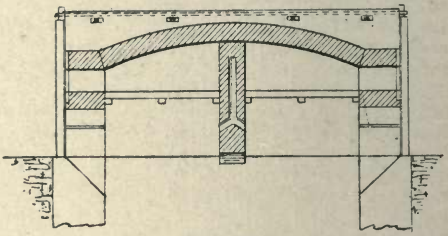


Fig. 15.

The *Fortschaufelungsröstöfen* is an example of the hand reverberatory roasting furnaces. There are, however, a number of forms of mechanical reverberatory roasting furnaces, some with stationary hearths and others with moving hearths, for the detailed description of which the reader is referred to Hofman's Metallurgy of Lead (New York and London, The Scientific Publishing Co.).

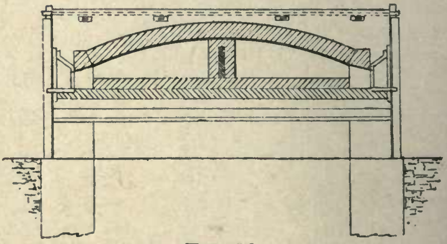


Fig. 16.

In 1896 Huntington and Heberlein introduced a method of treating galena, and concentrates consisting of galena mixed with pyrites and blende ; by this process the ore is rapidly desulphurised and obtained in a condition suitable for the blast furnace, and incidentally the sulphur dioxide produced may be utilised for the production of sulphuric acid. In this process the ore is mixed with from 6 to 15 p.c. of lime, according to the proportion of sulphur in the ore, and heated slowly in a reverberatory furnace. The partially desulphurised material is transferred to a pear-shaped vessel, made of sheet iron, styled a converter, in which it is submitted to the action of a blast of air ; during the blowing in the converter, energetic oxidation takes place, accompanied by other reactions resulting in a rise of temperature sufficient to bring about an agglomeration of the mass. In explanation of the Huntington-Heberlein process it appears, according to W. Maynard Hutchings (Engineering and Mining Journal, 1905, 726), that in the first action the lime is primarily converted into sulphate. 'The strong base, lime, apparently plays the part of "catalyser" in the most vigorous manner, the first SO_2 evolved being instantly oxidised and combined with the lime to sulphate, with so strong an evolution of heat that the operation spreads rapidly.' In the reactions in the converter silica plays an important part, decomposing the sulphates leading to the production of a basic silicate of lead, calcium, and other metals present with the elimination of all the sulphur. This explanation put forward by Hutchings (*l.c.*) is supported by the experiments of Hilpert (Metallurgie, 1908, 537 and 539) on the lead silicates, as also by the observations of Hofman and Mostowitsch (Trans. Amer. Inst. Min. Eng. 1909, 51), on the reactions between silica and calcium sulphate at temperatures between 1000° and 1250°, under which circumstances, it is shown that the sulphate is converted into silicate, sulphur dioxide and oxygen. Further, it is shown that ferric oxide effects a similar decomposition. In the light of these facts the Carmichael-Bradford process, used in Australia, is readily understood. In this method the ore is mixed with dehydrated gypsum and fed into a converter on to a small bed of glowing coal, which is kept glowing by a gentle blast of air. Another modification of the Huntington-Heberlein mode of treatment is the Savelsberg process, in which limestone is used in place of dehydrated gypsum. The new departure of 'blast roasting' or 'lime roasting,' inaugurated by Huntington and Heberlein, has been followed by the introduction of many modifications, amongst which may be mentioned the Dwight-Lloyd sintering process, which is a continuous one, and yields a porous sinter having a coke-like structure, and in a form suitable for treatment in a blast furnace. The essential feature of the Dwight-Lloyd process is that blast roasting is effected by a down-draught. The various types of machines employed embody, according to Hofman (Report of the Seventh International Congress of Applied Chemistry, London, 1909, sect. 111A, 18–23), the following three functions: '(1) a layer of ore is spread mechanically to the thickness of from 2½ to 5, average 4 inches, on a travelling herring-bone grate; (2) the ore stream thus formed passes first under an igniter, placed at right angles to the grate, to become ignited at the surface, and then over a stationary suction box, which, by down-draught, causes the roasting started at the surface to progress downward and be finished when the ore reaches the farther end of the suction box; (3) the sintered ore is discharged automatically in a size suitable for blast furnace treatment.' *Cf.* Bannister, Trans. Inst. Min. a. Metal. 1912.

Smelting for lead in blast furnace.—The roasted ore is next reduced by fusion with coke in a blast furnace, the form which has been adopted at Freiberg being a circular Pilz furnace resembling that used at Clausthal from which it differs in the manner of drawing off the gases and also in the arrangement used for charging the furnaces, and in having the sides of the furnace in the zone of fusion constructed of cast-iron boxes through which water circulates. The accompanying illustrations, Fig. 17 (from Percy's Metallurgy; Silver and Gold, part 1, 542), represent the Pilz furnace used at Freiberg in 1878. It is 25 feet high, is circular in section, 4 feet 11 inches diameter at the hearth, and gradually widening to 6 feet 7 inches at the top, and is supplied with eight twyers.

a, the hearth bottom, composed of four courses of bricks, the lowest common brick, resting on a circular plate of iron 1¼ inches thick, then three courses of fire-bricks, and is encased in boiler-plate, made in segments screwed together and further strengthened by hoops of wrought iron; *b*, channel extending through the brickwork and open at both ends; these channels, of which there are two, at right angles, allow of the escape of moisture; *c c*, brickwork forming the inner and upper part of the hearth; *c′ c′*, brickwork of the boshes; *c″ c″*, brickwork forming the shaft; *d d*, the tap holes, of which there are four; *e e*, two slag lips, along which the slag flows into the slag pot *p*, consisting of a cast-iron conical vessel; *f f*, blast pipes, the horizontal portions of which can be moved to and from the twyer holes; the vertical portions are supplied with a sliding screw by means of which they may be moved up and down; *g g g* are water-jackets made in sections, and of wrought iron, the construction of which is shown in detail in the accompanying illustrations. Water-jackets may also be constructed of cast iron instead of wrought iron, each segment being provided with an aperture for the twyer and also pipes for conveying the cold water and for the outflow of the heated water; *h h*, ring of angle iron, riveted to the outer case, serving for the support of the shaft during the repairing of the lower part of the furnace; *i i*, blast main of cast iron; *k*, ring of iron supported by the four cast-iron pillars *l l*; *m*, cast-iron cylinder, flanged at the top and inserted into the mouth of the furnace, in order that the fume and waste gases may be drawn off by the pipe *n*; *o*, charging floor; *q*, outer iron casing of the furnace. The water-jackets are composed of wrought-iron plates ⅓ of an inch in thickness, and are riveted to angle iron 2⅜ inches by ⅜ inch; *s s* are side plates overlapping by 2¾ inches top and bottom; *t*, pipes for supplying cold water; and *u*, pipe for the outflow of cold water; *v*, twyers, which are 2¾ inches diameter.

The following are four examples of the '*lit de fusion*' for such a blast-furnace, in tons of 1000 kilogs.:—

—	*a*	*b*	*c*	*d*
Roasted minerals . .	40·0	40·0	40·0	35·0
Foreign minerals (crude) .	1·20	0·6	0·6	0·6
Jewellers' sweepings . .	0·8	0·5	1·0	1·0
Residues from the manufacture of arsenic products (roasted)	6·00	6·00	6·00	7·00
Slags	27·5	25·0	27·5	27·5
Matte after a second roasting	1·00	1·00	1·00	1·00
Unroasted matte . .	0·75	0·75	0·75	0·75
	77·25	73·85	76·85	72·85

The products consist of a work-lead, a matte, occasionally a speiss, slags, and fume. The yield of work-lead from each of the above charges was the following :

a.	6 tons	450 kilogs.
b.	7 ,,	760 ,,
c.	7 ,,	940 ,,
d.	5 ,,	850 ,,

The lead contains many metallic impurities —*e.g.* copper, arsenic, antimony, bismuth, tin, iron, and sometimes cobalt and nickel ; the proportion of silver present is very variable, and dependent upon the proportion of foreign rich minerals used in the charge. If above a certain percentage of cobalt and nickel are present in

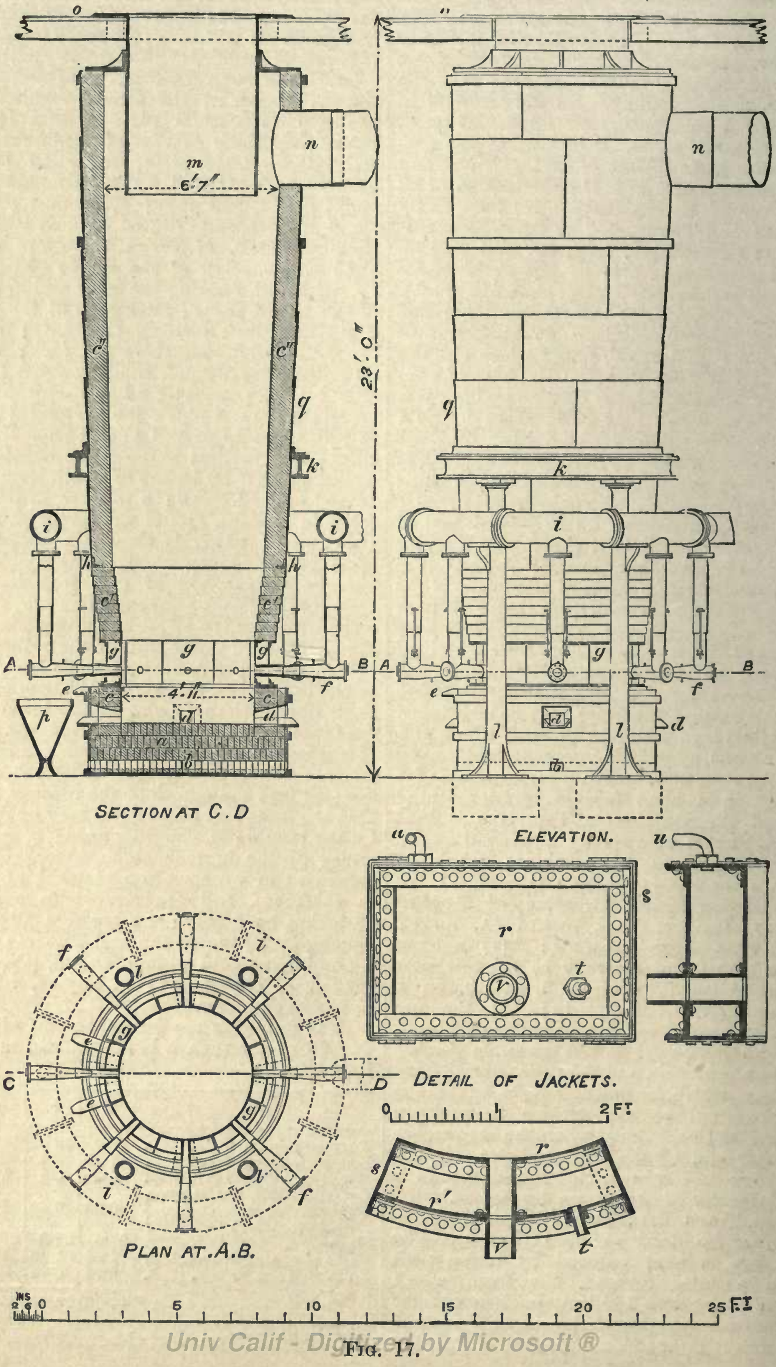


FIG. 17.

the materials smelted, a speiss is produced containing lead, copper, cobalt, nickel, and also silver. The average amount of matte produced from the above charges would be 1 ton 900 kilogs., and would contain from 15 to 20 p.c. of lead and from 10 to 12 p.c. of copper.

The slags produced consist chiefly of protosilicates, and are highly ferruginous. They contain 4–5 p.c. of lead, and, on an average, from 10 to 20 grammes of silver per 100 kilogs., in consequence of which they are in part returned to the blast-furnace and in part used in the subsequent smelting of the matte.

The amount of coke consumed is about 190 kilogs. per ton of roasted ore smelted.

The matte produced in the blast-furnace is first roasted in kilns and then in stalls, and the roasted matte is smelted in a blast-furnace similar to that used in smelting the ores, producing in this way a further quantity of lead, a second matte, and slag. The following is an example of the '*lit de fusion*' for first matte smelting:

	Tons
Slags from ore smelting . .	37·5
Matte (after three roastings) .	6·0
Matte (crude)	0·6
Foreign copper ores . . .	1·8
Slags from previous smelting .	2·5
'Abzug' from liquating furnace	1·6
Cupel bottoms	1·2
Drosses	1·5
	52·7

The amount of lead produced from these quantities was 3 tons 65 kilogs.; this lead is very impure, and contains on an average 400–500 grams of silver per 100 kilogs. The matte called second matte will contain 10–12 p.c. of lead, 12–15 p.c. of copper, and 140–150 grams of silver per 100 kilogs. The slags are usually thrown away; they may contain from 0·5 to 1 p.c. of lead, and 1–2 grams of silver per 100 kilogs. These slags are occasionally used for building purposes. The coke consumed is 116 kilogs. per ton of matte, &c.

This second matte, obtained in the operation described above, is treated in exactly the same manner as matte No. 1, and a further amount of work-lead rich in silver is obtained, which is submitted to liquation, and a third matte containing from 20 to 25 p.c. of copper, which is subsequently treated for the extraction of copper.

The different leads produced in the smelting of ore and of the mattes are very impure, containing about 5 p.c. of total impurities, amongst which are arsenic, antimony, tin, iron, zinc, bismuth, copper—at times cobalt and nickel. The purification and desilverising of the work-lead will be described subsequently.

At Leadville, in Colorado, lead ores are smelted in blast furnaces of the Raschette type, provided with water-jackets and also with a siphon tap which has been introduced into blast furnaces in this country and on the Continent. The siphon tap is a contrivance consisting of an oblique channel penetrating the bottom of the hearth of the furnace, by which the lead rises into a basin placed outside the furnace, and from which as it accumulates the lead is ladled out into moulds. The ores smelted at Leadville are locally styled *sand carbonates* and *hard carbonates*. The former consist of lead carbonate containing silver chloride, whilst the latter are a porous silicious material containing lead carbonate and silver chloride associated with hydrated oxides of iron and manganese. In some cases the ores contain considerable quantities of argentiferous galena, which is frequently covered with a coating of lead carbonate. The chief foreign ingredients, which are but few, are clay, limonite, and silica. Pyromorphite and anglesite are found in small quantities, as are also oxidised compounds of copper, arsenic, and antimony. In some mines bismuth and vanadium ores are found, and silver is found combined with iodine and bromine in addition to chlorine. The fuel used in smelting these ores is coke and charcoal; limestone, hæmatite and limonite are employed as fluxes, but in many cases the ores contain sufficient admixture of iron compounds to enable them to be treated directly in the blast furnace. The pig lead obtained, which is known as *base-bullion*, carries from 100 to 250 oz. of silver per 200 lbs, and from 0·25 to 0·14 oz. of gold; this is treated for silver and gold in the Eastern States. Each unit of lead produced requires the expenditure of 1½ units of fuel.

SMELTING ON SHALLOW HEARTHS.

The furnace known as the 'ore hearth,' or 'Scotch hearth,' is the one chiefly used in smelting galena in the northern counties. It varies considerably in dimensions and in external form at different works, but consists essentially of a shallow rectangular hearth built of cast iron, set in brickwork or stone. Fig. 18 is a vertical section of the 'ore hearth,' A the hearth bottom, 22 inches square, the iron plate being about 3 inches thick; the sides are also composed of iron of the same thickness, and the depth of the hearth will be about 4½–6 inches. In front of the hearth is the work-stone B, sloping from the front edge of the hearth to the metal pot C, in which the lead is maintained in a molten state by a fire below. The work-stone is about 3 feet long, 18 inches broad, and 2½ inches thick; it has a raised border of about an inch high on its two sides and along the front, and a narrow channel 2 inches wide and 1 inch deep runs diagonally across it. The work-stone is embedded in fireclay or a mixture of slime, ore, and bone-ash. At the back of the hearth is a prism of iron, called the back-stone, D, upon which rests the bellows-pipe, and above it is another prism E, called the pipe-stone, with an opening below to receive the bellows-pipe. The blast-pipe enters at a height of some 6½ inches above the level of the upper end of the work-stone, and when in work will be about 4 inches above the

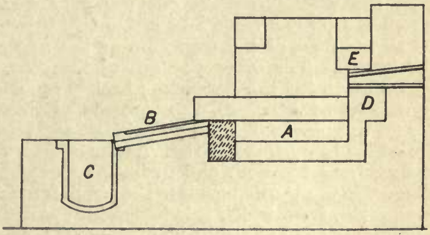


FIG. 18.

level of the metal in the bed. The hearth is covered by a hood of brickwork, opening at the back into a flue leading to the fume condensing chambers. Behind the hearth is a blind flue or pit into which 'hearth-ends' and other matter coming off with the fume may fall and collect, and from which it is removed as required. At the side of the hood is an opening in the brickwork communicating with the hearth, through which the ore and fuel are charged. The opening in front can be regulated by a movable iron plate, which in some cases is in the form of a sliding shutter, and by means of a counterpoise can be raised or lowered in its groove so as to nearly close in the front of the hearth.

The fuel used is either coal or peat, now more usually coal, and the blast is supplied by a Roots blower, and the ore may be either added in the raw state, or, as is more usual, after it has been roasted in a reverberatory furnace. The working of this hearth requires the constant attention of two men, and at the end of each shift the bottom should be nearly filled with lead, which in the molten state forms the bottom on which the charge rests. The mass of agglomerated ore, slag, and coke left at the end of each shift is called the 'browse.' In working, a fire of coal is made on the hearth, and then a moderate blast turned on. Ore is next thrown on, and when the hearth is provided with a shutter, this is closed down. After the lapse of a few minutes, the charge is stirred by a poker and fresh ore and fuel added from time to time. At intervals the shutter is raised and a portion of the charge drawn on to the work-stone, and then the workman picks out the grey slags, which are pushed aside and ultimately thrown on to the floor of the workshop at the side of the hearth. The other portions of the charge drawn on to the work-stone are broken up, and returned to the hearth, the contents of which are set up so as to distribute the blast, and fresh ore added in small quantities. As the lead forms it flows into the well, and overflows along the channel in the work-stone into the pot in front of the hearth, from which it is ladled into moulds. Towards the end of a shift no fresh ore is added, but the 'browse' is thoroughly worked up alone, and when the blast is stopped, the grey slags are separated from it, and a portion of the lead from the metal pot ladled back into the well in the hearth so as to fill it for the next shift. The process is essentially an air reduction process; the object being to oxidise the ore and then by subsequent admixture with ore to bring about the reactions between the unaltered sulphide and the oxy compounds resulting in the formation of lead. Formerly, as has been already stated, the ore was treated in the raw state, but is now more generally submitted to a calcination, by which a portion of the sulphur is removed and the slimes agglutinated, thus enabling them to resist the force of the blast and reduce the amount passing away in the form of 'hearth-ends' and fume. The influence of this previous calcination in reducing the fume and loss, &c., is shown by the following results obtained by the late Mr. Norman Cookson, in smelting 400 tons of ore, yielding on assay 81 p.c. of lead, one half of which was smelted raw and the other half after roasting (*v.* Local Government Report, 1878-9. Supplement containing the Report of the Medical Officer, 1878, 289).

	200 tons roasted	200 tons raw
Lead, first fire . .	73·10	60·80
Lead in grey slags .	2·50	1·80
Lead in fume, hearth-ends, loss, &c. .	5·40	18·40
	81·00	81·00

The American hearth, first introduced at Rossie, New York, is similar in construction and working to the Scotch hearth, from which it differs in having the two sides and back formed into an air chest, through which the air passes, from which it is conveyed by a pipe to a twyer at the back of the hearth. In this way the back and sides of the hearth are kept cool and a hot blast supplied, the latter has not, however, proved an advantage; the loss by volatilisation was found to be greatly increased, a fact which led to the replacement of this form of hearth by what is known as the American water-back ore hearth. The water-back ore hearth resembles the Scotch hearth, but has the three sides of the furnace formed into a water-cooled, cast-iron jacket. For the details of the construction of this and also of the Moffet ore-hearth, the reader is referred to Hofman's Metallurgy of Lead.

Slag hearth.—The various rich slags obtained by smelting in reverberatory furnaces, or in the ore-hearth, are usually smelted in a special blast furnace, known as the slag-hearth. In some establishments the Castilian blast furnace with three twyers is used, whilst in others furnaces similar in type to the Pilz furnace, and provided with water-jackets, are employed.

The ordinary slag-hearth is furnished with one twyer, and has the form of a deep hearth or shallow rectangular furnace. It is built of fire-brick and cast iron, incased in common brickwork, leaving an opening in front. The outer casing is prolonged, forming a shaft which is connected with the flues for condensation of fume, &c. The bottom is formed of a plate of cast iron, styled the *bed-plate*, and laid with a slight inclination forwards; on the bed-plate are placed two cast-iron *bearers*, which carry the side walls of the furnace. In front is a plate of iron, the fire-stone, placed so as to leave an interval of 7 inches between its lower edge and the bed-plate; the back of the furnace below the twyer is formed of another plate of iron. In front of the bed-plate is a cast-iron trough, the lead trough, which is usually divided into two unequal parts by a partition forming a part of the casting. The larger of these divisions corresponds in width with that of the bed-plate, and at the bottom of the partition is a hole through which the molten metal flows into the smaller division of the trough. The slags flow from an opening in the stopping of the breast into the larger division of the lead pan, and flow over from this into a pit sunk in the ground, through which a current of water flows. The outer brickwork surrounding the hearth is supported by iron plates braced together with tie-rods, the twyer passing through the plate which supports the back stone on which the nozzle rests. The outer brickwork is built so as to leave an opening in front of the hearth, and there is also an opening at one side for charging the furnace. The bed-plate is covered to within an inch of the twyer with coarsely sifted coal cinders, thus forming a bottom which slopes with the bed-plate towards the lower edge of the firestone. The space in front of the ash bottom, between the bearers and firestone, is plastered up with clay. The ash bottom serves as a filter to separate the slag from the lead, which percolates through to the bed-plate and then flows through openings in the clay stopping into the lead trough. This also is filled with cinders, through which the lead passes and finds its way to the bottom and through the partition into the smaller division of the trough, whilst the slag flows over into the slag pit, the sudden cooling of which by the water determines its disintegration, and renders easy the separation of any inclosed particles of metal. The fuel employed is coke and peat, and in commencing to work with this furnace, after making the bed of cinders as described, peat is piled up above the bed and ignited, then the blast turned on. When the peat is burning, coke is thrown into the furnace and a layer of grey slags added. This is continued as the operation proceeds, alternate charges of fuel and slag being added; lead is produced and a slag 'black slag,' free or nearly free from lead. Occasionally a bar of iron is thrust through the layer of cinders to liberate the slags and lead. The lead obtained from ore-slags is not as pure as that obtained at the first smelting; it is whiter and much harder, and is afterwards submitted to the calcining process to soften it. In some cases iron slags are added with the fuel and grey slags; especially when the grey slags contain much lime is this addition useful, the formation of an easily fusible slag being in this way promoted.

SOFTENING AND DESILVERISING.

The lead obtained by smelting may contain, in addition to silver, antimony or copper and other oxidisable metals, which may be present in quantities sufficient to interfere with the desilverising process; the metal is, therefore, when necessary, submitted to an operation known as *improving* or *softening*.

The *improving* or *softening* is effected in a reverberatory furnace, the bottom of which consists usually of a cast-iron pan, about 2 inches in thickness, length about 10 feet, width 5 feet 6 inches, and 10 inches in depth. All the angles of the casting are carefully rounded to prevent breakage by expansion or contraction, and the softened lead is drawn off by a hole bored in the bottom, near the outer edge, which is stopped by a well-fitting iron plug held in its place by a weighted lever. Such furnaces are usually made to hold from 8 to 12 tons of molten lead.

The fireplace is about 20 inches wide, and has a length equal to the width of the cast-iron pan, from which it is separated by a bridge 2 feet wide. The height of the furnace above the pan at the bridge end is 16 inches, and at the other end it is 8 inches.

The charge is introduced either in the form of pigs or is first melted in an iron pot set in brickwork at the side of the furnace, and subsequently ladled into a sheet-iron gutter, by which it is conveyed to the furnace. A softening furnace has been constructed with the iron pot for melting the hard lead, built above the calcining furnace, and so arranged that the heat required for the fusion is supplied by the furnace fire. The molten lead is run into the calcining pan by raising a plug at the bottom of the pot, the opening in which is immediately above the pan and a little to one side of the fire-bridge.

In this furnace the molten lead is submitted to the action of heated air, whereby the easily oxidisable impurities are converted into oxides, which, floating on the surface of the bath, are removed by an iron rake; in this way a fresh surface is constantly exposed to the action of the heated gases, and thus the greater portion of the impurity is removed. The progress of the operation is judged by taking a sample in a ladle and casting it in an iron mould; when the calcination has been completed the surface will present a peculiar flaky crystalline appearance. The calcined or softened lead is then tapped into an iron pot, from which it is ladled into the pig moulds, or is run from the furnace by a movable iron gutter into a series of pig moulds placed in readiness in front of the furnace.

In some districts hard lead is improved in a furnace with a slag bottom, which allows the operation to be conducted at a much higher temperature, and more rapidly than in iron pans. In Germany a marl bottom is used, whilst in some establishments these furnace bottoms are constructed of wrought-iron plates in form of a long shallow rectangular pan, the sides and bottom of which are lined with firebrick. Furnaces of this construction are made to hold as much as 70 tons of molten lead.

The calcined dross removed from the lead is reduced with coal, and the slag produced reduced in the slag hearth or in a cupola. In this way a very hard lead is obtained, which is again calcined, and the drosses formed yield on reduction a lead sufficiently rich in antimony to be sold to typefounders.

Leads containing a considerable proportion of copper are submitted to liquation before softening. The liquation is effected by heating the pigs of lead in a reverberatory furnace, the bed of which slopes from the fire-bridge and terminates in a sump or lead-pot at the flue end. The pigs are piled up at the upper end of the furnace-bed and subjected to a low heat; the lead first melts and flows down into the pot, whence, after skimming, it is ladled into moulds. The more refractory dross containing the copper, nickel, and a portion of the arsenic, and also sulphur, is left behind.

SILVER CONCENTRATION—DESILVERISING AND LEAD REFINING.

Concentration of silver in lead.—Before separating the silver from the 'improved' or softened lead it is submitted to a process having for its object a concentration of the silver to an extent sufficient to render its extraction economical. The silver concentration or enriching of the lead is performed by the Pattinson, the Rozan, or the Parkes' process. The first two of these processes are alike in principle, and are founded on the observation made by the late Hugh Lee Pattinson, of Newcastle-upon-Tyne, that when lead containing silver is melted and the molten mass allowed to cool slowly, at the same time being constantly stirred, then, at a temperature near the melting-point of lead, crystals begin to separate out. The crystals so produced are found to contain a smaller proportion of silver than the original lead, whilst the liquid alloy from which the crystals have been separated is proportionately richer in silver. This discovery was made the basis of a patent by Hugh Lee Pattinson, for 'An improved method of separating silver from lead,' the date of the patent being October 28, 1833, and at the meeting of the British Association held at Newcastle-upon-Tyne in 1838 the process was described in a paper by Mr. Pattinson. The introduction of this method of enriching lead has made it possible to extract the silver even when it is present in amounts so small as from 2 to 3 oz. to the ton, the desilverised lead retaining from $\frac{1}{2}$ to $\frac{3}{4}$ oz. of silver per ton. With present prices it would not, however, prove remunerative to Pattinsonise lead containing less than 4 oz. of silver per ton.

Pattinsonising, Pattinsonage, Pattinsoniren. The operation is conducted in large cast-iron hemispherical pans, capable of holding 6–10 tons of molten lead. The small 6-ton pots are now rarely used, and in some establishments pots capable of holding 18 tons of lead are employed, the larger size requiring the use of cranes in working the ladles. A series of nine to twelve of these pots is placed side by side in a line and resting on brickwork supports. Each pot is provided with a separate fireplace, the heated gases from which are conducted round the pan by a circular flue and thence pass into a flue running the whole length of the pots by which the gases are conveyed to the chimney. In addition to the large pots, there are sometimes smaller pots placed at the side between the larger pots, and heated by a separate fire; these serve to hold some melted lead for the purpose of heating and cleaning the ladles. Along both sides of the erection in which the pots are built is a platform on which the workmen stand. The pot at one end of the series is smaller than the others, being about two-thirds the capacity, this is called the *market pot*, which receives the poor lead and from which the lead is run into the pig moulds. The other apparatus used in this process consists of perforated ladles made of iron $\frac{1}{2}$ inch in thickness; when worked by hand the ladle would measure 16 inches in diameter and 5 inches deep, the holes being $\frac{1}{2}$ inch in diameter, whilst when cranes are used the ladle would measure some 20 inches in diameter, 6 inches in depth, and the holes would be $\frac{3}{4}$ of an inch. The handle of the ladle is some 9 feet 6 inches long, and $\frac{1}{2}$ an inch in thickness. In addition to the ladle, a chisel-pointed bar or *slice* is used in stirring the lead.

Fig. 19 shows the arrangement and mode of setting a range of pots.

The method of working will be best understood by supposing the lead to be treated contains some 20 oz. of silver to the ton; the metal in the form of pigs would be charged into one of the pots about midway between the *market pot* and the *rich pot*, the fire is set on and the lead melted; by the melting the surface of

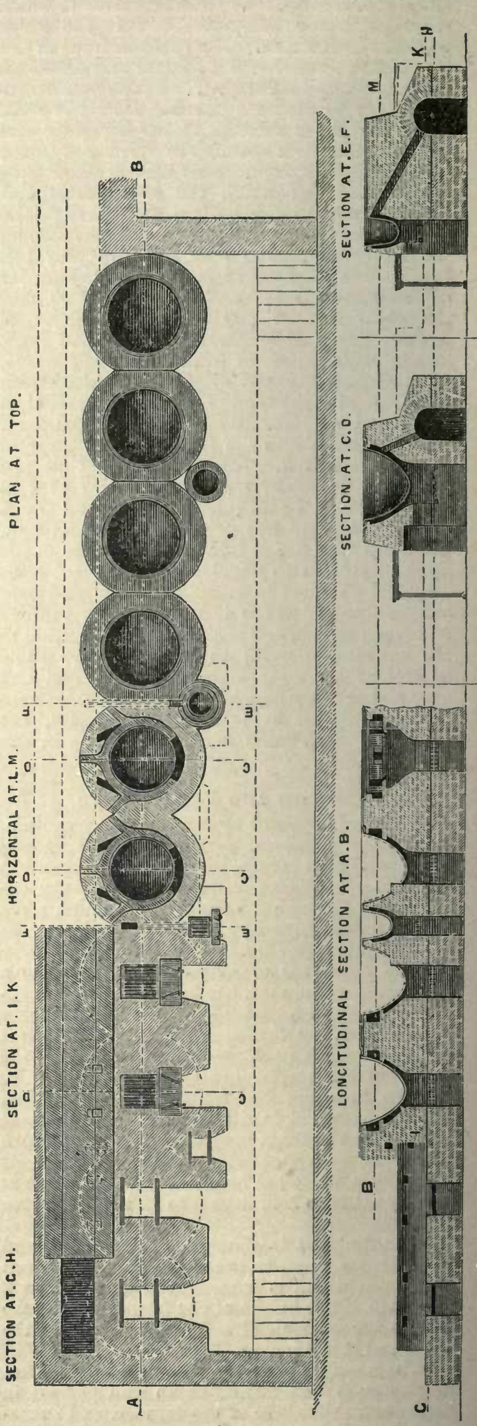


FIG. 19.

the metal is covered with a layer of dross, which is carefully removed by a ladle and the fire withdrawn. Water is sprinkled on the surface of the molten bath to promote cooling, and as the metal cools a cake is formed on the surface, which is detached and broken up by means of the slice, and the pieces stirred into the liquid. As the cooling proceeds the mass is kept continually stirred, and after a time crystals begin to make their appearance. The crystals are now removed by means of the large perforated ladle, which is plunged into the liquid and then gradually raised, the side of the pot serving as a fulcrum; the ladle is raised until it is completely out of the bath and is brought into a tilted position, and while in this position the crystals are allowed to drain. When drained the contents of the ladle are transferred to the next pot on the left, supposing the market pot to be at the left extremity of the range. This operation is repeated until two-thirds of the original charge has been transferred in this way. The remaining third, which represents the rich alloy, would be transferred to the next pot on the right —*i.e* toward the *rich pot*. The rich bottoms, as they are called, will contain 40 oz. of silver to the ton, and any lead that may be on hand having a similar silver content would be added to the enriched bottoms. The poorer lead from this single operation would contain about 11 oz. and similarly any lead to hand of this assay would be added to the metal obtained by this operation. A second charge would be next introduced into the pot in which the first operation was conducted and would yield further quantities of poorer lead and enriched bottoms, the former transferred to the left and the latter to the next pot on the right. The poorer lead would be similarly treated, and from it a further quantity of still poorer lead would be produced, which is passed on to the next pot to the right and so on until the lead which reaches the market pot will contain some 10 dwts. of silver per ton; the enriched lead gradually meanwhile making its way to the *rich pot*, but in the richer pots the separation is less complete than in the poorer ones, and the enrichment is not so rapid. In working the last pot, after two-thirds of the metal in form of crystals have been transferred, the enriched bottoms will consist of crystallised and liquid alloy, and the latter is separated from the former by pressing the mass with the back of the ladle, the fluid portion, the richer in silver, runs through the holes in the ladle and is removed by an ordinary ladle. Working in this manner a market lead is obtained at one end of the range in which the silver is reduced to the amount already stated, and at the other end of the range is produced lead containing from 600 to 700 oz. of silver to the ton, beyond which it is not possible to push the concentration by this method.

In the above description it has been assumed that the method of thirds or the high system was employed. This is the method most usually adopted in practice, but for special purposes the low system or method of eighths is sometimes used, in which seven-eighths of the contents of the pots are transferred to the poorer pot. In some works the method of seven-eighths is used for 'riching up' rich leads to the refinery grade of about 600 oz. In the seven-eighths system the lead should treble itself in assay in each operation, but this is seldom the case. In the two-thirds system each operation is supposed to result in the doubling of the silver content of the lead, but in practice this only obtains with leads ranging downwards from about 50-60 oz. of silver per ton.

As at each melting of the lead the metal is oxidised and a layer of dross formed on the surface, the bath is carefully skimmed after each melting and the drosses collected for future reduction. With a 20 oz. lead, the amount of drosses formed is 25 p.c. of the weight of the metal. The continual drossing of the metal naturally effects a purification of the lead, as the dross produced consists not only of lead oxide, but also of the oxides of the more easily oxidisable metals present. The value of the Pattinson process as a means of not only enriching the lead, but also of purifying it, is shown by the fact that lead to be used for white-lead making is frequently Pattinsonised, although the amount of silver present may be very small. Further, copper and iron are both separated with the silver in this process when the amount of copper does not much exceed 0·025 p.c.

The Rozan process or Pattinsonising by steam.—This process of crystallising by steam was first introduced in the works of Luce and Rozan at Marseilles, and has been described by Rozan in the Berg- und Hüttenmännische Zeitung for 1874, and also by Norman C. Cookson in a paper published in the Transactions of the Newcastle Chemical Society for 1878. In this system steam under pressure is forced into molten lead, and by the continual agitation of the mass produced in this manner the production of crystals poor in silver is favoured, and the separation of an enriched fluid lead facilitated. Cookson, in the paper referred to, is inclined to the opinion that the steam serves a second purpose, producing a chemical effect and aiding in the oxidation of the antimony, copper, iron, and arsenic, and other oxidisable metals present. This oxidation may be due to the air carried into the pot by the steam. In any case leads such as rich Spanish leads containing as much as from a $\frac{1}{2}$ to $\frac{3}{4}$ p.c. of foreign metals may be treated by this system without having been previously calcined or softened. The following is the description of the plant and mode of working taken from the paper already referred to:—

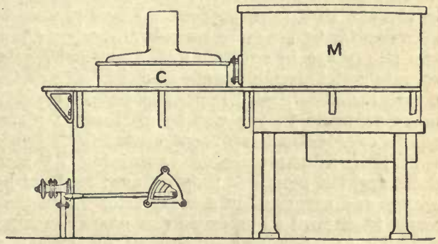


FIG. 20.

'The pot marked M (Fig. 20) is simply a melting-pot, and the lower pot C is the working, or, as it is commonly called, the crystallising pot. To illustrate the working, we will suppose the C pot contains 14 tons lead crystals from a previous operation, assaying, say, 80 oz. of silver per ton, and the M pot 7 tons original lead of similar silver content already melted; a moderate fire is set away in the firegrate of the C pot, and the contents of the M pot are skimmed of their dross; the hot lead from the pot M is then run on to the warm crystals in the C pot, and, with the assistance of the moderate fire already referred to, the whole contents of this pot (now 21 tons) are rapidly brought into a melted and working condition, when the charge is carefully skimmed; the M pot is at the same time charged with 7 tons of lead containing about 40 oz. silver per ton of lead, as this will be the assay of the crystals resulting from the operation shortly about to commence in the C pot. The fire under this pot is next drawn, and a small fire under each of the tapping spouts is set away, the object of this being to prevent the lead setting in them when tapping out the rich lead later on. Steam at 50-55 lbs. per square inch is next admitted through the valve V, and is distributed evenly through the pot by the baffle plate *b* (Fig. 21). To hasten the cooling and consequent crystallisation, thin streams of water are allowed to run on to the surface of the lead. This might be thought to cause the lead to set on the top, but the violent action of the steam entirely prevents this, and the crystals as formed and the liquid lead are uniformly distributed through the pot, and a more perfect crystallisation is effected than can be obtained in the old Pattinson process. When the workman sees that the charge is ready, *i.e.* when about two-thirds are in crystals and one-third liquid, he taps out through spouts at either side of the C pot the rich liquid lead, the poorer crystals being retained in the pot by perforated plates which effectually keep them back. This liquid lead is run into moulds containing 3½ tons each, and the blocks as they set are lifted out by cranes and arranged in a semicircle, where they await their turn to be again and again operated on. This process of crystallising, as in that of Pattinson, is repeated until the crystals are sufficiently poor in silver not to require further treatment, when, being fit for market lead, they are melted and run into pigs of the usual size, or into 3½-ton blocks, according to the purpose for which we require them. As regards the rich lead, it is worked up until its silver contents are of the standard fit for the refinery. A large portion of the foreign metals contained in the original lead is skimmed off in the state of oxides; and any one seeing these oxides for the first time will be struck by the fact that those from the operations in the richer charges will be very dark in colour, some in fact almost black, this being due to the impurities contained, while as they come down in silver contents they have the yellowish colour proper to the oxides of lead. A large portion, however, is carried off up the funnel above the C pot, with the escaping steam, and is deposited in the condensing chambers, of which we have several of good size. These oxides are of various metals, that of lead being in the proportion of 80-85 p.c., the remainder consisting of the oxides of copper, antimony, arsenic, iron, &c., but principally of the two first named.'

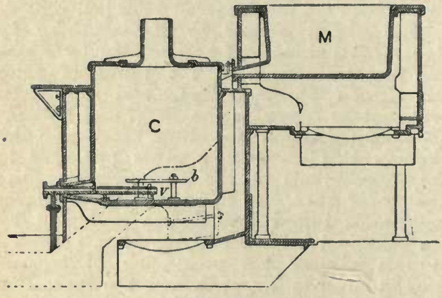


FIG. 21.

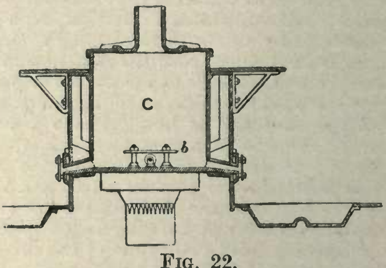


FIG. 22.

In the accompanying illustration of the plant used in the Rozan process, Fig. 23 is the plan of a battery, Fig. 20 is an elevation along the line S T, Fig. 21 a section along the line U V, and Fig. 22 a section along the line X Y.

The following table taken from Cookson's paper gives the silver assays of twelve crystallisations taken from an average of 350 operations:—

Ounces per ton of lead

570-315-202-112·5-62-33·75-19·5-10-5-2·5-1·25-14 dwts.

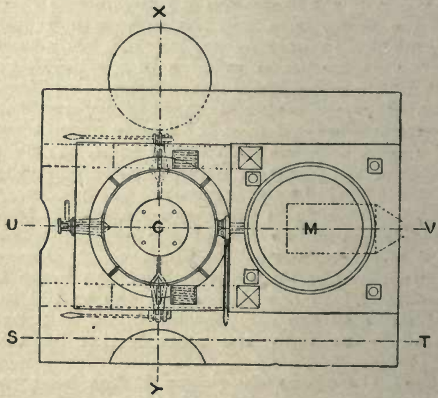


FIG. 23.

Mr. Cookson summarises the advantages of the Rozan system, as follows:—

'1. The entire saving of the cost of calcining all ordinarily hard leads, and in the case of extra hard leads, such as Greek lead, a very large saving.

'2. A cost for labour not exceeding one-fifth.

'3. A cost for fuel of about two-fifths.

'4. A saving of one-third in the oxides produced, which advantage any lead manufacturer will fully appreciate.

'Its defects are:

'1. A large capital outlay.

'2. A constant expense in repairs and renewals.'

The advantages of the system would appear to considerably outweigh the defects. The arrangement of the pots at different levels considerably reduces the labour of working a charge and at Messrs. Cookson & Co.'s establishment at Howden-on-Tyne, the working was still more simplified by having attached to each battery of Rozan pots a hydraulic crane, by which the blocks of lead, which are cast with an iron eye in circular moulds shown in section in Fig. 22, can be raised and lowered into the melting-pot or moved into any position at will. In fact, such is the perfection of the system of hydraulic cranes at this works that from the time the crude lead enters the work until it makes its exit as 'market lead' it is hardly ever touched by hand, but moved from place to place by cranes.

Parkes' system.—The method of desilverising lead by Parkes' process depends on the fact that when lead containing silver is melted with zinc, and the fluid mixture allowed to cool, the portion which first solidifies consists of a mixture of silver, lead, and zinc, and contains nearly the whole of the silver. Patents for this process were granted to Mr. Alexander Parkes, of Birmingham, in the years 1850, 1851, and 1852; and in 1859 the method was put in practice at Llanelly. It was subsequently tried at Tarnowitz, and, owing to the difficulties experienced in its working, finally abandoned at both places. The chief difficulties were (1) the removal of the zinc from the desilverised lead, which could not be performed sufficiently well to make the lead marketable; (2) the separation of the silver from the zinc alloy was attended by considerable loss; (3) the recovery of the zinc from the rich lead was somewhat difficult to accomplish.

The difficulties experienced in the use of this method have led to the proposal of several modifications of the original process, and the method as practised now at several establishments in this country, on the Continent, and in America, is comparatively simple, and is conducted as follows. At a height of some 8 or more feet from the floor level the several pots used in the process are set in brickwork, each being provided with a separate fireplace. The number of these pots will be determined by the quantity of lead to be treated. At one establishment visited by the writer the number of pots was five, two larger ones capable of containing 25 tons of lead, and three smaller ones each holding about 6 tons. The lead is charged into one of the larger pots and melted, and, when melted, a slab of zinc is laid in the bath and the temperature raised until the zinc melts. When this temperature has been reached, the remainder of the zinc to be added at this stage is thrown into the bath and the whole thoroughly well stirred. After stirring for a quarter of an hour the metal is allowed to cool, and, as soon as the crust of zinc alloy has become sufficiently solidified, it is removed by a perforated ladle, and the skimming continued until the lead begins to set. The skimmings are transferred to one of the smaller pots. The lead is again heated to the melting-point of zinc, and a further quantity of zinc thoroughly stirred into it, the cooling and skimming repeated as before, and the skimmings transferred to the smaller pot. After this second addition of zinc the entire operation is repeated with a third portion of zinc, and the pot subsequently carefully skimmed. The proportions of zinc used in the various additions will vary according to different practices. The following may be taken as representative of one method of working. The lead contained 550 oz. of silver; the total zinc required was 1130 lbs., which was distributed as follows: first addition 340 lbs. of zinc, for the second 340 lbs. also, and the remaining 450 lbs. were used in the last. The total amount of zinc used is determined by the richness of the lead, in accordance with the following table, which has been confirmed by experiments conducted at Clausthal:—

Lead containing	250	grams of silver, for 1000 kilos. required	1¼	p.c. of zinc.
,,	500	,, ,,	1⅓	,,
,,	1000	,, ,,	1½	,,
,,	1500	,, ,,	1⅔	,,
,,	3000	,, ,,	2	,,
,,	4000	,, ,,	2	,,

The desilverised lead left in the larger pot after skimming the third time is tapped or siphoned out, and run into an improving furnace placed at a lower level, where it is kept at a red heat for several hours and occasionally skimmed, the progress of the calcination being watched by withdrawing small samples, which are cast in a mould, and from the appearance presented on cooling the state of the lead is determined. When thoroughly calcined the lead is tapped into a cast-iron pot and then run into pig moulds.

For the recovery of the 0·7 p.c. of zinc retained by the desilverised lead Coda (D. R. P. 207104) proposes to add either an alloy of copper or copper-aluminium and lead, *e.g.* 5Cu : 94Pb, to the molten desilverised lead. This alloy has the property of taking up 10 p.c. of its weight of zinc and forms a crust, floating on the lead, which can be readily removed by skimming. From this crust the zinc is recovered by distillation.

The skimmings which accumulate in the smaller pots containing silver, lead, and zinc are gently heated to effect by liquation a separation of a portion of the lead and the argentiferous alloy which is separated from it by a perforated ladle. The liquated lead so obtained is added to the next charge of lead to be desilverised, whilst the solid alloy is next submitted to distillation, by which means the zinc is distilled off and obtained partly in a form in which it can be used over again, and partly in a pulverulent state consisting of zinc and zinc oxide. To this end the alloy is charged into a large fireclay crucible placed in a vertical furnace, heated by coke, and provided with a movable top, consisting of an iron framework with slabs of fireclay, and moved by a small crane. The mouth of the crucible is closed by a hemispherical cover provided with a tubulus for conveying the vapours of zinc to a vertical condenser, which stands on a vessel for receiving the condensed zinc. By this arrangement the crucible is converted into a retort in which the zinc-argentiferous alloy is distilled, the zinc volatilised, leaving behind the enriched lead, which is ladled out of the crucible. In this way some 40 p.c. of the zinc is collected in the metallic state and 20 p.c. in the form of dust mixed with oxide. Both are free from silver. The proportion of zinc recovered varies very much with the amount of zinc used, *i.e.* with the silver assay. Taking for an example the zinc used in the case cited above, 50–55 p.c. of this zinc would be recovered by distillation and a very little of it in the form of powder. Parkes's process, when worked as above described, is stated to cost considerably less than either of the other processes, and yields a market lead containing less silver.

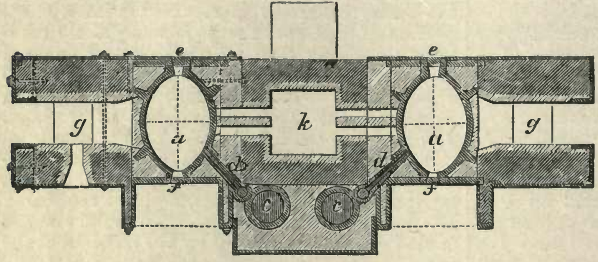


Fig. 24.

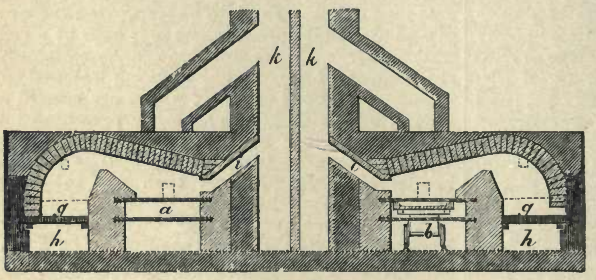


Fig. 25.

Cupellation or Refining.

The enriched lead obtained by either one or other of the above methods is next submitted to the process of cupellation or refining, in which the lead is oxidised and converted into litharge, and metallic silver obtained. In England the refining is performed in a reverberatory furnace, the bottom of which, called the test or cupel, is movable, and into this the lead is fed at intervals from a melting-pot containing the rich lead, and which is poured by a ladle into an iron gutter, serving to convey it to the test. In some cases the 'rich bars' are pushed down 'feed pipes,' so that they project into the furnace and are melted off as required. The oxidation of the lead is effected by means of a blast of air produced by a fan or other blower or by a steam injector. An English refinery in which two cupels can be worked at the same time is represented in Figs. 24 and 25.

a, a are the position of the tests, one of which is shown resting on the iron waggon, *b*; *c, c* the melting-pots for the rich lead; *d, d* the iron gutter to supply the test; *e, e* the point where the blast enters; *f, f* the opening along which the litharge flows into an iron pot placed below; *g, g* the fire-grates and *h, h* the ash-pits; *i, i* the flues, and *k, k* the chimneys.

The test or cupel is made of bone ash finely ground and prepared by moistening with a dilute solution of pearl ashes. This mixture is placed within an oval iron framework, consisting of an iron ring *a, a* (Fig. 26). This ring, known as the test ring, is held together by iron bars, *b, b*.

The mixture of bone ash and pearl ashes is beaten down thoroughly with iron rammers into this framework, and the centre of the mass scooped out by means of a small trowel, giving the test the form represented in the accompanying illustrations, thus forming a reservoir for the molten metals. It has been proposed to mould these tests by presses worked by hydraulic power. The test before use is allowed to dry in the air for some time and then placed on an iron waggon and run into position under the furnace; it is then wedged tightly against an iron ring built in the masonry. The fire is next lighted, and the test slowly and carefully heated, so as to thoroughly anneal it. When perfectly dry, the temperature is raised to a dull redness and the test is filled with rich lead. The lead is first covered by a greyish dross, which, as the heating continues and the temperature rises, gradually gives place to the formation of litharge. The blast is now turned on and the oxidation of the lead takes place, the litharge produced is blown by the blast to the mouth of the refinery and flows over the gate into an iron pot, placed below. These iron pots are built on wheels, and when filled with litharge are removed; the cake of litharge is easily detached after cooling, and is subsequently reduced, as will be described later on. As the oxidation proceeds, fresh lead is added to the test, and if a large stock of rich leads have to be treated, then the refining is only conducted sufficiently far to produce an enriched alloy, in

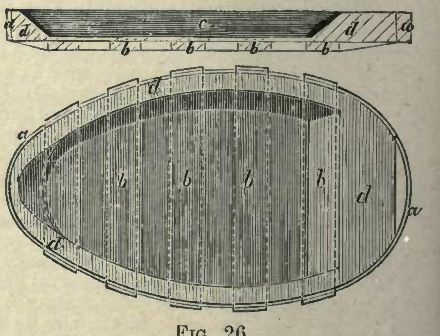


Fig. 26.

which the silver amounts to about 8 p.c. of the contents of the test. The concentrated argentiferous lead is tapped into an iron pot run on wheels, placed under the test bed, which is pierced by a drill. When the concentrated rich lead has been run off, the hole is made up with a pellet of bone ash kept in its place by an iron plate, and another charge is introduced. By this removal of the enriched lead, a distribution of silver through a large quantity of litharge is avoided. The concentrated rich lead is finally refined in another test. The end of the operation is indicated by the appearance of the surface, the brightening of the plate, as it is styled; the blast is then turned off and the fire removed from the grate. When the lead has been completely removed, the silver is usually tapped out into ingots direct, through a hole in the bottom of the test. In some cases the plate of silver is allowed to set, and when this has taken place the wedges are withdrawn and the test is lowered on to an iron waggon, on which it is removed and then allowed to cool. The plate, when solid, is detached from the test, and brushed with an iron brush to remove any litharge, slag, or bone ash.

In an ordinary refinery 4-5 cwt. of lead can be worked off in an hour, and the fuel required would be from 6 to 7 cwts. of coal per ton of lead oxidised. The plate of silver will vary in weight from 10,000 to 20,000 oz., and is usually pure, containing about 99·7-99·8 p.c. of silver. The test bottoms are saturated with litharge and contain some silver; they are usually broken up and those portions free from lead picked out to be used over again, whilst the remainder is smelted in a blast furnace. It has been proposed to extract the test bottoms with acetic acid, thus producing a solution of lead acetate and recovering the bone ash.

German Refinery.

In Germany the rich or enriched argentiferous lead is cupelled in a furnace known as the *Treibofen*, consisting of a reverberatory furnace with a circular hearth, and having a fireplace at one side. The bottom of this furnace is not movable, as in the English refinery, but composed of firebricks, on which lies a solid stratum of slag, and this again is covered by a coating of marl, well beaten down with iron rammers. The bottom is regularly hollowed out from the sides towards the middle, where a hollow is cut about an inch deep for the reception of the silver. The layer of marl is renewed for each operation. A dome of iron, plastered over with marl, covers the bed, and is moved as required by means of a crane. There are five openings into the side of the furnace, one serving to admit the flame from the fireplace, two smaller ones, near together, for the twyers by which the blast of air is forced on to the surface of the metal, and the litharge produced blown towards a fourth opening, by which it escapes in a fused state. The twyers are usually provided with valves, styled 'butterflies,' which serve to diffuse the blast over the surface of the metal. The fifth opening into the furnace is provided for the introduction of the lead. In working with unsoftened lead the charge for one operation would consist of about 5 tons of metal, some three-fourths of which would be introduced into the furnace before lighting up, the remainder being added from time to time as the cupellation proceeds. Much larger charges are treated when softened lead is used. The mode of working is as follows: the charge of lead, in form of pigs, is piled up in the middle of the hearth, and covered with wood, which is ignited by throwing on to it some burning charcoal. The iron dome is next let down and luted all round with clay. The blast is turned on and the fire in the grate made up. In the course of some 3 or 4 hours the lead has melted down and the bath is covered by a layer of dross, which is dark in colour and consists of a mixture of the oxides of the metallic impurities contained in the lead, and is called the *abzug*; it is raked out at the opening for the removal of the litharge. After the removal of the *abzug* the surface of the metal becomes clearer, and in a short time acquires a peculiar circular movement; the dross now rising to the surface is purer and more fluid than the *abzug*. This second product forms what is known as the *abstrich*, and is an impure litharge, which, as it is produced, flows through channels cut in the breast of the furnace. The temperature is kept sufficiently high to maintain the *abstrich* in a state of fluidity. The formation of *abstrich* is succeeded by the production of pure litharge, which flows out of the furnace through the channels already mentioned. After the litharge-stage has commenced, the remainder of the metal to be cupelled is added in small portions at a time; the pigs of lead being so placed that the lead gradually melts and leaves behind the more refractory *abzug* unmixed with the metal. The full charge of metal having been added, the operation is continued and the temperature maintained sufficiently high to keep the silver in a molten state until the greater portion of the lead has been oxidised and the bright metallic surface of the molten silver is observed. The blast is then turned off and the fire is damped down; water is also thrown on to the metal to harden it, and the cake of *blicksilber* is withdrawn from the furnace freed from marl, litharge, &c. The *blicksilber* contains from 90 to 95 p.c. of silver and is refined in small reverberatory furnaces, the beds of which are made of bone ash, or some material serving, like bone ash, for the absorption of the litharge formed by exposing the *blicksilber* at a temperature above the melting-point of silver to the oxidising action of the air.

The cupellation of a charge of 10-15 tons of lead lasts from 70 to 80 hours, and the loss of metal amounts to from 3 to 6 p.c.

Reduction of Litharge and Pot Dross.

The litharge produced in the cupellation of argentiferous lead, as also the various drosses formed in the Pattinson process, are reduced to the state of metal. The reduction is in this country usually performed in a reverberatory furnace, the sole of which slopes from the fire-bridge to a point near the flue, where an iron gutter, built in the furnace bed, serves to convey the molten lead to an iron receptacle outside the furnace. The reducing agent employed is coal. The sole of the furnace is prepared by covering it with small coal which is partially coked by the heat, and thus a porous covering is formed on the brickwork of the furnace bottom. On to this sole, so prepared, the litharge broken into lumps and mixed with coal is thrown, the ignition of the fuel and the reducing gases in the furnace soon effect a reduction of the litharge, and the molten lead trickling through the porous mass gradually finds its way into the metal gutter, by which it is conveyed to the metal pot. The charge is turned over from time to time, and when the reduction is completed the residue, termed *cinders*, is raked out. The litharge cinders are, together with other lead refuse, such as test bottoms, &c., treated in a cupola or slag-hearth, whereby a further quantity of lead is obtained from them.

In some establishments the litharge is reduced in blast furnaces similar to those employed in smelting ores; the fuel used is either coke or charcoal, and the litharge is mixed with slags from a previous reducing operation. The lead produced by reduction of the litharge is softened and desilverised when necessary, and inasmuch as the litharge produced towards the completion of the cupellation is richer in silver than that formed in the earlier stages, it is frequently reduced apart from the rest, and yields a lead containing from 70 to 100 oz. of silver per ton.

Refining lead by electrolysis.—A process, due to Keith, for refining lead by electrolysis, has been in use at New York for some years. The anodes of the electrolysing cells are made of the furnace lead, which is cast in thin plates about 4 feet long, and weighing 45 lbs.; these are inclosed in muslin bags, which serve to retain the gold and silver and other insoluble matters. The cathodes are plates of pure lead, and are placed about 2 inches from the anodes in a bath consisting of a solution of lead sulphate in sodium acetate. The bath is heated by steam to about 38°, and the electricity is supplied by a Weston dynamo, working at 1500 revolutions per minute. When the electric current is passed through such a series of cells the anodes are corroded and dissolved, an equivalent amount of lead being precipitated on the cathodes as a loose crystalline powder, which falls to the bottom of the cell, whilst the matters formed by the disintegration of the anodes are collected in the muslin bags. The action is continued until only 2 or 3 p.c. of the lead forming the anodes remains undissolved. In a series of 48 decomposing cells each containing 50 anodes, 10 tons of 180-oz. silver lead with 2¼ p.c. of antimony and arsenic, can be refined daily by a 12 horse-power steam engine. The precipitated lead contains 11 grains of silver per ton, and is compressed by hydraulic pressure before melting.

Amongst other electrolytic methods of refining lead that devised by Betts is of special interest. The electrolyte is a solution of lead fluosilicate, produced by dissolving the carbonate in aqueous hydrofluosilicic acid. The anodes, consisting of the lead to be refined, are cast in closed or in horizontal moulds; they are 1 inch in thickness and 3 feet long by 2 feet wide. The cathodes are formed of thin slabs of pure metal, cast by pouring molten lead on a sloping iron plate. The electrolyte liquor is contained in a series of vats, arranged in cascade; through these by aid of a pump a continuous circulation of the liquor is maintained. The vats are made of wood coated with asphalt, each vat taking from 22 to 28 anodes, and from 23 to 29 cathodes, separated from one another by a distance of about 1¾ inches. Electricity is conducted along the vats by means of copper bars, to which the anodes and cathodes are suitably attached. The electrolyte is maintained at a temperature of 30°–35°, at which temperature the resistance is 3·6 ohms. per cubic metre. The cathode deposit of pure lead is smooth, dense, and coherent, a condition largely contributed to by the addition of gelatin to the electrolyte, in the proportion of from 400 to 500 grams per 1000 kilogs. of lead deposited. The anode mud, which adheres to the anode, is scraped off, washed, and filtered in a press, from which it is discharged on to trays, and dried. The dried mud subsequently melted down in a reverberatory furnace yields an antimonial slag, a rich silver alloy containing bismuth, and may also give a copper matte containing silver.

The cost of treatment with a plant dealing with from 60 to 100 tons *per diem*, is given at four dollars per ton, and the loss of hydrofluosilicic acid as from 3 to 5 lbs. per 1000 lbs. of lead refined.

It is stated that electrolytically refined lead contains more silver than that refined by Parkes' process, but is free from bismuth (Hofman, Mineral Industry, 1909, 504; *see* also Betts, Lead Refining by Electrolysis, J. Wiley & Sons, 1908).

Condensation of Lead Fume.

In consequence of the volatility of lead at high temperatures a certain proportion of the metal and some of its compounds are carried away by the heated gases in the operations of smelting, refining, reducing, &c. To prevent the loss and minimise the nuisance which would arise from allowing the gases produced in these various operations to pass direct into the chimney, the furnaces are connected with a series of flues or condensing chambers in which the gases are cooled and so deposit some of the solid matter held in suspension, before they issue from the chimney. These flues are cleaned out at stated intervals, and the 'fume' collected. The lead exists in the 'fume' chiefly in the form of sulphate and oxide, and is recovered by roasting and smelting it alone or mixed with ores and slags. A certain proportion of silver is always found in fume lead, the amount being considerably less than that obtained directly from the ores from which it was produced.

The method of fume condensation most usually relied on, and the one stated to be the most efficient, is simply to connect up the various smelting and other furnaces in a works with a series of long flues of large transverse area. In some establishments the flues used for this purpose have an aggregate length varying from 3 to 5 miles, and a cross section of from 6 feet by 7 feet to 8 feet by 9 feet. Jets of steam and water have in some cases been introduced at different points in the flues with the object of facilitating the fume deposition; but lead smelters differ in opinion as to the advantages gained by the use of either steam or water. Various devices have been proposed to effect a condensation of lead fume without the necessity of constructing long flues or large condensing chambers.

Stagg's condenser consists of a large rectangular chamber divided by partitions springing alternately from the top and bottom of this chamber, leaving free spaces above and below; the lower part of the chamber is filled with water, so that the gases pass first down one side of a partition through the water, and rising in the next compartment pass over the next partition and down again through the water. The gases are drawn through the chamber by means of air-pumps attached to the exit flue. The fume is in its passage through the condenser thus drawn through water, and the greater portion of the solid particles is removed, the solid matter collecting in the water is drawn off from time to time into tanks where the fume subsides.

In Stokoe's method of condensing, the gases are drawn off from a flue by means of a fan and are then forced into the condenser, which consists of two chambers placed side by side; these chambers are divided into several compartments by partitions which alternately reach the top and dip below the surface of water at the bottom of the chamber. The chamber is divided horizontally by two floors made of open joists upon which faggots are laid, thus forming filtering beds, which are washed by water in the form of fine spray falling from a cistern on the top of the condenser. The gases extracted from the flue by the fan are forced through the series of compartments of the condenser and meet in their passage with the fine spray of water, and must also pass through the several filtering beds, where the fume as it collects is washed away by the water which accumulates in the lower part of the chamber. When the water has reached a certain height it is drawn off into tanks, and here the solid matter collected by the water gradually separates out.

In 1878 Messrs. Wilson and French patented a condenser, which has been adopted at the Sheffield Smelting Company's works, and was also used by Messrs. Bewick and Partners, Limited, of Hebburn-on-Tyne. At Messrs. Bewick's works the gases from the ore-hearths and slag-hearths and reverberatory furnaces passed first into a long flue, which ascended the ballast hill at the back of the works, and after making a circuit round the top of the hill, the gases were drawn off from the flue down a series of narrow flues to the condensers. In this way the gases are thoroughly cooled before they reach the condenser, and a certain portion of their solid burden will have been deposited in the flues, which were cleaned out from time to time; the remainder is obtained in the condenser. The condenser consisted of a wooden box *aa*, Fig. 27, having a shelving bottom where the solid matter arrested collects, and at the lowest point a tap *b*, by which the contents of the condenser are run off from time to time. The box is filled with water to the level of *c*. The gases are forced into the box by a fan, along the pipe *h*, which opens into a chamber *g*, formed by a partition running parallel with the side of the box. Below, this chamber opens into a series of triangular tubes *i*, running across the box; these tubes are perforated above, and through these fine openings the gases are forced into the water by which the box is partially filled. Near the surface of the water at *d* is fixed a series of three or four copper wire screens, or screens made of wickerwork, and held in position by the supports *e* and *f*. The gases pass out finally by the pipe *j* in the top of the box, and are conducted by flues to the chimney. By this arrangement the gases are forced through a layer of water of a given depth, and further intimate contact between the water and the particles of the fume, &c., is insured by the wickerwork or copper wire screens. The fume, &c., arrested by the water collects in the lower part of the box, and is drawn off into settling tanks, and after removing the greater portion of the water, is dried and smelted. With three wire-gauze screens and a depth of 8½ inches of water, Mr. French states that at the Sheffield Smelting Company's works, the quantity of lead and silver arrested amounts to from 95 to 98 p.c. of that contained in the smoke as it leaves the furnace.

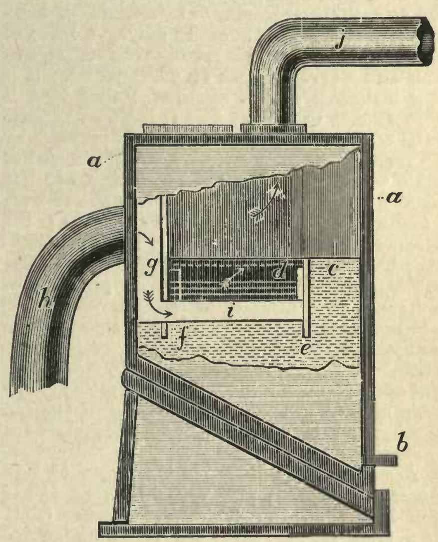


Fig. 27.

The application of electricity to fume condensation has been suggested by Sir O. Lodge, and its use patented by Walker. Experiments made with electricity at the Bagillt works of Messrs. Walker, Parker & Co., Limited, yielded satisfactory results when working on a small scale, but did not prove successful when applied to the flues of the works. One of the chief difficulties was the efficient insulation of the conductors.

Composition of lead fume.—The following analyses taken from Percy's Metallurgy of Lead (p. 451) will serve as examples of the composition of lead fume. The samples analysed were collected from the flues of the lead-smelting works at Bagillt, and represent the fume from reverberatory furnaces and slag hearths.

Lead oxide . .	46·54	62·26	46·88
Lead sulphide .	4·87	1·05	—
Ferric oxide and alumina . . .	4·16	3·00	10·00
Zinc oxide . .	1·60	1·60	4·14
Lime	6·07	3·77	6·73
Sulphuric anhydride .	26·51	25·78	14·15
Insoluble residue .	10·12	1·97	14·40
Carbonaceous matter	—	—	3·37
	99·87	99·43	99·67

PROPERTIES AND USES OF METALLIC LEAD.

Properties of lead.—Lead is a bluish-grey metal, the freshly cut surfaces exhibiting a distinct metallic lustre, which soon disappears owing to superficial oxidation. Its crystalline character is well shown by the beautiful fern-like crystalline growths which are seen on the pigs of best market lead, or as they form on the surface of a casting as the molten metal gradually cools. It can easily be obtained in the form of regular octahedrons by melting lead and allowing the molten metal to partially solidify, and pouring off the portion still remaining liquid. It is deposited in arborescent forms, known as the lead tree, by the decomposition of a solution of lead acetate either by zinc or by electricity. Lead is a very soft metal, is easily cut by a knife or scratched by the nail; it readily receives impressions and leaves a streak on white paper. It is very malleable and is ductile. Rolled lead is more ductile than cast lead; both its malleability and ductility are injuriously affected by the presence of impurities. Lead is a metal of feeble tenacity, a wire $\frac{1}{12}$th of an inch will not support a weight of 20 lbs. When struck with a hammer pure lead emits a dull sound; the presence of antimony, however, makes it sonorous, hard lead being easily distinguished from soft lead by this property. The presence of antimony, zinc, arsenic, or silver increases the hardness and brittleness of the metal. The hardness of lead is also increased by repeated meltings; this is stated to be due to the formation and dissolution by the molten metal of the oxide of lead formed by the action of the air. In practice it is found that the lead is improved by every melting.

According to Schweitzer the sp.gr. of lead (Amer. Chem. J. 7, 174) varies between 11·344 and 11·377 at 4°. St. Claire Deville (Phil. Mag. [iv.] 11, 144) gives the following as the results of his observations on lead prepared in different ways:—(1) cooled slowly from fusion, 11·254; (2) cooled quickly from fusion 11·363; (3) electrolytic lead, 11·542; (4) lead obtained by electrolysis, then fused and cooled quickly, 11·225. The influence of pressure on the sp.gr. of lead is shown in the following results obtained by Spring (Ber. 16, 2724). (1) Not pressed, 11·350 at 14°; (2) once pressed, 11·501 at 14°; (3) twice pressed, 11·492 at 16°. The sp.gr. of molten lead is given as 10·37 and 10·65 by Roberts-Austen and Wrightson (Ann. Chim. Phys. [v.] 30, 181), and 10·952 by Quincke (Pogg. Ann. 135, 642).

Lead begins to melt at 325° and is completely fused at 335°; its boiling-point has been determined by Carnelley and Williams (Chem. Soc. Trans. 1879, 35, 566) and is stated by these observers to lie between 1450° and 1600°.

The specific heat of lead according to Regnault is 0·0314 at temperatures between 10° and 100°, and for molten lead according to Person it is 0·0402 between 380°–450°. The latent heat of lead is such that 1 part by weight of lead in solidifying gives out heat sufficient to raise the temperature of 5·369 parts by weight of water by one degree centigrade. It is a poor conductor both of heat and electricity.

Lead is tasteless, but emits a characteristic odour when rubbed between the fingers. It can be welded in the cold by pressing the clean surfaces together.

Lead is easily oxidised by exposure to the air, and in the finely divided state, as obtained by the decomposition of the tartrate by heat, is pyrophoric. Pure dry air, freed from carbon dioxide, has no action upon lead, nor is it attacked by air-freed water; but easily suffers corrosion under the combined influence of air and moisture, or of water and air. By the action of air and water lead hydroxide is produced, which dissolves in the water and is converted into a basic carbonate by the carbonic acid present. The action of water on lead is materially influenced by the presence of small amounts of salts dissolved in the water; nitrates are supposed to further the action—this is especially true of ammonium nitrate—whereas chlorides, sulphates, carbonates, and phosphates are said to retard the action. Chlorides, sulphates, and carbonates, especially the latter, diminish the solvent action of nitrates and in some cases destroy it altogether. The action of distilled water on lead is reduced by addition of chlorides, sulphates, and carbonates. Water saturated with carbon dioxide under ordinary pressure has but little solvent action on lead, but when saturated with carbon dioxide under a pressure of six atmospheres, the solvent action is considerably increased. In this case also the presence of ammonium nitrate and of potassium carbonate tends to retard the action. These conclusions are drawn from a series of observations on the influence of salts on the solvent action of water on lead, made by Muir (Chem. News, 33, 102, 125, 145; 34, 223, 324), who has also studied the influence of salts on the solubility of the basic carbonate

$$(PbCO_3)_2,Pb(OH)_2,$$

which is formed on the surface of the exposed lead or deposited at the bottom of the vessels. The order of the solubility of the basic carbonate agrees very nearly with that of metallic lead in solutions of the same salts (Muir, Chem. Soc. Trans. 31, 660). The influence of small quantities of free sulphuric acid on the corrosion of lead by water has been studied by W. Carleton Williams (J. Soc. Chem. Ind. 6, 111). In these experiments distilled water saturated with air was used to dissolve certain salts, and to these solutions sulphuric acid in amounts equivalent to from 1 to 5 grains per gallon was added, and the amount of lead dissolved from pieces of sheet lead immersed in these different solutions was determined. The presence of 1 grain per gallon of free acid notably increases the action, a greater quantity of lead in a given time being found in the solution than when the salt solutions are used alone. The total action as measured by the loss of lead is less in presence of free sulphuric acid than with the salt solutions alone. Allen (Chem. News, 46, 145) found that water taken direct from the main in one town in Yorkshire, and having an acid reaction, when left in contact with lead, dissolved an amount of lead equivalent from 0·42 to 0·56 grains per gallon, but after the water had been made slightly alkaline the amount of lead dissolved was equivalent to 0·14 grains per gallon only. Crookes, Odling, and Tidy refer the activity of water towards lead as due to a deficiency of silica, and are of the opinion that from 0·5 to 0·7 parts of silica per 100,000 is sufficient to prevent the action. In many cases the corrosion of the lead pipes would appear to be due to the presence of a free acid in the water supply, as is apparently the case with one of the water supplies of Sheffield, and also the water supply at Huddersfield (Allen, *l.c.*, also Chem. News, 46, 88). The waters most liable to act upon lead are those obtained from upland gathering grounds, waters which are soft and usually of remarkable purity. The activity of such waters is by many attributed to the presence of free acid (*cf.* P. F. Frankland, J. Soc. Chem. Ind. 8, 241) (*v.* WATER).

Inasmuch as air facilitates the solvent action of water, an intermittent water supply is favourable to the contamination of the water, and as lengthened contact with lead in the case of an active water will naturally result in a considerable proportion of the metal being dissolved, it is advisable to run off the water that has been standing over night in the pipes, as such water may, by the long contact with lead, be unfitted for drinking purposes.

Lead is dissolved easily by dilute nitric acid; the action of concentrated acid is arrested by the formation of lead nitrate in white granular crystals. Dilute hydrochloric and dilute sulphuric acids do not attack lead, but it is dissolved by boiling concentrated hydrochloric and sulphuric acids, lead chloride and lead sulphate being formed.

Composition of commercial lead.—Market lead is usually pure, containing traces of antimony, copper, iron; occasionally zinc, tin, bismuth are found, and small but varying amounts of silver are usually present. The following analyses serve to show the impurities in commercial lead :—

—	*a*	*b*	*c*	*d*	*e*	*f*	*g*	*h*
Copper . . .	0·0014	0·0526	0·0053	0·0004	0·0002	0·012–0·046	0·05–0·10	0·00011
Antimony . . .	0·0037	0·0074	0·0074	0·0011	0·0013	0·016–0·040	0·02–0·10	0·00016
Iron	0·0016	0·0015	0·0015	0·0003	0·0014	0·004–0·035	0·02–0·05	0·00037
Zinc	0·0016	0·0018	0·0018	0·0007	0·0003	traces to 0·009	—	0·00013
Silver . . .	0·0080	0·0040	0·0040	0·0001	0·0009	—	—	—
Bismuth . . .	—	—	—	0·0034	0·0555	—	—	0·00063
Tin	—	—	—	0·0001	—	—	—	—
Arsenic . . .	—	—	—	—	—	—	—	0·00005
Total of foreign metals	0·0163	0·0673	0·0200	0·0061	0·0596	0·032–0·110	0·09–0·25	0·00145
Specific gravity . .	—	—	—	11·3580	11·3440	11·365–11·395	11·369	—

(*a*) Bleiberg. (*b*) Newcastle; both analysed by Hampe. (*c*) Lead manufactured by Foster, Blackett and Wilson, Newcastle-on-Tyne, analysed by Michaelis (1868) (Kerl, Hüttenkunde, 19). (*d*) and (*e*) Schweitzer (*l.c.*). (*f*) Lead from Upper Hartz, purified by Pattinson's process. (*g*) Freiberg lead, refined by Pattinson's process. (*h*) Lead from Ems, desilverised by zinc and refined by steam. *f*, *g*, and *h* are quoted from analyses given by Kerl (Hüttenkunde).

Lead is largely used in building construction in the form of sheets, gutters, spouts, &c., also for the manufacture of pipes for gas and water, for making shot and solders. Its power of resisting the action of acids, &c., renders it of great service in the construction of chemical plant, *e.g.*, sulphuric acid chambers. The lead preferred for the construction of sulphuric acid chambers is that obtained by remelting old lead, which is hardened by a small amount of antimony. Experiments of Johnson and Calvert (Compt. rend. 56, 401), of Hasenclever (Wag. J. 1872, 239), and of Bauer (*ibid.* 1875, 364) have shown that ordinary leads resist the action of sulphuric acid more effectively than pure lead.

Sheet lead.—For the manufacture of sheet lead, market lead is cast in a plate several inches in thickness by running molten metal into a mould consisting of a large rectangular iron framework. When the plate is somewhat cooled it is transferred to the rolling mill, which consists of a pair of massive iron rollers, about 18 inches diameter and some 8 feet wide, which are worked by engines with reversing gear. The rolls are placed in the middle of a long bench, a little wider than the rollers, and about 3 feet high; at intervals of a foot along the bench are placed wooden rolls on the same level as the rollers, which serve to facilitate the movement of the sheet to and fro. By passing and repassing the plate between the rollers it is gradually extended into a sheet, which, when too long for manipulation in the ordinary way, is cut into smaller sheets which are rolled separately. Or the sheet may be doubled over, the surface being previously chalked to prevent the adhering of the two sheets, and the doubled sheet rolled out to the required thickness. The lead having been rolled out, the edges and ends of the sheets are cut straight and the sheet wound on to a cylinder at the end of the bench.

Lead pipes are usually made in machines worked by hydraulic pressure. Over the piston of the press is a reservoir which contains the metal, and which may be heated by an annular fireplace. The reservoir is filled with molten lead by a spout through an aperture in the top; when filled the spout is withdrawn and the aperture closed tightly by an iron plug, kept in position by an iron key. The size of the pipe is regulated by a steel die of the diameter of the outside of the pipe fitted at the top, the internal diameter of the pipe being determined by a mandril which passes directly through the centre and is moved upwards by the rising piston, the semi-molten metal being at the same time forced through the die. As the pipe passes out at the top it is coiled on to a drum. The pipes used for gas-services are usually made of metal to which either tin and antimony have been added directly, or these metals may be supplied by the addition of a harder lead containing them.

Lead shot is made by alloying the metal with arsenic, which is added either in the form of white arsenic or arsenical dross from the improving furnace. The addition of arsenic serves to impart a greater fluidity to the metal and increases the tendency of the metal to assume a spherical form in passing through the air. The molten metal is made to run through cullenders pierced with holes, and to fall through a considerable height into vessels holding water. The height required for the fall is either secured by means of a shot tower, or, as in some places, by means of a deep well, the shaft of an old coal pit being in some cases adapted for this purpose. The size of the shot is determined by the size of the holes in the cullender, by the height from which the lead falls, and by the temperature and consequent fluidity of the molten metal.

The shot, taken from the vessel in which it has solidified, is sorted by sieving into different sizes, and the imperfect ones separated by causing the shot to roll down an inclined polished metal surface, the globular ones running down easily, and are collected in a box at the bottom of the inclined plane, whilst the imperfect ones remain on the sides of the plane. The shot is finally polished by shaking with a little plumbago in a cask revolving on a horizontal axis.

Lead Compounds used in the Arts.

Lead oxide, lead monoxide, or *plumbic oxide* PbO. The two commercial varieties of this compound are *massicot* and *litharge.* The former is obtained when molten lead is heated at a moderate temperature in the air, the molten lead being constantly stirred. It is the product formed in the first stage of the manufacture of red lead. After grinding and levigation it is obtained as a brownish-yellow powder. Another variety is obtained as a lemon-yellow powder by heating white lead (the basic carbonate).

Litharge is produced when the oxidation of the lead takes place at a temperature sufficiently high to melt the oxide formed, as in the cupellation process of which it is one of the products. When litharge is manufactured for sale, the purest lead is submitted to cupellation; if the lead used is not quite pure, then the portions of litharge first formed and that produced towards the end of the operation are rejected. The litharge as it forms is collected in large iron pots fitted on wheels, in which it is allowed to cool slowly. When the pots are emptied, the litharge 'falls,' the central portions which have cooled more slowly being somewhat lighter in colour and possessing a scaly crystalline structure. The more friable portion is broken up and passed through a circular temse or screen, the litharge collected and packed in casks and sold as *flake litharge.* That portion of the litharge which does not fall, but remains in hard coherent masses is ground between horizontal stones in a stream of water, by which the powdered litharge is carried into settling tanks in which it accumulates. The litharge after separating from the water is dried at a low heat in a reverberatory furnace, packed, and sold as *levigated litharge.* The colour of lead oxide varies from lemon-yellow to reddish-yellow, and on heating it becomes brownish-red. The sp.gr. of different varieties of lead oxide are given by Geuther (Ann. Chim. Phys. 19, [ii.] 60–61) as follows: yellow cryst. 9·29 at 15°; red cryst. 9·126 at 15°; red cryst. 9·125 at 14°; red powder, 9·09 at 15°; and red, very pure, 8·74 at 14°.

Litharge is used in the manufacture of flint glass; as a glaze for earthenware; for the preparation of lead acetate, lead nitrate, lead plaster, and for drying oils.

Red Lead, Minium, or *Plumbic Tetroxide* Pb_3O_4. The manufacture of red lead consists in the oxidation of lead, which is effected in two stages, the first process being the conversion of the lead into massicot or the 'drossing' of the lead, and the second the conversion of the monoxide into tetroxide or a red lead of the required shade. These operations are usually conducted in two different furnaces. The first of these, the drossing oven, is a low-arched furnace with a bed of fire-brick laid on a bed-plate of cast iron having raised borders on each side and at the back. The bed of the furnace is made to slope slightly towards a median line, and also from back to front. On either side of the furnace bed is a low wall, the spaces between which and the wall of the furnace form the two fireplaces. In front are three openings closed by hinged doors of cast iron; the two side ones communicate with the fireplaces, and serve for the introduction of fuel, whilst the central one, which is larger than the other two, serves for the introduction and the working of the charge, as also to allow of the escape of the products of combustion, which pass into an arched space or hood of brickwork in front of the furnace, this hood forming in fact the base of the short vertical chimney attached to each furnace. In front of the working door is hung a chain with a hook at the end; this serves as a fulcrum for the rabble used in working the charge. Below the working door a space is formed by two vertical plates of cast iron on brick walls, resting on a slab of stone or plate of iron on the floor, and supported by the iron plate which forms the lower part of the front of the furnace. This space in front serves to collect any of the oxidised product which may fall in transferring it to the waggons. The length of the furnace is about 11 feet, and the width between the bridges is about 8 feet 4 inches. The 'colour oven' is in most essentials similar to the 'drossing oven;' the bottom is flat and the slope from back to front not so great as in the latter. Coal is used as fuel in these ovens; in some cases where the ovens are constructed with fire-grates and ash-pits, small coal may be used.

The mode of working is as follows. A charge of from 22 to 31 cwt. of pig lead is introduced into the furnace, and a dam is made across the furnace of rough oxide intermingled with lead obtained from the grinding, &c., of a previous charge. The temperature is so regulated as to melt the lead, which forms a pool behind the dam; the molten lead is agitated by means of a rabble and splashed over the furnace bottom. In this way the oxidation is promoted, and as the oxide forms it is pushed toward the back of the furnace, the still unoxidised lead flowing to the front, and as the oxidation proceeds the pool becomes smaller and smaller. The oxidation is promoted by adding some slag lead from time to time, the antimony contained in it being favourable to a rapid drossing. This addition of slag lead, whilst it curtails the length of the operation, is not permissible in the manufacture of the better varieties of red lead, such as are used in the manufacture of flint glass; the red lead used for this purpose should not contain copper. In practice it is found the oxidation of the lead is so materially promoted by the use of slag lead, that in many works special alloys of antimony and lead are prepared and used to replace slag lead in the manufacture of the best varieties of red lead.

When the oxidation is completed the charge is raked out into iron waggons, and in these allowed to cool. It is next passed to the grinding mill, where it is ground between millstones with a regulated supply of water. The heavier particles of lead oxide and metallic lead which sink in the troughs leading to the settling cisterns are collected and used in the drossing oven to dam up the charge of lead. The finely ground massicot is carried by the stream of water into settling tanks where it subsides, and after the water has been run off, it is transferred to iron barrows, in which it is conveyed to the 'colouring' oven, upon the bed of which the contents of the barrows are emptied. The mass is thus quickly dried, and is then spread out over the bed of the oven in furrows and ridges resembling a ploughed field, and heated at a carefully regulated temperature for some hours, until it has assumed the required shade. The oxidation is aided by stirring the mass from time to time, and the progress of the operation watched by withdrawing a sample by means of a paddle, and from the appearance presented by the sample the completion of the operation is determined. When hot, the red lead has a rich purple tint, which, when the oxidation is completed, assumes a bright red colour on cooling.

A variety of this same compound, styled orange lead, is made by submitting white lead to a similar process. The lighter particles of white lead which form as a froth in the grinding and levigating white lead are collected, and when heated in the red lead ovens yield a very soft and bright coloured orange lead.

The red lead is withdrawn from the ovens, and after cooling is re-ground and dried, and after sieving is packed in barrels. Orange lead is ground and levigated, as the decomposition of the carbonate requires a temperature so high that some of the oxide of lead produced is partially fused.

Red lead is a granular crystalline powder, the colour of which varies somewhat, this variation is supposed to be in part due to the presence of orange lead formed from the lead carbonate contained in the massicot, and produced by the absorption of carbon dioxide from the air, but in all probability it is to be accounted for by the difference in composition of the lead from which the red lead is made. When heated, red lead assumes a darker shade of red, becoming violet and ultimately black, regaining its original tint on cooling. The sp.gr. of red lead, as given by different observers, varies from 8·62 to 9·19 (Clark's Constants of Nature, 47). When strongly heated it yields oxygen, and is converted into the monoxide. It is decomposed by nitric acid, lead nitrate and the puce-coloured peroxide PbO_2 being formed; when digested with nitric acid and a little sugar, the red lead is completely dissolved. Red lead is used as a pigment, in the manufacture of flint glass, as a cement in making steam-joints, and in the manufacture of secondary batteries. Commercial red lead may contain some metallic lead, lead sulphate, and also oxides of antimony tin, copper, and iron.

White lead, Céruse, Blanc de Plomb, Bleiweiss. The commercial article known as white lead is essentially a basic lead carbonate, of the formula $2PbCO_3{\cdot}Pb(OH)_2$, which is produced by the decomposition of a basic lead acetate by means of carbon dioxide. The method of manufacture which according to experience yields a white lead best adapted for the production of paint, one of the chief uses of white lead in the arts, is a modification of the old Dutch process.

The Dutch method consists in exposing thin sheets of metallic lead, rolled into coils and placed in earthenware pots containing a small amount of vinegar, to the combined action of the acetic acid contained in the vinegar, air, moisture, and carbon dioxide; the carbon dioxide and the heat necessary to further the corrosion of the lead being obtained by the fermentation of horse manure and stable litter, in which the earthenware pots and their contents are embedded. The 'blue' or metallic lead is gradually corroded and converted into white lead, which after being separated from the unaltered metallic lead, is ground and washed.

The English method differs from the Dutch method chiefly in the replacement of horse dung and stable litter by spent tan in a state of fermentation, and the substitution of dilute acetic acid, prepared from pyroligneous acid, for the vinegar. The substitution of spent tan for stable litter minimises the risk of discolouration of the white lead by the production of sulphuretted hydrogen, but the fermentation is somewhat slower, and consequently the conversion of the 'blue' lead into white lead requires a greater length of time. The lead used for the manufacture of white lead should be of the purest and softest description, and the manufacturer usually purifies the lead used for this purpose by the Pattinson, the Rozan, or the Parkes process already described. The presence of small amounts of copper or antimony tends to produce a white lead having a dull grey tint. A red or pink colour, at times observed in the manufacture of white lead, has been attributed to the presence of a suboxide of lead by Bannow and Kraemer (Ber. 1872, 545; 1873, 21), an explanation admitted by Lorscheid, whilst according to Baker the colouration is caused by the presence of finely divided oxy compounds of silver. The lead is cast into thin sheets of lattice work or gratings, so as to expose a large surface to the corrosive action of air and acid vapours, &c., by pouring molten lead on to a sloping grooved iron plate, from which, on solidifying, the crates, buckles, plates, straps, or wickets, as they are variously styled, are easily detached. Some of this lead is cast in thin circular discs or stars. In some of the works in this country and in America, the 'plates' and 'wickets' are cast by machinery. The machine consists of an endless band of square plates of iron linked together, each plate being a mould, into which the lead is poured as the plates are slowly moved under the spout of the lead-pot. The castings are delivered at the end on a leather belt covered with plates of sheet iron to prevent the hot lead injuring the leather, and are thus carried away from the machine. This machine can make from 50–60 castings per minute. The corrosion of the lead is effected in what are known as stacks, built in brickwork chambers, a series of which are usually built side by side along one side of a shed. The dimensions of the chambers vary at different works, the most convenient dimensions being an area of 12 feet by 20 feet, or 16 feet square, and a height of some 25 feet. The front wall of the chamber is provided with an opening, 4 feet wide, running from the top to the bottom, serving for the introduction of the materials used in the construction of the stack. As the building of the stack proceeds the opening is closed by boards fitting into slots. The stack is built up as follows. First, the floor of the chamber is covered with a layer of ashes, upon this is spread spent tan, already in a state of fermentation; the height of this first bed of tan is some three feet. The tan is beaten down and the surface levelled, and on the bed so formed is placed a series of earthenware pots, partially filled with a 2 to 3 p.c. solution of acetic acid. These pots are placed together, leaving a space about 6 inches wide between the outside rows and the walls of the chamber. The pots ordinarily used are of two sizes; the larger ones, which are provided with a rim on the inside, are placed on the outer edges of the series, and in the mouths of these pots are placed the discs of metallic lead, resting on the rims already mentioned. These larger pots serve to support the wooden bearers which carry the flooring boards used to cover in the bed. In some establishments, pots of one size only are used, and the flooring boards are supported by blocks of wood. On the top of the earthenware pots are placed the crates of metallic lead, so as to form a layer of lead about 5 inches in depth; between the lead and the cover of flooring boards is left a space of from 6 to 8 inches. The space between the walls of the chamber and the pots is filled in with tan on all sides, the opening in front being closed by boards. On the bed so constructed another bed is built in exactly the same way, with the exception that in the construction of the upper beds the layer of tan is only about 1 foot in thickness. In this way the chambers are filled up to a height of some 20 feet or more, with beds consisting of pots, lead, and tan, the topmost bed being covered with a layer of tan. In stacks of an area of 12 feet by 20 feet, a bed will represent 3 tons of lead, which will lie on about 1000 pots of 5½ inches diameter, containing 200 gallons of diluted acetic acid. The weight of lead in a stack will vary with different practices, with the size of stack and weight of wickets. In stacks 28 feet by 14 feet, each bed might represent as much as 7 tons of lead, and with twelve beds the total lead being 84 tons. As the building of the stack proceeds the opening in front is gradually built up with loose boards, and when the stack is completed the opening at the top is left unclosed, so that the stack may be examined from time to time, and if necessary the tan rearranged, as during the fermentation the system of beds gradually falls away from the side walls. In some cases it is usual to provide ventilation in the form of wooden spouts placed in the corners of the chamber; these spouts are pierced with holes which may be closed by tan. Such ventilators are only used in stacks of large area, and they provide an escape for the steam which is produced in considerable amounts during the first stages of the fermentation; in the case of smaller stacks this takes place with sufficient regularity at the surface of the side walls. After the stack is built it is left to itself for about three months, and during this time the fermentation of the tan proceeds producing heat, the temperature in some cases rising to 140°F., which serves to volatilise the acetic acid and water, and at the same time develop carbon dioxide. Under the combined influence of these agents the blue lead is gradually converted into white lead. At the end of the time mentioned above, the stack is unloaded, the top covering of tan is removed, the bark which is not mouldy is used to add to fresh tan in the construction of another stack. As the covering of boards is removed, the corroded crates and discs are loaded into trays and carried away to the mill, in which the white lead is separated from the unaltered metallic lead. The 'corrosions' preserve the form of the castings of the metal, but are more bulky, and present a white opaque appearance, and vary in texture. The best corrosions are hard and porcellanous, and can be easily handled without crumbling, whilst the poorer are of a floury character and crumble easily when touched. In places the white lead is discoloured; the discolouration may be either due to the tarry matter present in the acid used or to the droppings of water from the tan. Before removal of the corrosions from the stack, each layer as it is exposed is thoroughly moistened with water. The white lead taken direct from the bed is not uniform in composition; it consists mainly of a basic carbonate $2PbCO_3 \cdot Pb(OH)_2$, but some of the corrosions approximate more nearly to the formula $3PbCO_3 \cdot Pb(OH)_2$, whilst in some cases the composition is very nearly that of the normal lead carbonate $PbCO_3$. All white lead corrosions contain some lead acetate locked up in the particles, and this is dissolved out in the washing and grinding to which the corrosions are next submitted. It is usual to find the earthenware pots quite empty and dry, or at the most a few may contain a little water; the pots are washed and drained, and when dry are used over again. The pieces of white lead which fall on the bed of tan are picked up by hand, the surface of the bed is also raked and a further quantity of white lead is got from the tan by washing it on sieves in a stream of water.

The trays of corrosions are taken from the stack to the grinding mill, where the unaltered or blue lead is separated from the white lead and the latter finally ground into an impalpable powder. The mode of conducting the grinding and levigation varies in different works; the trays are usually sunk in a cistern of water and the contents are directed by means of rakes between corrugated rollers running under a stream of water. The emptying of the trays is effected in this manner to insure a complete soaking with water, and thus further obviating the production of clouds of poisonous dust. The production of dust in the treatment of the corrosions is greatly reduced by watering them before they are removed from the stacks. After the blue lead has been separated, the white lead is crushed by passing through a pair of smooth rollers, made of gun-metal, and raked about over a perforated plate under a constant spray of water. The coarse white lead next passes to horizontal grinding stones, to which it is fed by a ladle or by an endless band. After passing through these stones, the white lead issues in the form of a thick white mud, and is again passed through other grinding stones until it has been reduced to a state of subdivision so fine that it is carried along by the stream of water to the settling tanks; the white lead which settles out in the troughs used to convey the water to the tanks is returned to the grinding stones. The grinding and levigating are conducted in such a way that the water may be used over and over again, and is usually found to contain lead salts in solution, which, before discharging the water, are precipitated by sodium carbonate. In the tanks the white lead gradually settles and forms a thick white paste, from which the water is siphoned off, and when the mud has attained a sufficient consistence it is ladled out into the dishes used for drying it. The dishes are shallow clay saucers, 12 ins. diameter and 3 ins. deep, and made of clay similar to that employed in making flower pots. The dishes are stacked in drying stoves upon shelves made of iron bars, the stoves are heated by iron pipes made to circulate round the floor of the stove, and connected with a fireplace outside the stove, the products of combustion from the fire passing through the pipes. In this way the pulp, which contains some 25–30 p.c. of water, is gradually dried, the temperature of the stoves should not rise above 180°F. The white lead when dry is taken from the stoves and either packed in casks or ground and mixed with oil to form a paint. Boiled linseed oil is used for this purpose, from 8–9 lbs. of oil is needed for every hundredweight of white lead. During the grinding, some manufacturers add a small quantity of a blue colouring matter such as Prussian blue or indigo to the white lead to modify the somewhat yellowish tint due to the stains from the bark.

To obviate the dangers attending the method of drying the pulp, as described above, drying in vacuum pans has been used in some places, but where the white lead is to be made into paint, the method patented by Ismay (Eng. Pat. 23969, 1895) has been adopted with considerable success. In this process, the white lead pulp is mixed with oil and thoroughly agitated in a pug-mill, with the result that the greater portion of the water is displaced by the oil; the last portion of water is driven off by using a pug-mill, provided with a heating jacket, in which the mixture may be subjected to heat in a partial vacuum. In this process, the drying in stoves is entirely obviated.

The explanation given by Liebig in his Handwörterbuch der Chemie of the chemical changes which take place in the corrosion of the lead in the stacks, has been practically substantiated by the experiments of Hochstetter. These experiments demonstrate the first change to be the conversion of the lead into a basic acetate by the agency of air and acetic acid vapours. The basic lead acetate is next converted into white lead and normal lead acetate by means of carbon dioxide and aqueous vapours. The normal acetate is next converted into white lead, and acetic acid liberated by the combined action of carbon dioxide and aqueous vapour. The acetic acid so liberated is free to take part in the corrosion of a further quantity of blue lead, the conversion of which into a basic acetate precedes the formation of the basic carbonate. The basic carbonate $2PbCO_3{\cdot}Pb(OH)_2$ is, according to Hochstetter, not only the product of this combined action, but is also formed when carbon dioxide is passed into a solution of the basic lead acetate. Further, this compound resists the action of carbon dioxide alone, and can only be converted into the normal carbonate in presence of free acetic acid. In the light of this investigation, white lead would appear to consist of lead carbonate and hydroxide in the proportion of two molecules of the former to one of the latter, and the increased proportion of the carbonate frequently observed is to be explained as due to an admixture of normal carbonate produced by the action of carbon dioxide in presence of acetic acid vapours upon the basic carbonate. All white lead corrosions contain some normal acetate, but the amount of this compound will be less in white lead made by the Dutch or English methods than that produced by the German method in which the production of carbon dioxide, acetic acid, and aqueous vapour ceases simultaneously.

The proportion of lead corroded when working in stacks is from 50–70 p.c., the average result will be about 65 p.c.; the increase in weight is 20 p.c. of the lead used. The uncorroded lead is collected and after drying is weighed and remelted to be used over again.

The percentage of corrosion is chiefly determined by the thickness of the wickets, some manufacturers prefer to cast heavy wickets, and get a low percentage corroded, as it is found that the ‘blue’ lead is so much more efficiently separated from the ‘white’ lead.

The German method, as practised at one time at Krems, and now chiefly at Klagenfurt, consists in exposing thin sheets of metallic lead suspended in wooden boxes to the action of the vapours produced from a mixture of wine lees and vinegar, which is spread over the bottom of the boxes. The boxes are packed in stoves heated to about 85°F. This mode of procedure has been modified by suspending the sheets of lead in heated chambers, on the floors of which are placed vessels containing diluted acetic acid, air and carbonic acid gas being led into these chambers.

Whilst this method is much more rapid than the English method, it labours under the disadvantage that the white lead produced does not compare favourably with that produced by the older and slower procedure.

French or Clichy method.—The process by which white lead is manufactured in France is due to Thenard, and consists, first, in the production of a solution of basic lead acetate by digesting litharge with a pyroligneous acid of a sp.gr. 1·056; the litharge is added to the acid in a vessel in which it is kept constantly agitated by mechanical means until the sp.gr. of the solution is 1·145. The liquor is then run into another vessel, in which insoluble matter, such as lead, lead sulphate, silver chloride, &c., settles out, and the clarified solution is conveyed into a vessel where it is exposed to the action of carbon dioxide, which is forced through it by means of a fan and distributed throughout the liquid by a series of small pipes. The carbon dioxide used is produced by heating a mixture of coke and chalk in a kiln, the gases from the kiln passing into a vessel in which they are washed, and are then drawn off by a fan and forced into the decomposing vessel. The gas is passed through the solution of acetate for 12 to 14 hours, the white lead produced is allowed to settle, and the solution of normal acetate pumped back to the vessel, in which it is digested with litharge and converted into basic acetate. The white lead is run off into a tank and repeatedly washed with water; the first washings, as they contain lead acetate, are used over again for the production of basic acetate.

Milner's process.—This method of manufacturing white lead consists, first, in the production of a basic lead chloride by the mutual action of litharge, common salt, and water; the change takes place when these substances are mixed at the ordinary temperature; the mixture swells up, becoming gradually white and pasty. The reaction is attended by a considerable evolution of heat, and the solution becomes alkaline. This decomposition is, on the large scale, effected in a pug mill made of white pine, the arms of American elm; the litharge used is flake litharge which has been carefully ground and levigated; it is mixed with salt and water in the proportion of 1 of salt, 4 of litharge, and 16 of water. These materials are mixed with one another, the agitation being continued for 3 hours, as it is found that unless a sufficient time is allowed, the mass becomes stiff and pasty, and has to be removed from the mill by hand, whereas if the mixing be continued for the time specified, the mass obtained is more fluid, and can be easily removed. The mixture of basic lead chloride and caustic soda so obtained is next run into a large iron cylinder with spherical ends, the cylinder is lined with lead, and is 16 feet high and about 8 feet diameter. In the top end of the cylinder are two openings, one serving to introduce the mixture from the pug mill, and the second is closed by a valve by which the pressure is regulated. In this vessel the conversion of the basic lead chloride into a basic carbonate is effected by means of carbon dioxide, which is introduced by a pipe, the portion inside the vessel being provided with a number of perforations for the distribution of the gas. At one side of the lower part of the cylinder is a tap for the withdrawal of the white lead and of samples, which are taken from time to time during the carbonation. The carbonator is supplied with paddles or stirrers attached to a horizontal shaft running across the cylinder, and set in motion by machinery. As in the Clichy process, the carbon dioxide is produced by heating a mixture of limestone and coke in a kiln, from which it passes up a coke tower, in which it is washed by a stream of water and then forced by a pump or fan into the carbonator. The fluid mixture of basic chloride, caustic soda, &c., is submitted to the action of carbon dioxide until it is completely converted into white lead and common salt. The completion of the conversion is ascertained by the appearance and properties of samples withdrawn from the carbonator. The end of the reaction is shown by the liquid no longer exhibiting an alkaline reaction, the mixture forming a viscid, homogeneous mass, which, when shaken up in a glass vessel, which it partially fills, coats the sides, forming a uniform very thin layer, like frost on a window pane, and after standing a few seconds, the clear liquor separates from the carbonate, leaving arborescent patterns on the sides of the glass. If after this point has been attained the gas be passed through the mixture, the product loses its value, becoming granular and no longer coats the glass, but settles out rapidly. At the end of the carbonation the charge is run off into cisterns in which it is thoroughly washed with water to free it from salt, and, when completely washed, it is drained and dried in the usual manner. The white lead made by Milner's process resembles in composition that produced by the methods already described, and, like these products, is well adapted for use as a paint. This method of white lead manufacture was in operation at the Sankey White Lead Company's works, near Warrington, and at one time employed at one of the white lead establishments on the Tyne, but has been abandoned at both places.

Many processes have been devised for the manufacture of white lead; the production of white lead by the decomposition of a basic lead nitrate with carbon dioxide has been made the basis of one of the proposed methods. Another proposal is to submit a pasty mixture of litharge and lead acetate solution to the action of carbon dioxide, and it has been suggested to utilise the corrosion of finely divided granulated lead by air, water, and carbon dioxide as a method of making white lead. Attempts have also been made to manufacture white lead by precipitating solutions of basic lead acetate with solutions of sodium carbonate. These and many other processes have been suggested and patented; and whilst basic lead carbonates, or mixtures of the normal carbonate and lead hydroxide, are yielded by these methods, none has proved sufficiently successful to supplant the older methods, the greater portion of white lead manufactured at the present time being that produced by the English method, which, despite the slowness of the first stage and the dangerous character of several of the subsequent operations, maintains a supremacy. It would appear that the slow conversion of lead into white lead, such as obtains in the Dutch and English methods, is favourable to the production of this substance in a form possessing high covering properties, and specially adapted for use as a pigment. To perfect this mode of manufacture, what is needed is a method of detaching the corrosions, of washing and drying the white lead, which will minimise the risks of poisoning to the workpeople. Despite the regulations in force at all white lead manufactories in this country and the constant medical examination of the individuals engaged in these processes, cases of lead-poisoning are not infrequent, and in some instances these terminate fatally. Careful and frequent medical examination and immediate attention to the first symptoms of lead-poisoning have proved in the experience of a manufacturer with whom the writer is acquainted that it is possible to produce white lead by the English process without serious consequences to the people employed. No doubt one of the chief obstacles in the enforcement of the sanitary regulations is the negligence and carelessness of the workpeople themselves.

Properties of white lead.—White lead is a white, earthy, heavy powder, which, from its behaviour to polarised light, undoubtedly possesses a crystalline structure. Examined under the microscope, it appears to consist of rounded, circular, or oval grains. The grains are transparent; they vary in diameter from 0·0001 to 0·00004 of an inch. Commercial white lead varies in composition, and is apparently a mixture of the basic carbonate $(PbCO_3)_2{\cdot}Pb(OH)_2$ and normal lead carbonate, $PbCO_3$. This view of the constitution of white lead is not only supported by the observations that samples of white lead have been found on analysis to have a composition represented by the formulæ $3PbCO_3{\cdot}Pb(OH)_2$ and $5PbCO_3{\cdot}Pb(OH)_2$, and in some cases to consist of nearly pure $PbCO_3$, but is borne out by the investigations of Hochstetter, already referred to. For Hochstetter has shown the basic carbonate $(PbCO_3)_2{\cdot}Pb(OH)_2$ to be the product of the action of carbon dioxide on a solution of the basic lead acetate, and also of the action of sodium or potassium carbonates on the solution of the basic acetate. This compound is also produced by the action of carbamide on a solution of the basic lead acetate (Bourgeois, Bull. Soc. chim. [ii.] 50, 83; Chem. Soc. Abstr. 1889, 21). Further, this basic carbonate is converted into the normal carbonate by carbon dioxide in presence of acetic acid, and it is conceivable that in the stacks the compound $(PbCO_3)_2{\cdot}Pb(OH)_2$ should be in part converted in this way into the normal carbonate, and thus the varying composition of commercial white lead may be explained. The presence of the basic carbonate, or at any rate of a proportion of lead hydroxide, would appear to be essential to a white lead in order that it may be useful as a pigment and of good covering power. This conclusion is borne out by a series of experiments made by Wigner and Harland, who, by artificially preparing mixtures of lead carbonate and lead hydroxide, have shown that the covering power, the opacity, and the ease with which it can be applied as a pigment are greatly impaired when the proportion of carbonate to hydroxide exceeds that of three molecules of the former to one of the latter. In mixing white lead with oil, a considerable rise in temperature is observed, and it is supposed by white lead makers that a portion of the oil is saponified in this process. If this be the case, then it is probable that the lead hydroxide takes part in this decomposition of the oil, and an explanation is given of the fact that those corrosions, which consist mainly of the normal carbonate of lead are practically worthless as pigments. The covering power of white lead is further dependent upon the density; the greater the density the smaller the amount of oil absorbed and the thicker the colour. The covering power may be tested by triturating equal weights of the samples to be compared with equal quantities of linseed oil, and then determining the weights of equal volumes of the pigments thus obtained; that having the greater density will possess the higher covering power.

Weise (Monatschr. des Gewerbe-Vereins Cöln; also Dingl. poly. J. 208, 434) has examined different corrosions obtained by the German method, and concludes from the analysis of the same that the best varieties are those approximating most nearly to the composition of the basic carbonate $2PbCO_3{\cdot}Pb(OH)_2$, and that an increase in the proportion of normal carbonate results in a reduction of covering power. The following are the analytical results obtained by Weise:

	Lead oxide	Carbon dioxide	Water	
1.	86·80	11·16	2·00	Best quality
2.	86·24	11·68	1·81	Seconds—still good as a paint
3.	86·03	12·28	1·68	Thirds—useful as a paint
4.	84·69	14·10	0·93	Residue from washing apparatus
5.	83·47	16·15	0·25	Useless for paint
6.	93·70	5·31	0·90	„

The following represent the composition of the normal carbonate and of the basic carbonate:

	Lead oxide	Carbon dioxide	Water
Normal carbonate	83·52	16·48	—
Basic carbonate $2PbCO_3{\cdot}Pb(OH)_2$	86·32	11·36	2·32

The pigments known as Venetian, Hamburg, and Dutch whites are made by mixing white lead with heavy spar, Hamburg white containing these materials in the proportion of 1 to 3, and Dutch white in the proportion of 1 to 2.

Substitutes for white lead.—Several proposals have been made to replace the basic lead carbonate by other compounds of this metal. Amongst these may be mentioned lead oxychloride which was at one time manufactured at Washington, in the county of Durham, by a process patented in 1849 by the late Hugh Lee Pattinson. In this process, lead chloride is produced by treating finely ground galena with concentrated hydrochloric acid; the lead chloride formed in this way separates out by reason of its sparing solubility in water. The lead chloride is collected and dissolved in hot water, and this solution is treated with a quantity of milk of lime sufficient to neutralise any free acid and precipitate any iron that may be present, the solution during this operation being maintained at a temperature sufficiently high to keep the lead chloride in solution. After allowing the iron oxide to settle, the clear liquor is run off into a vat, and then treated with half the quantity of lime required to decompose the lead chloride. The lead oxychloride so produced is collected, drained, and washed, and finally dried in stoves on porous earthenware plates. The composition of the lead oxychloride is represented by the formula $PbCl_2{\cdot}Pb(OH)_2$ or $PbCl(OH)$; it is a white solid, possessing considerable covering power, and at one time was used as a paint. The manufacture of Pattinson's white lead at Washington has been given up for many years.

Lead sulphate is another of the compounds which it has been proposed to utilise as a white lead. In 1839, Richardson suggested the preparation of this compound by decomposing with sulphuric acid a solution of lead acetate, made by dissolving litharge in acetic acid. The pigment styled 'galenite' is said to be a basic lead sulphate, and can be made by treating finely powdered galena at a low red heat in open retorts or furnaces. Lead fume consists chiefly of lead sulphate, and occasionally a paint of a greyish shade is made with the fume collected in French's and other forms of fume condensers.

Hannay's 'white lead' is essentially a lead sulphate produced directly from galena, which is placed with live coke in a furnace of special construction, and volatilised and oxidised by a blast of air. The fume thus produced is conducted into specially constructed condensers, which are very similar to French's condenser, where it is collected. The material is washed, and finally dried. The patentee also describes the treatment of this condensed fume with various oxidising agents, such as *aqua regia*, to complete in this way the conversion of the sulphites and other similar compounds into sulphate. By this method a powder of great whiteness is obtained, which is stated to have considerable covering power and to form a useful paint when mixed and ground up with oil.

If, as has been already mentioned, a partial saponification of the oil by white lead takes place when the white lead is mixed with oil, it is not easy to understand how any normal salt of lead can efficiently replace white lead.

LEAD POISONING.

The salts of lead, more especially the soluble ones, are strongly poisonous, and since lead is a cumulative poison its salts and compounds, such as the oxide and carbonate, produce serious results if taken into the system even in minute quantities for any length of time. One of the forms in which lead is introduced into the system is by the use of drinking waters, some varieties of which easily attack the lead of the pipes used for conveying the water. Again, the workpeople engaged in the manufacture of lead and lead compounds, more especially white lead, are liable to suffer from the poisonous action of the compounds of this metal. In course of time the disease becomes chronic, the symptoms of which are pain in the abdomen, constipation, loss of appetite, thirst, a nervous prostration known as lead palsy, epileptic fits, and total paralysis. One of the signs of chronic lead poisoning is a blue line at the edges of the gums, due to the deposition of lead sulphide. This line is frequently seen in the case of painters and decorators, who are liable to this form of poisoning, produced in their case by the white lead used in making paint. The blue line is also to be observed in the workpeople engaged in the manufacture of white lead, or in manufactures in which this compound is employed. A portion of the lead taken into the system is excreted by the kidneys, and in cases of chronic lead poisoning it is stated that the administration of potassium iodide aids in the elimination of lead from the system. The mode in which the compounds of this metal are distributed in the different organs of the body is illustrated by the following results of an examination made by the writer in conjunction with Dr. Drummond and Sir Thomas Oliver in the cases of three workpeople who succumbed to the influence of this form of poisoning:—

Description of organ, &c	Lead found expressed as metallic lead in parts per million			Lead in grains calculated on total weight of organ		
	I.	II.	III.	I.	II.	III.
Large intestine	14·6	37·7	—	—	—	—
Small intestine	9·2	—	—	—	—	—
Muscle	3·1	—	—	—	—	—
Lung	2·2	7·6	—	—	—	—
Heart	6·7	4·12	5·0	0·0243	0·0189	0·0164
Mamma	4·8	—	—	—	—	—
Kidney	15·5	10	13·3	0·027	0·0229	0·0261
Spleen	14·7	12	39·0	0·0193	0·0341	0·0853
Liver	47·7	37·8	41·6	0·918	1·000	0·728
Cerebellum and pons	36·9	—	—	—	—	—
Grey matter of basal ganglia	53	—	—	—	—	—
Brain grey matter of cortex	40·9	—	—	—	—	—
white substance	18·9	—	—	—	—	—
Spinal cord	—	1·16	—	—	—	—
Brain	—	9·8	21·6	0·688	—	—
Cerebellum	—	24·8	8·59	—	—	—
Pons	—	22·6	—	—	—	—
Brain and cerebellum	—	—	—	—	0·779	0·634

P. P. B.

OTHER COMPOUNDS OF LEAD.

Oxides. Besides the two oxides described above several others exist.

Lead suboxide Pb_2O is formed when lead oxalate is heated in the absence of air at a temperature below 300°; or when lead oxide is reduced with carbon monoxide at 300° (Brislee, Chem. Soc. Trans. 1906, 154). It is a black velvety powder of sp.gr. 8·342 at 18°, which is readily decomposed into the metal and the monoxide when heated or when treated with caustic soda or acids.

Lead sesquioxide Pb_2O_3 is generally considered to be a compound of the mono- and di- oxides $PbO{\cdot}PbO_2$, into which it is decomposed by acids. It is a yellowish-red powder, formed by adding a solution of sodium hypochlorite to a cold potash solution of lead oxide or by precipitating an acetic acid solution of red lead with dilute ammonia.

Lead peroxide (*Lead dioxide* or *Puce-coloured oxide of lead*) PbO_2 is found native in *plattnerite*, which crystallises in black hexagonal prisms of sp.gr. 9·4. It may be prepared by the action of nitric acid on red lead, by the action of chlorine on a lead salt in the presence of an alkali or better by the action of bleaching powder on lead chloride (Fehrmann, J. Soc. Chem. Ind. 1882, 407). A lead peroxide suitable to the requirements of the aniline manufacturer may be obtained by adding the required amount of lead oxide to molten caustic soda at the highest possible temperature, with constant stirring, and then sufficient sodium nitrate for oxidation. The mass is then extracted with hot water, washed and dried (Minor, J. Soc. Chem. Ind. 1894, 940).

Normal or basic lead sulphate may be converted into lead peroxide, by mixing it with magnesia, suspending the mixture in water and passing in chlorine. It is purified by treatment with boiling 10 p.c. caustic soda, then with hot nitric acid. The yield is almost theoretical, and the oxide is of 97 p.c. purity, containing only traces of chlorine (Friedrich, Mallet, and Guye, Monit. Scient. 1906, 20, 514).

The reaction may be represented thus:

$$PbSO_4+MgO=MgSO_4+PbO\,;$$
$$PbO+MgO+Cl_2=PbO_2+MgCl_2.$$

Lead peroxide may also be obtained electrolytically when water containing less than 1 p.c. of acid, alkali, or salt is electrolysed, using a lead sulphide anode: $PbS+H_2O+5O=PbO_2+H_2SO_4$ (D. R. P. 162107; *see* also D. R. P. 124512; Eng. Pat. 12186, 1901; J. Soc. Chem. Ind. 1897, 743; *ibid.* 1902, 620; Hollard, Compt. rend. 1903, 136, 229). (For other methods of preparing the peroxide *see* Eng. Pats. 11962, 1889; 6954, 1903; Warren, Chem. News, 1896, 144.) Lead peroxide is a dark brown, almost black, powder of sp.gr. 8·9–9·2, which is said to keep best when moist (Fehrmann, *l.c.*). It loses oxygen readily on heating, forming the monoxide, and on exposure to sunlight forms red lead. It has a powerful oxidising action, taking fire when triturated with sulphur, and igniting sulphuretted hydrogen when the latter is passed over it, the heat of this reaction being such that explosives like guncotton or picrate can be fired and metallic powders ignited by its aid (Vanino and Hauser, Ber. 1900, 33, 625). A large number of organic compounds when triturated with it also cause an evolution of heat and light. It decomposes or oxidises some mineral acids, forming the corresponding lead salt with, often, a violent evolution of gas. Lead peroxide is often employed as an oxidising agent in the analysis of organic compounds containing sulphur, and it has also been used in inorganic analysis for the removal of excess of sulphuretted hydrogen or ammonium sulphide (Bogdan, Bull. Soc. chim. 1903, 29, 594). Lead peroxide has been used as a mordant and also for the precipitation of other oxides on the fibre (Bonnet, Bull. Soc. Ind. Mulhouse, 1894, 69; Compt. rend. 1893, 117, 518). It has also been used in the voltaic battery and in electrical and metallurgical operations (Eng. Pat. 16608, 1886; J. Soc. Chem. Ind. 1888, 37). Lead peroxide acts as a weak basic oxide, forming unstable tetravalent lead salts and also as an acid-forming oxide yielding the *plumbates. Orthoplumbates* of the composition M_4PbO_4 and *metaplumbates* $M_2PbO_3,3H_2O$ or $M_2Pb(OH)_6$ have been prepared (Fremy, Ann. Chim. Phys. 1844, [iii.] 12, 490; Grützner and Höhnel, Arch. Pharm. 1895, 233, 512; Bellucci and Parravano, Gazz. chim. ital. 1905, 35, ii. 500).

The orthoplumbates evolve oxygen when strongly heated, and on this fact has been based a method of obtaining oxygen on a large scale; the calcium salt has also been used as an oxidising agent (Kassner, Arch. Pharm. 1890, 228, 109; *ibid.* 1894, 232, 375; *ibid.* 1895, 233, 501).

When calcium meta- or orthoplumbate is heated in a current of air at 200°–280°, *calcium perplumbate* $CaPb_2O_6$ is formed (Kassner, Arch. Pharm. 1899, 237, 409; *ibid.* 1900, 238, 449).

When potassium plumbate is treated with water at the ordinary temperature it is completely hydrolysed, and *plumbic acid* H_2PbO_3 remains in solution in the colloidal state (Bellucci and Parravano, Atti. R. Accad. Lincei, 1906, v. 15, ii. 542, 631; Parravano and Calcagni, Gazz. chim, ital. 1907, 37, ii. 264).

Lead hydroxide $Pb(OH)_2$ is formed when potassium nitrate is electrolysed, a lead anode being used (Lorenz, Zeitsch. anorg. Chem. 1896, 12, 436). It may also be prepared by heating lead carbonate with water or steam (Eng. Pat. 9521, 1893), or by treating lead sulphate with excess of alkali hydroxide (U. S. Pat. 787541, 1905; *see* also U. S. Pat. 808141, 1905; Fr. Pat. 401473, 1909). It acts as a very weak acid (Hantzsch, Zeitsch. anorg. Chem. 1902, 30, 308; Rubenbauer, *ibid.* 331), and has also been obtained in a colloidal form (Sziland, J. Chim. Phys. 1907, 5, 636). The action of lead hydroxide on sugars is similar to that of the alkali hydroxides, inducing molecular rearrangement (Lobry de Bruyn and Eckenstein, Rec. trav. chim. 1896, 15, 92; U.S. Pat. 726130, 1903).

Two *basic lead hydroxides* are known, $2PbO{\cdot}H_2O$ or $PbO{\cdot}Pb(OH)_2$ and $3PbO{\cdot}H_2O$ or $2PbO{\cdot}Pb(OH)_2$. The former is obtained as a white powder by the action of air and water on the metal or by precipitating a lead salt with a small quantity of alkali or ammonia. It may also be obtained in hexagonal crystals by exposing a cold solution of lead monoxide in caustic potash to the air (Lüdeking, Amer. Chem. J. 13, 20). The latter basic hydroxide has been prepared by precipitating basic lead acetate with ammonia (Payen, Ann. Chim. Phys. 1866, [iv.] 8, 302). It forms a white crystalline powder or glittering octahedra, according to the method of preparation.

Halogen compounds of lead. *Lead chloride* (*horn lead, plumbum corneum*) $PbCl_2$ occurs native in the craters of volcanoes as the mineral *cotunnite*, and may be prepared readily by treating the oxide or carbonate with hydrochloric acid or by precipitating a fairly concentrated solution of a lead salt with a soluble chloride. On a large scale it may be prepared by heating litharge with a slight excess of hydrochloric acid at 200° and 25 atmos. pressure, in an autoclave lined with an acid-resisting material (Eng. Pat. 12953, 1895; *see* also Eng. Pats. 16213, 1889; 8914, 1895; J. Soc. Chem. Ind. 1890, 941; *ibid.* 1895, 873; *ibid.* 1896, 357). In a colloidal form it can be obtained by mixing together lead acetate or the lead salt of any other organic acid with an alkali, or alkaline earth chloride (van de Velde, Chem. Zeit. 17, 1908).

Lead chloride forms a white crystalline precipitate or white silky rhombic needles of sp.gr. 5·8. When heated in absence of air it melts at about 485°, and volatilises at 861°–934°. It is less soluble in dilute hydrochloric acid and in solutions of chlorides than in water, but dissolves more readily in concentrated hydrochloric acid (André, Compt. rend. 1883, 97, 1302; Lichy, J. Amer. Chem. Soc. 1903, 25, 469). It dissolves in alkali acetates and in thiosulphates, forming a lead thiochloride $Pb_4S_6Cl_2$ (Hofmann and Wolfl, Ber. 1904, 37, 249).

Lead chloride forms double salts with ammonium and other metallic chlorides (André, Compt. rend. 1883, 96, 435; Lorenz and Ruckstuhl, Zeitsch. anorg. Chem. 1906, 51, 71; Ephraim and Barteczko, *ibid.* 1909, 61, 245; Foote and Levy, Amer. Chem. J. 1907, 37, 119; J. Soc. Chem. Ind. 1909, 707).

A large number of lead oxychlorides are known. The compound $PbCl_2,PbO$ occurs in nature as the mineral *matlockite;* it forms long thin colourless needles, decomposing at 524° into a mixture of $PbCl_2,2PbO$ and PbO, which fuses completely at 615°. $PbCl_2,2PbO$ occurs as *mendipite,* and forms long glistening needles, m.p. 693°. The compound $PbCl_2,4PbO$ has m.p. 711°, and forms glistening lamellar crystals, which give an intense yellow powder (Ruer, Zeitsch. anorg. Chem. 1906, 49, 365; *see* also Strömholm, *ibid.* 1904, 38, 429; Berl and Austerweil, Zeitsch. Elektrochem. 1907, 13, 165). The compound known as *Cassel yellow* has the approximate composition $PbCl_2,7PbO$, together with a little lead, and is usually prepared by fusing together 1 part ammonium chloride, and about 10 parts massicot, white lead, or minium. It is used as a pigment.

Lead tetrachloride $PbCl_4$ may be formed by passing chlorine into lead chloride, suspended in strong hydrochloric acid at 10°–15°. On adding ammonium chloride, *ammonium plumbichloride* $(NH_4)_2PbCl_6$ separates (Hutchinson and Pollard, Chem. Soc. Trans. 1899, 212; Seyewetz and Trawitz, Compt. rend. 1903, 136, 686; Bull. Soc. chim. [iii.] 29, 261; Elbs and Nübling, Zeitsch. Elektrochem. 1903, 9, 776).

When this ammonium compound is added little by little to ice-cold concentrated sulphuric acid, lead tetrachloride separates as a yellow highly refractive oily liquid, which fumes in air, smells like hypochlorous acid, and induces a sweet taste in the mouth. It has sp.gr. 3·183, is stable under sulphuric acid, but is liable to explode, especially when heated, forming chlorine and lead chloride. It solidifies at −15° to a transparent yellow crystalline mass. With hydrochloric acid it forms a crystalline compound H_2PbCl_6, which dissolves on further addition of acid, and is decomposed by water into lead dioxide and hydrochloric acid (Friedrich, Monatsh. 1893, 14, 505; *see* also Ber. 1893, 26, 1434; de Coninck, Bull. Assoc. belge Chim. 1902, 16, 94).

Lead chlorite, chlorate, and *perchlorate* are also known.

Lead bromide $PbBr_2$ is obtained by treating lead oxide with aqueous hydrobromic acid or by precipitating a lead salt with a soluble bromide. It forms white shining needles, which darken when exposed to sunlight (Norris, Amer. Chem. J. 1895, 17, 189); sp.gr. 6·6. It resembles the chloride in properties.

It forms double bromides and oxybromides.

Lead iodide PbI_2 is formed by dissolving lead in hydriodic acid or by precipitating a solution of a lead salt with a soluble iodide. It forms yellow crystals of sp.gr. 6·1, which on heating become yellowish-red, bright red, and finally brownish-black. It also forms double salts and basic salts.

The chloride, bromide and iodide yield double salts with pyridine and quinoline (Elbs and Nübling, *l.c.*).

A number of mixed halogen compounds are known (Thomas, Compt. rend. 1898, 126, 1349; *ibid.* 1899, 128, 1234, 1329; Fonzes-Diacon, Bull. Soc. chim. 1897, [iii.] 17, 346; Hertz and Bogg, J. Amer. Chem. Soc. 1897, 19, 820).

Lead fluoride PbF_2 is formed in the same way as the corresponding iodide. It is a white powder, almost insoluble in water and in hydrofluoric acid, but readily soluble in hydrochloric and in nitric acid. It yields a basic fluoride and a chlorofluoride (Fonzes-Diacon, *l.c.*).

Lead tetrafluoride PbF_4 is said to be formed in a colloidal state by the action of strong sulphuric acid on the *acid plumbifluoride* $3KF,HF,PbF_4$, but has never been obtained pure (Brauner, Chem. Soc. Trans. 1894, 393). The above acid plumbifluoride is obtained by the action of hydrofluoric acid and potassium fluoride on lead tetracetate.

Lead and nitrogen. *Lead nitrate* $Pb(NO_3)_2$ is formed by dissolving litharge in nitric acid of sp.gr. 1·35. The solution is evaporated until it has the sp.gr. 1·6, and is then allowed to cool. It forms milk-white crystals of sp.gr. 4·5 and dissolves in water with a reduction of temperature. It has an astringent metallic taste, detonates with brilliant sparks when thrown upon red-hot charcoal and deflagrates when triturated with sulphur. When heated it commences to decompose at 283°, and in a sealed tube at 357°, it decomposes thus:

$$Pb(NO_3)_2 \leftrightarrows PbO+O+2NO_2$$

(Baekeland, J. Amer. Chem. Soc. 1904, 26, 391; Morgan, J. Phys. Chem. 1904, 8, 416; Colson, Compt. rend. 1909, 148, 837). Lead nitrate is used in dyeing and calico printing, for the preparation of mordants and of chrome yellow. Several basic lead nitrates are known (Senderens, Bull. Soc. chim. [iii.] 11, 365; Mailhe, Compt. rend. 1902, 134, 233; Peters, Zeitsch. anorg. Chem. 1896, 11, 116).

Basic lead nitrate is said to be a very useful decolorising agent for sugar solutions (Herles, Zeitsch. Zuckerind. Böhmen, 1896, 21, 189; Neuman, *ibid.* 183; Zeitsch. angew. Chem. 1897, 123; Pellet, Bull. Assoc. Chim. Sucr. Dist. 1897, 14, 794; *ibid.* 1905, 23, 638; Horne, *ibid.* 635).

Lead nitrite $Pb(NO_2)_2$ is obtained by decomposing silver nitrite with lead chloride and concentrating the solution in a vacuum (Lang, J. 1862, 100; *see* also Chilesotti, Atti. R. Accad. Lincei, 1908, [v.] 17, i, 824). It forms yellow prisms, soluble in water, the solution on evaporation losing nitric oxide and yielding a basic nitrite. A number of these basic salts are known (Chilesotti, *ibid.* 1908, v. 17, ii. 173, 288, 377, 474; Meldrum, Chem. Soc. Proc. 1908, 97).

Lead hyponitrite $Pb(NO)_2$ is a yellow crystalline powder, which explodes on heating (Kirschner, Zeitsch. anorg. Chem. 16, 424; Divers, Chem. Soc. Trans. 1899, 121).

Lead nitrohydroxylamine PbN_2O_3 is an unstable salt (Angelico and Fanara, Gazz. chim. ital. 31, [ii.] 15).

Lead imide PbNH is obtained by the action of potassamide on lead iodide in liquid ammonia. It is a reddish-brown explosive substance. If the lead iodide be in excess, a white basic salt $NPb_2I{\cdot}NH_3$ is formed (Franklin, J. Amer. Chem. Soc. 1905, 27, 820).

Lead nitride PbN_6 is said to be formed by the action of aqueous ammonia or of nitrides on lead salts (Curtius and Rissom, J. pr. Chem. [ii.] 58, 261).

Lead cobaltinitrite, lead cyanide, and cyanate, the corresponding thio- compounds, and lead ferro- and ferri- cyanides are known.

Lead Phosphates. *Tribasic lead phosphate* $Pb_3(PO_4)_2$ is an amorphous white powder obtained by precipitating an excess of lead acetate with a small quantity of sodium phosphate at 100° or by boiling the dibasic salt in water for 5–6 hours.

Dibasic lead phosphate $PbHPO_4$ is prepared by precipitating a somewhat dilute solution of lead nitrate with hot dilute phosphoric acid at 100°. It forms a fine crystalline powder.

Monobasic lead phosphate $Pb(H_2PO_4)_2$ is formed by dissolving the dibasic salt in strong phosphoric acid by the aid of heat and allowing the solution to crystallise. It may then be recrystallised from phosphoric acid. It forms fine needles stable in air, and is decomposed by cold and even more readily by boiling water, forming first the dibasic and finally the tribasic salt (Alders and Stähler, Ber. 1909, 42, 2261).

Lead pyrophosphates, a number of complex phosphates and *thiophosphates* (Gerhardt, Ann. Chim. Phys. 1848, [iii.] 22, 505; Ouvrard, Compt. rend. 1890, 110, 1334; Friedel, *ibid.* 1894, 119, 260; Ferrand, *ibid.* 1896, 122, 886), and also *lead phosphites* (Amat, *ibid.* 1890, 110, 901), have been prepared.

The following are naturally occurring lead phosphates and arsenates isomorphous with apatite, a portion of their chlorine often being replaced by fluorine:

Pyromorphite $Pb_3(PO_4)_2Pb_2ClPO_4$; *Polysphærite* $(PbCa)_3(PO_4)_2(PbCa)_2ClPO_4$; *Mimetesite* $Pb_3(AsO_4)_2Pb_2Cl(AsO_4)$; and *Kampylite* $Pb_3[(As,P)O_4]_2Pb_2Cl[(As,P)O_4]$.

Lead arsenate may be formed by suspending litharge in a solution of arsenic acid in the presence of nitric or acetic acid as catalyst (U.S. Pats. 892603, 903389, 1908; J. Soc. Chem. Ind. 1908, 1019, 1203), or by roasting a mixture of white arsenic and a lead salt in combining proportions in the presence of oxygen or an oxidising agent (U.S. Pat. 929962, 1909).

Lead arsenate is used as an insecticide and is largely employed in the United States for the protection of fruit trees from the larvæ of the gypsy moth. For this purpose, it is said to be best prepared by adding a solution of lead acetate or nitrate to sodium arsenate until an iodine test paper shows the presence of excess of lead (Haywood and McDonnell, J. Soc. Chem. Ind. 1910, 1027; *see* also Pickering, Chem. Soc. Trans. 1907, 312). For spraying plants, it is often mixed with lime-sulphur solution; in this case, the normal lead salt should be employed, and it is best to avoid using water containing much alkali carbonate, as the tendency of the latter is to make the arsenic soluble (Brady and Tartar, J. Ind. Eng. Chem. 1910, 2, 328; *see* also Griffen, *ibid.* 1909, 1, 659; Moreau and Vinet, Compt. rend. 1910, 150, 787).

Lead silicates. Silica fuses with lead oxide forming a yellow glass. Lead silicate also forms a constituent of flint glass. Two silicates have been isolated (Cooper, Shaw, and Loomis, Amer. Chem. J. 1909, 42, 461). *Lead orthosilicate* Pb_2SiO_4 forms colourless hexagonal tablets, and has m.p. 746°.

Lead metasilicate $PbSiO_3$ has m.p. 766°, and has been found to exist naturally in Mexico as *alamosite.* It is analogous to *wollastonite*, calcium silicate, and occurs in radial aggregates of colourless transparent fibres (Palache and Merwin, Amer. J. Sci. 1909, 27, 399; *see* also Hilpert and Weiller, Ber. 1909, 42, 2969; Hilpert, Metallurgie, 1908, 5, 535).

Lead silicofluoride is formed by heating galena or other lead-containing material with hydrofluosilicic acid, air being blown through the mixture and water being then added (U.S. Pats. 754667, 1904; 779091, 779092, 1905). (For the use of lead silicate in glazes *v.* FRITTS and GLAZES.)

Lead borates and lead boric glasses have been prepared (Faraday, Phil. Trans. 1830, 1).

Lead and **sulphur.** *Lead sulphide* PbS occurs in nature as *galena*, usually in the form of cubes, possessing a bluish-grey colour, and sp.gr. 7·25–7·7 (Hannay, J. Soc. Chem. Ind. 1894, 639). It may be formed by passing sulphur vapour over lead, by fusing lead oxide with excess of sulphur, or, in an amorphous condition, by passing sulphuretted hydrogen into a solution of lead nitrate. When heated in a current of certain gases, it sublimes in cubes, whilst if fused with potash and sulphur, it forms octahedral crystals. In a current of sulphur dioxide it has been said to form the compound PbS_2O_2; but this has been disputed (J. Soc. Chem. Ind. 1894, 813).

Lead sulphide has m.p. 1120°±10° (Friedrich, Metallurgie, 1907, 4, 479; *ibid.* 1908, 5, 23); according to Lodin (Compt. rend. 1895, 120, 1164), the m.p. is 935°. It is converted by nitric acid into nitrate and sulphate, and is decomposed by hot strong hydrochloric acid, sulphuretted hydrogen being evolved. Lead sulphide forms double compounds with the halides of lead (Hünenfeld, J. pr. Chem. 1836, 7, 27; Parmentier, Compt. rend. 1892, 114, 299; Lenher, J. Amer. Chem. Soc. 1895, 17, 511; *ibid.* 1901, 23, 680), and also with bismuth sulphide (Ducatte, Compt. rend. 1902, 134, 1061). The reactions between lead sulphide and its oxidation products have been studied in detail by Schenck and Rassbach (Ber. 1907, 40, 2185, 2947; *ibid.* 1908, 41, 2917).

A *polysulphide* PbS_5 is formed as an unstable purple-red precipitate by precipitating lead nitrate at 0° with calcium pentasulphide and washing the precipitate with carbon disulphide (Bodroux, Compt. rend. 1900, 130, 1397).

Lead sulphate is found native as *lead vitriol* or *anglesite*, in transparent rhombic crystals isomorphous with *celestine* and *heavy spar.* It may be obtained as a white powder by precipitating a lead salt with sulphuric acid or with a soluble sulphate, or by the action of sulphur dioxide on lead peroxide (Marino, Zeitsch. anorg. Chem. 1907, 56, 233). It may also be obtained crystalline (Manross, Annalen, 1852, 82, 360). Lead sulphate has sp.gr. 6·2–6·3, and is said to melt without decomposition at a red heat, but according to Schenck and Rossbach (*l.c.*) it does not melt below 1100°. It is soluble in pure water to the extent of 0·0824 gram of lead sulphate per litre or 1 in 12135 at all temperatures, but the solubility diminishes on addition of sulphuric acid (Sehnal, Compt. rend. 1909, 148, 1394; *see* also Dolezalek and Finckh, Zeitsch. anorg. Chem. 1906, 51, 320). Lead sulphate is also soluble in alkalis, in ammonium and in calcium acetates, and in a number of other salts (Long, Amer. Chem. J. 22, 217; Reichard, Chem. Zeit. 1903, 27, 924, 943; Fox, Chem. Soc. Trans. 1909, 878). It forms double salts with the sulphates of tin (Weinland and Kühl, Ber. 1906, 39, 2951); with potassium (Belton, Chem. News, 1905, 191); and with arsenic (Kühl, Arch. Pharm. 1907, 245, 377).

Lead disulphate or *Plumbic sulphate* $Pb(SO_4)_2$ is obtained at the anode when pure sulphuric acid, of sp.gr. 1·7–1·8 is electrolysed between lead electrodes. It is a white or faintly greenish-yellow crystalline powder, giving a green solution in strong sulphuric acid. It is decomposed by water, forming sulphuric acid and lead peroxide, and is a powerful oxidising agent. It forms double salts with the alkali metals and also with aniline and with dimethyl and diethyl aniline (Elbs and Fischer, Zeitsch. Elektrochem. 1900, 7, 343). On the preparation and use of basic lead sulphate, *v.* above.

Lead sulphite and *lead thionates* are also known.

Lead selenide (Pélabon, Compt. rend. 1907, 144, 1159); *selenites* (Marino, Zeitsch. anorg. Chem. 1909, 62, 173); and *selenates* (Mathers, J. Amer. Chem. Soc. 1908, 30, 1374), also exist.

Lead organic compounds. The lead alkyl compounds are prepared by the interaction of alkyl iodides and lead-sodium or by the action of lead chloride on zinc alkyls (Buckton, Annalen, 1859, 109, 222; Cahours, *ibid.* 1862, 122, 65; Ghira, Gazz. chim. ital. 24, i. 44. 320; Frankland and Lawrance, Chem. Soc. Trans. 1879, 245; Klippel, J. 1860, 383).

Lead ethoxide $Pb(OEt)_2$ has been prepared by suspending thin sheets of lead over absolute alcohol through which a stream of ozone is passed. When washed with alcohol and dried *in vacuô* over sulphuric acid, it forms a light yellow friable powder, soluble in, but readily hydrolysed by water (Perkin, Chem. Soc. Proc. 1908, 179).

Lead tetraphenyl may be obtained by the action of lead chloride on an ethereal solution of magnesium phenyl bromide (Pfeiffer and Truskier, Ber. 1904, 37, 1125; Polis, Ber. 1887, 20, 3332).

A number of other aromatic and aliphatic alkyl and halogen alkyl compounds have been prepared (Pfeiffer and Truskier, *l.c.*; Polis, *l.c.*, and 717).

Lead thiocarbamide halides $Pb(CH_4N_2S)_2X_2$ ($X=Cl,Br,I$) are described by Rosenheim and Meyer (Zeitsch. anorg. Chem. 1906, 49, 13).

For the lead salts of organic acids, *see* the respective acids. Z. K.

LEADHILLITE. A rare mineral approximating in composition to the formula

$$PbSO_4·2PbCO_3·Pb(OH)_2.$$

The monoclinic crystals have the form of six-sided plates or pseudo-rhombohedra with a perfect basal cleavage and pearly lustre. As indicated by variations in the optical characters and chemical composition, there appear to be at least three varieties or modifications. The mineral is found in the upper oxidised portions of veins of lead ore at but few localities, notably at Leadhills in Scotland. It has also been met with in lead slags left by the Romans. 'Susannite' is a variety from the Susanna mine at Leadhills, and the name 'maxite' has been applied to crystals from Sardinia. L. J. S.

LEAF GREEN. *Chrome Green* (*v.* PIGMENTS).

LEATHER. When the skins of animals are treated with infusions containing any of the vegetable tannins, the gelatinous tissue is converted into the tough imputrescible substance known as leather, while the process by which it is made is called 'tanning.' Certain mineral salts, as well as oils and fats which undergo oxidation in the skin, have a somewhat similar effect, and more recently, aldehydes, and especially formaldehyde, have been successfully employed. It is proposed in the following article first to describe the structure and chemical composition of skin, and the preliminary processes it has to undergo to deprive it of hair and to render it fit for tanning, and then to deal with the different tanning materials and the various processes by which they are employed in practice.

The skin, as it exists on the animal is much more than a mere covering, and contains a variety of organs, both of sense and of secretion, and some knowledge of its anatomy is necessary to a proper understanding of the tanning process.

The skin consists of two layers, which arise in embryonic development from the inner and outer layers of the ovum, and which throughout retain the strongly marked differences which correspond to this diversity of origin. The *epidermis* or outer layer of the skin is derived from the outer layer (epiblast) of the ovum, while the inner layer, *corium*, *derma*, or *cutis*, together with all the other connective tissues of the body, takes its rise from the middle of the ovum (mesoblast). Though the skins of different animals differ in details, that of the calf, of which a section is illustrated in Fig. 1, may serve as a type of most of those used in the manufacture of leather. The outer layer or *epidermis* consists, as has been said, of simple nucleated cells, which at the surface are dead, hardened, and flattened, but where they rest on the *corium* are soft and spherical, and constitute the so-called 'mucous layer' (*rete mucosum*). This is not supplied directly with blood-vessels, but derives its nourishment from the fluids of the *corium*. Here growth takes place, and the cells probably multiply by fission, though this has not been actually observed. The hairs, though deeply rooted in the *corium*, are really products of the *epidermis* which surrounds them and passes down into the *corium* in the form of a bulb-shaped sheath. The nourishment of the growing hair is supplied by a knob of connective tissue called the hair-papilla, furnished with blood-vessels, and passing up into the centre of the hair-bulb. The hair itself is composed of modified and hardened cells, forming exteriorly irregular overlapping scales, giving the outline a serrated appearance, which is especially marked in wool. Within this 'hair-cuticle,' as it is sometimes called, is the fibrous portion of the hair, composed of long spindle-shaped cells, and sometimes in the centre of this is a cellular pith containing air. The hair, except in white animals, contains a good deal of pigment, and some is also present in the epidermis cells forming the hair-sheath. The new hair, both in fœtal development and in ordinary growth, begins as a thickening of the *epidermis* layer, forming a knob which gradually sinks into the *corium*, and becomes a bulb in which the hair is developed and forces its way to the surface much as an onion does to the surface of the ground. In animals which change their coats in spring, the young hair generally originates in this way from a new bulb formed below the old one, and passes up into the old sheath. This deep-seated origin explains the great difficulty found in removing these young hairs for technical purposes. Besides the hairs, sudoriferous and sebaceous glands are similarly developed from the *epidermis*. The sebaceous glands are seated round the stems of the hairs, and their ducts discharge oily matter which serves as a lubricant into the hair sheaths near the surface of the skin. The sudoriferous glands are more deeply placed, usually extending even below the hair roots; they are less convoluted than in man, and discharge through narrow sinuous ducts to the surface.

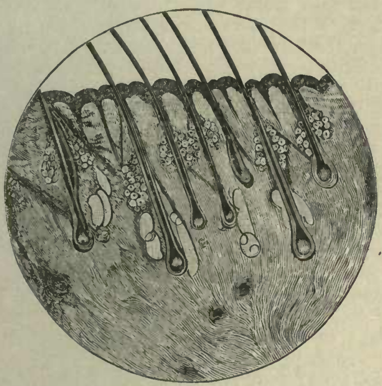


FIG. 1.

The *corium* consists mainly of connective tissue, which, on boiling with water, readily dissolves, and is wholly converted into gelatin. In most animals the principal part of the hide (*pars reticularis*) is composed of bundles of interlacing fibres, each of these bundles being formed of a multitude of fine fibrils. Towards the outer surface these bundles disappear, and the separate fibrils combine in a closely-matted felt (*pars papillaris*), which is technically known as the 'grain.' In the pig, and possibly also in the seal, this close-textured part is thick, and is all that is valuable for tanning, the reticular part being so slightly developed as not to be distinguishable from the looser fatty tissue (*panniculus adiposus*), which underlies the true skin. Consequently, these skins are remarkable for extreme toughness. In addition to this gelatinous structure, the true skin contains certain yellow fibres called 'elastic,' and distinguished by their very difficult solubility in boiling water, acids, and alkalis.

Between the *corium* and the *epidermis* is an extremely fine membrane, known as the hyaline layer. This is very difficult to demonstrate microscopically, but has been separated in some technical operations, and is probably the cause of the clear brown or buff colour of the grain surface of tanned leather, while the finely matted tissue below it remains nearly white.

The *corium* has also blood-vessels, nerves, and minute muscles for erecting the hairs; but none of these is of much technical importance, and for further details the reader may be referred to Procter's Leather Industries Laboratory Book, Principles of Leather Manufacture, or to the larger anatomical works.

A few words must, however, be said about the practical microscopic examination of skin. For this purpose it is necessary to produce extremely thin sections, and the skin must be previously hardened. To this end it may be cut into strips about ½ inch long by ¼ inch wide, with their length at right angles to the direction of the hair, which should be cut short with scissors, with which also the loose fatty subcutaneous tissue should be removed. The strips are placed in a closed vessel with several times their volume of methylated spirit diluted with an equal quantity of water. The next day this must be replaced by stronger alcohol, and finally by absolute. In 4–8 days, the hide will be hard enough to cut, and may be held between the finger and thumb, and shaved by a drawing cut with a very sharp razor flooded with alcohol and resting on the tip of the forefinger. The cut should begin at the grain side, and must be exactly parallel with the hairs to give good results. For this reason a microtome is of very little service, as it is more difficult to adjust the fragment of hide in it than to make the sections by hand. They are floated off the razor in alcohol, and must be stained in order to make the details visible. Various methods of staining are described in the microscope text-books, one of the simplest being to immerse in aqueous solution of picrocarmine. The carmine stains the connective tissue and the nuclei of the cells red, while the structures derived from the *epidermis*, the *erectores pili* muscles, and the blood-vessels, absorb the picric acid only, and become yellow. The section may now be soaked in glycerol to clear it, and examined in a drop of glycerol under a thin cover-glass; or may be permanently mounted in glycerol or Farrant's fluid; but for this purpose it is generally better, instead of clearing with glycerol, to soak the sections again for some time in absolute alcohol containing a little picric acid, till quite deprived of water, clear in clove oil, and mount in a drop of solution of gum dammar in benzene, or of Canada balsam.

Kathreiner has described a method which, while it is less striking for demonstration of the different tissues, is better adapted for practical work when a knowledge of the general appearance of the structures has been attained. The fresh hide (and it is important in preparing type specimens that the animal should not have been killed more than a few hours) is cut into small strips as described, and then immersed for 4–8 days, according to the thickness of the hide, in about twelve times its volume of an aqueous solution containing 1 p.c. of osmic and 2½ p.c. of chromic acids. This solution must be kept from light and dust in a stoppered bottle and in a cool place. Care must be taken to avoid the fumes, which cause severe catarrh of the mucous membranes. The hide pieces must now be soaked in about twelve times their volume of absolute alcohol several times renewed for 4–8 days, and are then cut as described. No further staining is required, as the chromic acid colours the tissues yellow, while all traces of fat, as for instance, the oily matter of the sebaceous glands, are stained grey or black by the osmic acid. They may be cleared at once with clove oil, in which they may be examined, or mounted in dammar.

A third method may be mentioned which is very useful for rapid observations, especially when it is desired to ascertain how far the cellular structures have been affected in preparing the hide or skin for tanning. The section, which need not be so thin as when intended for more detailed study, may be cut either after a short hardening in alcohol, or in the case of hide swollen with lime, simply by cutting a small strip ¾ through from the grain, and turning it back so as to put the tissue on the stretch, and then cutting from flesh to grain with a razor flooded with distilled water. If the wet section be placed in a drop of water on a slide under a cover glass, and examined by reflected light with a 1-inch objective, the fat glands will be seen as yellow masses embedded in the white fibrous tissue. If now the section be moistened with a mixture of equal parts of glycerol and glacial acetic acid, the connective tissue will become quite transparent, and the glands and hair-roots may be examined, even with a moderately high power, by transmitted light.

The principal chemical constituents of the skin are proteids, fats, and water; and the most important of these is collagen, of which the white fibres, forming the main fabric of the hide, are composed, and which, on boiling with water, is converted into gelatin (glutin). The remaining proteids (keratins, elastins) are mostly albuminoids, but glycoproteins (mucins) and those of the blood and lymph (serum albumens, hæmoglobin, &c.) are also present.

The *epidermis* and its products, hair, horns, hoofs, &c., all belong to the class of keratins, which are allied to coagulated albumen, but differ in their composition (*e.g.* in their percentage of sulphur), and in their behaviour towards chemical reagents. They can hardly be said to be soluble in water, though by prolonged boiling under pressure they are finally dissolved to an extract which does not gelatinise on cooling. The softer structures are easily soluble in dilute caustic alkalis in the cold, whilst hair and horn are gradually softened, but only yield to strong solutions aided by heat. They are reprecipitated by acids, and these precipitates mixed with oil have been proposed as a ‘filling’ for alumed leather in place of flour and egg-yolk, but have not come into practical use. Lime and other alkaline earths act like the alkalis, and hence milk of lime, while it scarcely attacks the hair, easily loosens it, by dissolving and softening the *epidermis* and root-sheaths. Strong solutions of the alkali and alkaline-earth hydrosulphides, on the other hand, seem to attack the harder tissues by preference, and reduce the hair to pulp without affecting the *epidermis* cells so much as milk of lime.

Collagen forms nearly 95 p.c. of the dry matter of the *corium* and is insoluble in cold water, dilute acids, and common salt solution (Reimer's statement that it is soluble in 10 p.c. solution of NaCl has not been confirmed), and it is but slowly attacked by dilute alkaline solutions, but strong acids and alkalis have a hydrolysing action, yielding soluble products. Boiling water has a similar effect, the first stage in this case being gelatin, which is slowly further attacked, continued hydrolysis yielding hemicollin and semiglutin, and later gelatoses and glutin peptones.

Hofmeister, who has studied these changes, proved that the production of gelatin from collagen is merely hydrolytic, with an increase of weight of about ¾ p.c. As final products of prolonged hydrolysis, ammonia, and amino-acids are formed, among the latter, glycine (amino-acetic acid), glutaminic acid, leucine (amino-caproic acid) arginine, lysine, and α-proline being the most important, while tyrosin and tryptophan are absent. Thus all the products of collagen belong to the antigroups of proteids, and aromatic groups are almost absent, in this respect showing a marked difference from keratin and the albumins.

Hydrolysis of collagen is also produced by pepsin (in slightly acid solutions), but trypsin has no dissolving action on collagen if the latter has previously been treated with water at 70° or with acids. Putrefactive bacteria rapidly lead to the final products of hydrolysis (amino acids, &c.).

Elastins form the substance of the ‘yellow’ or ‘elastic’ fibres which act as a sort of soft framework to the connective tissue, and are remarkable for their great resistance both to putrefaction and to chemical reagents.

Mucins are present both in the mucous layer and in the substance which cements the fibrils into fibre-bundles. The nature of this interfibrillar substance, called coriin by Reimer, has been much disputed. Rollet,[1] who first studied it, considered it of a mucous nature, but Reimer [2] claimed that it differed from mucins, and was a hydrolysis-product of the fibres themselves. Körner [3] held a similar view, taking it to be collagen rendered more soluble in alkalis by swelling and hydration. Both Halliburton [4] and Van Lier,[5] on the contrary, favour its mucin character, and the latter names it coriomucoid (in distinction from tendo-mucoid).

[1] Sitz. Ber. Wien. 1858, 30, 37.

[2] Dingl. poly. J. 205, 143.

[3] Jahresbericht der deutscher Gerberschule, Freiberg, 1898.

[4] Jour. Pathol. & Bacteriol. 1892, 1.

[5] Zeitsch. physiol. Chem. 61, 1909.

The mucins are easily soluble in even dilute alkaline solutions, and are dissolved during the process of liming, allowing the epidermis to be mechanically removed and isolating the fibrils.

Fats.—A distinction must be made between those of the *epidermis*, which are largely unsaponifiable, and consist mainly of cholesterols and liquid waxes; and those of the fat-cells of the *corium*, which are almost entirely triglycerides like most ordinary fats. The former exist not only as products of the sebaceous glands (wool-fat, &c.), but are combined with the keratins, rendering the *epidermis* more resistant, and thus fulfilling a similar function to the waxes in plants (Liebreich [1]). The fats of the *corium*, like those of the body, vary in composition, and especially in the proportion of olein to stearin and palmitin, with the age, sex, and food of the animal, but are usually of lower melting-point than the corresponding internal fats. They are liquid during life but in warm blooded animals solidify after death.

Fresh hides and skins contain 50–70 p.c. of water of which the larger proportion is in the *corium*, and the total is highest in young animals. In the adipose tissue below the skin, the proportions of fat and water are approximately equal.

Hides and skins reach the tanner in various states. Most of those from animals killed in this country are either fresh or very slightly salted, but those from greater distances are treated in various ways to preserve them. Perhaps the simplest and best is the use of salt, either sprinkled on the flesh side repeatedly, or used in the form of brine. In this way most European hides, and many of those from North and South America, are cured. In countries remote from the sea, hides are frequently first salted and then dried, so as to save weight in carriage, and at the same time to preserve them better. This is called 'drysalting.' A still commoner method, especially where salt is scarce and costly, is simply to dry the hide or skin either by hanging in the shade or by stretching on the ground in the sun. Many hides from Texas and Central and South America are thus treated, as well as smaller skins from more temperate countries. The hides of the small cattle of India, called 'kips,' are dried and then plastered on the flesh side with a mixture of a sölute saline earth containing sodium sulphate and water, to preserve, and incidentally, to weight them. Sometimes a portion of arsenic is used to prevent the ravages of insects. It has been proposed in Germany to substitute sodium sulphate for common salt in the curing of skins, both on account of the tax on salt, and because the former retains water, and consequently increases the weight of the hide. The advantage of this to the tanner does not seem obvious. In Russia and other cold climates, hides are sometimes preserved by freezing.

Preparation of hides for tanning.—Preliminary to any other treatment, it is necessary to soften hides and skins, and to free them from blood and dirt. When fresh, a few hours, or at most a day or so in one or two changes of fresh water is sufficient to accomplish this; and for sole leather the cleansing does not need to be so thorough as for the finer sorts, whilst too long soaking is apt to lead to incipient decomposition, and to yield a soft and light-weighing product. Where goods are salted, a much more thorough washing is desirable, and it is advisable to give three or four changes of water to remove the salt as rapidly as possible, and to swell the tissue, which is more or less dehydrated by salting.

When hides have been dried, a mere soaking is in most cases insufficient to produce complete softening, and in addition mechanical and chemical means have to be employed. Eitner has pointed out that the higher the temperature at which the original desiccation took place the greater is the difficulty of softening; calfskin which has been dried at 60° refusing to soften sufficiently for tanning either by soaking or mechanical means. This is analogous to the fact that gelatin dried at 130° becomes insoluble even in boiling water. For thin skins, such as calf or sheep, dried in the open air in temperate climates, a simple soaking of some days in cold fresh water, assisted by working over the beam with a blunt knife, is enough. On the other hand, for the sun-dried kips of India or the heavy ox hides of Texas and South and Central America, such treatment would be quite ineffectual, and the method was formerly adopted in this country of soaking for 2 or 3 weeks in water, which being seldom changed and highly charged with organic matter from previous parcels of hides, was in a state of active putrefaction. Such soaks will soften much more rapidly than fresh water, and are effectual where even prolonged treatment with it would fail. In India, hides are softened by the native tanners within 24 hours, by plunging them into pools in which all the refuse of the tannery is allowed to collect and putrefy. It has, however, come to be recognised by observant tanners that this putrid soaking is very dangerous and unsatisfactory, especially where the hides are destined for sole leather, since it has always a destructive effect on the tissue, and it is found that a much more rapid and satisfactory softening may be effected by the use of very dilute solutions of sodium hydroxide, or sodium sulphide, or of weak organic acids. When the hides or kips were so far softened that they could be bent sharply without danger of breaking the fibre, they were worked in the 'stocks' or 'hide-mill,' which is a machine in which two large hammers or plungers work the hides with a sort of kneading action, but this violent treatment has been rendered unnecessary by the chemical treatment, and at most a drumming with warm or tepid water in a rotating 'tumbler' like an immense barrel-churn is all that is needed. A machine in use on the Continent for the same purpose consists of two rollers studded with rounded pegs, or of which one is grooved and the other pegged. The hides are passed back and forwards between these, and undergo a sort of kneading action. A solution of sulphurous acid of about N/20 strength followed by cold water, has also been successfully used, and from its antiseptic effect, seems particularly suited for hot climates. When the hides or skins are thoroughly softened they are ready for depilation.

Depilation.—With a few exceptions, which scarcely come properly under the head of

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[1] Virchow's Archiv. 121, 183.

'leather,' it is necessary to remove the hair preparatory to the tanning process. Probably the oldest way of doing this is by putrefaction, or as it is technically called, 'sweating.' This was formerly accomplished by leaving the hides or skins, folded or laid together, in a warm and moist place, till the destruction of the *epidermis* liberated the hair. But though the *corium* was somewhat more resistant to putrefaction than the mucous layer of the *epidermis*, the putrefactive change frequently spread into it, and injured at least its surface. This simple form of sweating may now be considered obsolete, and where putrefaction is still employed, it is by what is known as 'cold sweating,' which, though little used in England, is still employed in America in the treatment of dried hides. In this method the hides are suspended from tenterhooks in well-ventilated chambers, usually almost buried in soil or spent tan, so as to maintain an equable temperature (which is generally somewhere between 15° and 20°, the higher the more rapid being the action). The air is kept saturated with moisture, and the temperature regulated by admitting steam under a false bottom, or a spray of water from pipes provided for the purpose. The hides, which if dried must previously have been thoroughly softened, are ready for unhairing in 3–7 days, and during the latter part of the time must be examined from hour to hour, and, as soon as the hair is loosened, taken down and placed in piles on the floor. As the thick parts take longer to unhair than the thinner, and the process proceeds more rapidly at the top than the bottom of the chamber, the position of the hides must be altered as the action progresses. When the hair is fully loosened, it is removed either by scraping with a blunt two-handled knife on a sloping 'beam,' or by fulling with stocks. Some American tanners now give a light liming before unhairing to slightly plump the goods and check the decomposition. A similar process is largely employed in Europe for unwoolling sheepskins; in this case to avoid the injurious effect of lime upon the wool. The process is not wholly bacteriological, since ammonia, which is largely evolved, acts as a caustic alkali on the epidermis and is itself capable of loosening the hair without putrefaction.

In England, both for sole and dressing goods, the hair is almost universally loosened by the use of lime. The pits are usually, though by no means invariably, worked in sets of three, of which one is old and nearly exhausted, the second fairly good, and the third freshly made or strengthened. The duration of the process is very variable, ranging from 4 or 5 to 14 days or more, and the quantity of lime used is yet more indefinite, being variously stated at from 1 lb. to 12 lbs. per hide. The fact is, that, lime being very scantily soluble in water, any quantity beyond that required to maintain a saturated solution has but little effect. Lime is only soluble to the extent of about 1¼ oz. per cubic foot, but of course is continuously absorbed by the hide, so that an excess is required which may be less the more often the hides are moved and brought in contact with fresh portions of the lime liquor. Hides lime well and rapidly, suspended from frames in pits, especially if rocked or frequently shaken, and in any case the more frequently they are moved, the better and more uniform is the action; mechanical motion is largely in use on the Continent, and to a limited extent in England. In America, the hides are usually tied together by the shanks and wound from one pit to another over a 'reel' or skeleton drum, turned by hand or power. The old lime liquors become charged with ammonia and organic products from the hides, which materially modify their action, rendering more lime soluble, but diminishing its plumping effect. One result of this is that hides unhair more readily out of a somewhat old lime than they do out of one freshly made, and a change from an old into a newer and stronger lime sometimes actually sets the hair firmer at first, by plumping the tissue and so grasping the root-bulbs. Experiments seem indeed to render it probable, however, that lime alone in the complete absence of putrefaction, will not loosen the hair in any reasonable time. If hides be limed for 1 to 4 days in a sharp new lime in which they are frequently drawn, and are then transferred into a pit of water maintained at a temperature of 40°–50° for some hours, they will part readily with their hair, and at the same time be to a considerable extent freed from lime. This plan, which is of American origin, and is sometimes called the Buffalo method, may be highly recommended for sole leather, giving good weight and colour and a firm solid texture. Of course, the relative amount of liming and hot water may be varied to a considerable extent.

Unhairing may also be hastened by warming the limes themselves. The heat increases the solvent power of the lime, but at the same time checks the plumping, and the tendency is to produce a soft and porous leather. Hence the method is ill adapted for sole, and even for dressing leather is undesirable, since the same effects are obtained better in other ways.

It has naturally been proposed to substitute the caustic alkalis for lime, and it is probable that it might be done in some cases with advantage, or at any rate that small quantities might be added to the limes to hasten their action; but so far their use has not found much favour with tanners, except as constituents of such secret preparations as 'Inoffensive.' One cause of this is probably that from their easy solubility and powerful action, great care is required, and where used by 'rule of thumb,' serious injury is readily done to large quantities of costly raw material. It is one of the virtues of lime that, from its very limited solubility, it is almost impossible to destroy a pack of hides by its use, and the injury which it does when carelessly handled is often attributed to other causes. Naturally it might be thought that the alkalis would be easily removed from the hide by simple washing, and that the solubility of their soaps would favour the removal of grease; but it is found that alkalis form a sort of compound with hide-fibre, from which they can scarcely be removed until they have first been neutralised with acid, while practically the grease is not saponified but merely emulsified, and for this purpose lime answers just as well as a stronger alkali.

In liming sole leather the principal object is to enable the hair to be removed and to free the hide from grease with as little solution of its fibrous structure as possible. The English tanner frequently desires also to raise or swell the hide, and so to split up the fibrous bundles into their constituent fibrils as to prepare it for tanning, though this may also be done by the presence of acid in the earlier tanning liquors, or in some cases by the direct use of an acid bath. It is a question on which there has been much difference of opinion whether the unhairing is best accomplished by the use of strong fresh limes for a short time, or of old limes charged with ammonia for a longer period. It is now, however, generally recognised that the continued action of old limes is too dangerous, usually injuring the grain surface of the hide or skin, and the compromise is usually adopted of beginning the process in the older limes and finishing in fresh ones. It is very dangerous in hot weather to let limes get too stale and loaded with organic matter, as in this case even the presence of caustic lime does not prevent putrefaction, which is fatal to the manufacture of plump and solid leather. In fact, by microscopic examination of such stale limes it is easy to detect the presence of active bacteria. It is a mistake to suppose that such limes are 'weak,' since the excess of lime is always sufficient to maintain them as saturated solutions, and in addition they contain much dissolved lime as organic salts, and considerable quantities of ammonia and bacterial enzymes, which, though they prevent swelling, assist in the solution of the hide. If in any case the liming is too low, it will be impossible to eradicate grease from the hides of very fat cattle, although the leather may be of excellent quality. In the manufacture of dressing leather a somewhat more thorough liming is generally desirable, since it is not only required to remove the hair but to dissolve a proportion of the cementing matter of the fibrous tissue, and so render the leather softer and more pliable. This is especially true in the manufacture of glove or 'glacé' kid and lamb leather, in which the property of stretching in any direction is largely dependent on a proper liming. In the continental manufacture of these goods it is customary to 'sharpen' the limes by the addition of realgar (arsenic sulphide). This produces, with the lime, calcium hydrosulphide, sulpharsenate, and some metallic arsenic, and considerably hastens the unhairing. The hydrosulphide seems to be the active agent, V. Schroeder and Delimitz-Dumont (Dingl. poly. J. 1896) having shown that the arsenic compounds are inoperative and not even antiseptic; and, many years since, the desirability of finding a substitute for the very poisonous red arsenic led Böttger to propose the use of calcium hydrosulphide, prepared directly by passing sulphuretted hydrogen into milk of lime. This produces a paste which is greenish from the presence of traces of iron sulphide, and which acts as a rapid depilatory, and if applied as a paste on the hair-side will in a few hours reduce the hair to a pulp, whilst from the rapidity of the action, the hair bulbs and the various glands are much less affected than with an ordinary liming. Mixed with lime in smaller proportion and used in pits in the ordinary way, it loosens the hair rapidly without actually destroying it, principally by attacking the mucous layer, since the harder part of the epidermis frequently comes off with the hair roots in it in sheets of considerable size. Unfortunately for its use in practice, for which otherwise it is excellently fitted, it keeps very badly, and must be freshly made as required which is both costly and troublesome. A concentrated solution of calcium hydrosulphide was formerly produced by the Washington Chemical Company, and promised to be a valuable depilatory; but unfortunately its manufacture proved unremunerative. Gas-lime, which often contains a considerable quantity of calcium hydrosulphide, has been used as a substitute, but is too uncertain in its composition to be satisfactory, and has been almost superseded as a gas-purifying agent by oxide of iron. None of these disadvantages attends the use of sodium sulphide, which has been strongly advocated by Eitner, a director of the Austrian Government Research Institute at Vienna, to whom the leather trade probably owes much of its impulse to scientific improvement. It is now manufactured commercially, in a crystallised form; it keeps well and possesses great depilatory powers, both alone and in union with lime, with which it forms calcium hydrosulphide and caustic soda. A paste containing 2–4 lbs. to the gallon of water, and thickened with lime to a soupy consistence, will, if painted on the hair side of a hide, completely destroy the hair in a few hours, so that it may be swept off with a stiff brush. This mode of proceeding has been much recommended for sole leather, and it makes a firm and solid article, but the difficulty of getting it so thoroughly brushed into the hair that it will destroy every part of it, is very considerable, while, if any part has been missed, the short hair is very difficult to remove. For this reason, and because it leaves all the hair-roots and glands in the skin and so prevents a clean buff, it is only suitable for very common classes of leather, though it will do good service on dried hides instead of the cold sweat. Such a paste is also much used for unwooling sheepskins, being in this case applied to the flesh side and allowed to penetrate the skin. Used in pits with lime to the extent of $\frac{1}{4}$–$\frac{1}{2}$ lb. per hide, sodium sulphide does not materially injure the hair, while it quickens the unhairing and yields good weight and excellent quality; but it must be borne in mind that sulphides do not swell the hide so much as caustic alkalis, so that the after process of tanning must be so arranged as to get the plumping in the liquors. Where plumpness is not desirable, but a tough, solid texture is required, as in some descriptions of light leathers, its use would promise special advantages. Since sodium sulphide, however, dissociates in solution to sodium hydrosulphide and sodium hydroxide, the effect of the latter leads to more swelling of the grain than is desired, and it is found that this may be lessened by the addition of an equivalent quantity of calcium chloride which substitutes calcium hydroxide for sodium hydroxide with formation of common salt.

The total soda existing in commercial sodium sulphide as sulphide, carbonate or hydroxide may be determined with standard acid, using methyl-orange as an indicator, since this colour is quite unaffected by the presence of either hydrogen sulphide or carbon dioxide. The sulphur is advantageously estimated by ammoniacal zinc solution, using alkaline lead tartrate as an indicator by placing drops of it and of the solution being tested near each other on filter paper. Solutions containing sodium sulphide together with dissolved sulphur and polysulphides obtained by boiling sulphur with caustic soda or soda ash and lime possess considerable depilatory power, but it is not easy to determine the amount of available sulphur. Somewhat similar solutions are obtained by forcing air through the 'tank waste' of alkali works, suspended in water, or, naturally, in the 'bog-liquor,' which in some works drains from the waste-heaps, and where these can be cheaply obtained, they may in some cases be used advantageously.

Examination of lime liquors.—Considerable information may often be obtained by a simple examination of lime liquors. Free ammonia may be determined by rapid distillation of, say, 30 c.c. of the filtered liquor, preferably with the addition of a little magnesium sulphate to remove caustic lime. The ammonia is absorbed in a measured quantity of standard acid which is titrated back with caustic alkali. If it be desired to estimate free lime in the same sample, the magnesium sulphate must be omitted, which, if the distillation is short, does not lead to serious error. The sample should be drawn from the middle of a lime pit well plunged up, and rapidly filtered in a funnel covered with a clock-glass.

The caustic lime in the portion from which the ammonia has been withdrawn may now be estimated with normal or decinormal acid, using phenolphthalein, and the total lime (and any other alkalis present) existing in a free state or in combination with organic matter and weak organic acids with methyl orange or red as an indicator. Litmus is unsuitable for the purpose from the presence of these weak organic acids, which render its end-reaction quite indefinite, but do not affect methyl-orange so much. For the same reason this indicator will be found very useful for many determinations required in a tannery. Phenolphthalein cannot be accurately used in presence of ammonia. An estimate of the organic matter present is obtained by evaporating 50 c.c. of the filtered liquor to dryness in the water-oven in a platinum crucible, weighing, and then igniting and estimating by loss. This method can of course lay no claims to strict accuracy, but is sufficient to give valuable information as to the condition of the liquor; and, if a uniform course of liming be adopted, as to the amount of matter dissolved out of the hides in the process, or the comparative quantities by different liming methods. For more accurate work the liquor may be evaporated to dryness or very small bulk in a flask with the addition of a little excess of sulphuric acid to retain ammonia, and the nitrogen estimated by Kjeldahl's method. It is easy to calculate very approximately the amount of matter which the nitrogen represents, since both the gelatinous and horny tissues contain about 17·5–18 p.c. of nitrogen.

Bateing and drenching.—If lime or other alkalis have been used in depilation, they must be removed before tanning, and in sole leather it is desired to do this with as little loss of pelt as possible. Formerly a mere suspension in water was considered sufficient, and when the water is hard, a little lime was added to remove the free carbonic acid and calcium hydrogen carbonate present, which would form insoluble carbonate with the lime contained in the hide, and afterwards by combining with tannin would produce bad coloured leather. A further cleansing may be effected by 'scudding,' or working the grain-side with a blunt knife on a beam, which expresses much of the *débris* of hair-roots and fat glands, as well as lime. When a clean buff is desired this precaution should never be omitted.

It is, however, impossible really to remove the whole of the lime by soaking in water, since it forms a sort of loose compound with the fibrous tissue, from which it can only be dislodged by the aid of acids, and at present, even for sole leather, acids are usually employed after removal of as much lime as possible by washing in 'softened' water.

Very dilute sulphuric acid will perform the service satisfactorily, although great care has to be used to keep the hides in constant motion, to add the acid in small successive doses as it is absorbed by the hides, and to avoid even a small excess. Some trouble is often experienced in the use of commercial acids from the precipitation of the iron which they contain as an impurity on the fibre of the hide, where it subsequently produces stains by combining with the tannin. The ammoniacal salts of the stronger acids may also be used, but boric, formic, acetic, lactic, and other organic acids are generally employed in solutions not exceeding about N/20 strength. For sole purposes, hydrochloric acid should be avoided, as the chlorides have a great effect in preventing the plumping of the hide which is so desirable in this class of leather. Instead of actually removing the lime it might be sufficient in many cases to convert it into a neutral and insoluble form, as, for instance, by the action of acid or neutral phosphates, oxalates, or arsenates. Some of the sulphonic acids of various coal-tar products have also been tried for the purpose with some success; and they are, at the same time, powerful antiseptics.

In the case of most light leathers where softness is aimed at, it is found necessary to use, either alone or as a supplement to some process of removing the lime, a putrefactive or fermenting bate, which has the effect of reducing ('abateing') the plumpness of the hide, and at the same time of softening it by attacking the fibrous tissue. Either an infusion of dung (pigeons', hens,' or dogs') called *bate* or *puer* (the latter probably having some connection with the French *puant*), or of bran (drench), and frequently both, are used successively. Probably the putrefactive organisms themselves or their products are active agents of the process, and the problem has been partially solved by Wood in England, and by Popp and Becker in Germany, who have introduced an artificial puer under the name of 'erodin,' consisting of a suitable culture of selected bacteria and a dry powder which when dissolved in water forms a suitable nutritive fluid for their rapid multiplication.

Dr. Röhm, following up an experiment of Wood's, has also introduced under the name of 'Oropon,' a mixture of ammonium chloride with a small quantity of the pancreatic ferment, which, for some of the finer leathers, has been very successful.

In the preparation of 'shaved' and 'dressing' hides, a bate may contain about 1 peck of hen or pigeon dung to 25 or 30 hides, in which they are handled frequently for 3–7 days. This time may be much shortened by warming the bate and working the goods with a drum or paddle tumbler. The latter consists of a tank or pit, generally having a curved bottom to favour the motion of the liquid, and agitated by a paddle-wheel with 6–8 floats. A short 'stocking' out of the bate is also sometimes employed. Tumbling with warm water before bateing will wash out a good deal of lime and reduce the plumpness, and so save both time and material; and French tanners make excellent shaved hides and calf-skins without bateing by careful working at the beam, long washing with cold water (during which probably a slight putrefactive action takes place), and the use of weak and stale liquors. Shaved hides are so called because, after the bateing, the thicker parts of the butt are reduced by shaving on an upright beam with a currier's knife having a turned edge.

Still lighter and more flexible sorts of leather, such as morocco and kid, are usually puered with fermented dog-dung, infused in hot water, and strained through a basket. This is frequently followed, after scudding, by a drench made by pouring boiling water on bran, and allowing to ferment. In this case, lactic acid is the most active product, although its plumping action is controlled by some putrefactive fermentation going on at the same time. Wood (J. Soc. Chem. Ind. 9, 27) has shown that starch is destroyed by the active ferment, and considerable quantities of methane evolved. In hot and thundery weather the lactic ferment is liable to be replaced by another, partially the butyric, when the skins plump rapidly and become transparent, and are finally perforated or dissolved. The best precautions are to scald out the tubs thoroughly, and to wash the bran before using with cold water to remove the flour, which furnishes the nourishment required by the butyric ferment.

In the brief space available it is impossible to give more detail as to these preparatory processes, which are, however, of the first importance from a practical point of view. From the scientific aspect, it must be noted that the plumping and 'falling' which the fibrous tissue suffers through the action of various reagents, is closely connected with osmosis, and is at least as much a physical as a chemical phenomenon.

Tanning materials. Before speaking of the actual tanning process, a few words must be said about the chemistry of the vegetable products on which the operation depends.

The tannins, or tannic acids, are widely distributed through the vegetable kingdom, and form a large and varied class, differing considerably in chemical constitution as well as in properties. The one point which they all have in common is the power of precipitating gelatin from its solution as an insoluble compound. They are also all derivatives of the aromatic series of carbon compounds, and, so far as is known, all contain either pyrocatechol $C_6H_4(OH)_2$ or pyrogallol $C_6H_3(OH)_3$, and sometimes the isomeride of the latter, phloroglucinol. This difference usually corresponds to well-marked differences in constitution. As a rule, the pyrogallol tannins give a blue-black with ferric salts, and a whitish deposit on the surface of the leather, well known to the tanner as 'bloom'; whilst the pyrocatechol derivatives give a greenish black, and deposit red insoluble matters, probably anhydrides of the tannins. All catechol tannins give insoluble precipitates with bromine water, and with formaldehydes in presence of hydrochloric acid. Oak bark occupies an intermediate position, yielding both bloom and reds, and apparently containing both pyrogallol and pyrocatechol. In such cases, however, it is not very certain whether we have to deal with a complicated tannin or with a mixture of two dissimilar ones, since tannins, being neither crystallisable nor volatile, are very difficult to separate. It is known that many of the bloom-yielding materials, such as myrobalans, contain gallotannic acid, which yields no bloom, and ellagitannic acid, which yields a copious bloom of ellagic acid.

It is, of course, only the pyrogallol tannins which yield gallic acid as a decomposition product, while the pyrocatechol tannins contain the corresponding protocatechuic acid. Many of the pyrogallol tannins yield glucose on decomposition, but in the pyrocatechol class it seems to be absent.

A complete list of tannin-yielding plants would embrace a large part of the vegetable kingdom, but the following are those in most extensive practical use. (*Cf.* art. TANNINS.)

Oak bark is one of the oldest and best of tanning materials, producing excellent but not heavy leather; and, from its comparative weakness in tannin (8–12 p.c.) its action is somewhat slow. It yields a good deal of whitish bloom.

Valonia, the acorn cup of the *Quercus Ægilops* (Linn.) and *Q. Macrolepis* (Kotschy), contains up to 35 p.c. of a tannin very similar to that of oak bark, but giving more bloom and a darker colour, and at the same time a heavier leather.

Myrobalans, the fruit of *Terminalia Chebula* (Ratz.) (India), contains 25–35 p.c. of gallotannic and ellagitannic acids, and, consequently, blooms freely. It gives good colour and fair weight, and though alone it yields a porous and soft leather, it is very useful in mixture with dark coloured materials, such as hemlock extract, for sole leather, and as a cheaper substitute for sumach, on the lighter descriptions.

Divi-divi, pod of *Cæsalpinia coriaria* (Willd.) (S. America), contains 30–50 p.c. of a tannin somewhat similar in effect to that of valonia. It produces a heavy-weighing leather, but is dangerously liable to a sudden fermentation, which produces a deep-red stain on all leather in contact with it.

Sumach, the pulverised leaves of *Rhus Coriaria* (Linn.), &c. (Sicily), yields 20–30 p.c. of tannins very similar to those of myrobalans, but paler in colour. It is principally used for light leathers, though warm sumach liquor is used to brighten the colour of heavy tannages. There are also several American species used for tanning.

Mimosa bark, the product of several species of *Acacia*, principally Australian, contains 20–40 p.c. of a red tannin derived from pyrocatechol, and yielding no bloom, but giving considerable weight and firmness to the leather. An extract has recently been introduced into commerce. Babool bark from *Acacia arabica* (Willd.) is one of the principal tanning materials of India (*A. Catechu* (Willd.) and *A. Catechu* var. *Sundra*, see below).

Cassia auriculata (Linn.), Turwar or Tanghadi bark, from a leguminous bush allied to senna, is the principal tanning material for sheep and goat skins (so called ‘persians’) in Southern India.

Hemlock bark, known in this country principally in the form of extract, is produced by the hemlock pine, *Tsuga* [*Abies*] *Canadensis*, (Carr.) of North America. The bark contains 8–10 p.c., and the extract 20–30 p.c. of a tannin similar to that of mimosa, but giving a larger proportion of red anhydrides, and consequently a heavier leather, but at the same time one of a still more pronounced colour, which is less easily modified by other agents. It is the staple tanning agent of North America.

Gambier (*Terra Japonica*), pale catechu, an inspissated extract from the leaves of *Uncaria Gambier* (Roxb.) of the East Indies, contains 30–40 p.c. of a peculiar catechol tannin, which penetrates leather rapidly, but has less astringency and adhesion to the hide fibre than most other tannins. These properties make it very valuable in certain stages of the tanning process, although alone it produces a leather of very inferior quality. Cutch (dark catechu), though somewhat similar in its chemical relations, is a very different product practically, and is derived from the wood of *Acacia Catechu* (Willd.) and *A. Catechu* var. *Sundra*, and, consequently, more allied to the mimosa bark, which has already been described. Gambier comes to this country in blocks of about 2 cwt., covered with mat and pasty in the centre, and also in cubes of about an inch square, which are much purer, and internally are quite white with crystals of catechin. Cutch comes in masses of a glossy dark-brown fracture, and is principally used for dyeing.

Quebracho wood from *Quebrachia Lorentzii*, (Griseb.), a large tree of South America, and especially of the Argentine Republic, contains about 20 p.c. of rather difficultly soluble catechol tannin, principally used as extracts which are often decolorised and rendered soluble with bisulphites.

Mangrove barks from various species of *Ceriops* and *Rhizophora*. Extracts principally manufactured in East Indies. Barks vary a good deal in strength but may contain up to 40 p.c. of a dark red but fairly soluble catechol tannin.

Mallet bark from *Eucalyptus occidentalis* (Endl.) or ‘flat-topped yate’ of Western Australia. Rich in a brown catechol tannin producing rather hard leather if used alone.

Ulmo bark, said to be from *Eucryphia cordifolia* (Cav.) of Chile, produces a dark red extract strongly resembling mangrove.

Exhaustion of tanning materials.—Most tanning materials require to be ground before lixiviating. This is accomplished either by a mill, on the principle of the ordinary coffee mill, with grooved iron or steel cones, or by one of the numerous forms of ‘disintegrator,’ in which the grinding is done by dashing the material against a serrated or grated casing, by beaters revolving 2000 or 3000 times a minute. Valonia and myrobalans are frequently crushed between fluted or toothed steel rollers. The grinding should not be so fine as to render percolation difficult. The actual exhaustion takes place in this country mostly in large square sunken vats, constructed like the other pits of the tannery and worked in series, the liquors being either pumped from one to the other or allowed to run through wooden boxes, connecting the space below the perforated ‘false bottom’ of one pit with the top of the next. In America the ‘leaches,’ as the extracting vessels are called, are usually immense circular tubs, fitted with perforated ‘false bottoms’ and heated by steam coils. These are generally employed in groups of 6 or 8, water or weak liquor being run on the most nearly exhausted, and forced or pumped round the series to the newest and strongest vat. Hot extraction is more rapid than cold, and usually more complete, but the liquor is darker in colour, and contains more non-tanning matters, and the question of temperature must be decided by the particular material and conditions, some tannins being decomposed at temperatures which are not injurious to others.[1]

Tanning extracts now form an important portion of the materials used by the tanner, and in many cases render available materials which from their bulk and low percentage, or their remote origin, would not pay for transit, or yield sufficiently concentrated liquors for modern requirements. Among those of leading importance may be mentioned those of the woods of oak, chestnut, and quebracho, and of the barks of mangrove and hemlock pine. Valonia, myrobalans, and sumach are also extracted. The materials are prepared and extracted as above described, woods being previously reduced to chips or shavings by machines similar to those employed for dyewoods, and heat, occasionally under pressure, being freely used in extraction, especially with the weaker materials, such as oakwood, which only contains 2–3 p.c. of tannins. When this is done, decolorising methods are frequently employed to remove the dark and difficultly soluble matters dissolved by heating; the most approved method being partial precipitation by blood or blood-albumen, dissolved in the warm infusion, which is then heated beyond the coagulation temperature. Metallic precipitants are also sometimes used, and sulphurous acid and bisulphites, not merely as bleaching agents, but to render the phlobaphenes and ‘reds’ more soluble. A so-called ‘pinewood extract’ is on the market, made by concentration of the sulphite liquors of cellulose manufacture, which analyses well, but contains no true tannin and is used mainly as an adulterant. After settling or filtering the decolorised liquors, they are concentrated in the vacuum pan to 50–60 p.c. of water for liquid extracts and 20–25 p.c. for those intended to solidify, the Yaryan evaporator being largely used for concentration up to about 20Bé.

Imperfect exhaustion is one of the most serious sources of waste in tanning, and the residues deserve more careful testing than is usually given to them.

Quantitative determination of tannins.—Many methods have been proposed for the

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[1] J. Soc. Chem. Ind. 1895, 635; 1898, 116.

purpose, several of which are capable of application under special conditions, but the only two that have stood the test of general practical work, and are valuable for different purposes, are the hide-powder method, which is the gradual development of the work of several chemists, among whom Simand may be specially mentioned, and the permanganate and indigo process of Löwenthal.

The first of these permits an actual gravimetric determination of the matters absorbable by hide, but these include colouring matters, acids, and other substances not strictly tannins. It has been found that the absorption of these matters is lessened by a light preliminary chroming of the hide-powder, and it must also be remembered that the method is purely empirical, and must therefore be carried out with absolute adherence to the smallest details if comparable results are to be obtained.

The following is the method of the International Association of Leather Trades Chemists, which is the official standard in Europe and only differs in minor details from that of the American Leather Chemists' Association.

Preparation of infusion.—Such a quantity of material shall be employed as will give a solution containing as nearly as possible 4 grams of tanning matter per litre, and not less than 3·5 or more than 4·5 grams. Liquid extracts shall be weighed in a basin or beaker and washed with boiling distilled water into a litre flask, filled up to the mark with boiling water, and well mixed, and rapidly cooled to a temperature of 17·5°, after which it shall be accurately made up to the mark, again well mixed, and filtration at once proceeded with. Sumach and myrobalans extracts should be dissolved at a lower temperature.

Solid extracts shall be dissolved by stirring in a beaker with successive quantities of boiling water, the dissolved portions being poured into a litre flask, and the undissolved being allowed to settle and treated with further portions of boiling water. After the whole of the soluble matter is dissolved the solution is treated similarly to that of a liquid extract.

Solid tanning materials previously ground till they will pass through a sieve of 5 wires per centimetre, are extracted in Koch's or Procter's extractor with 500 c.c. of water at a temperature not exceeding 50° and the extraction continued with boiling water till the filtrate amounts to 1 litre. It is desirable to allow the material to soak for some hours before commencing the percolation which should occupy not less than 3 hours, so as to extract the maximum of tannin. Any remaining solubles in the material must be neglected, or reported separately as 'difficultly soluble' substances. The volume of liquid in the flask must be made up accurately to 1 litre after cooling.

The *total solids* must be determined by drying a weighed portion of the material, or a measured portion of its uniform turbid solution at a temperature between 98·5° and 100° in shallow flat-bottomed basins, which shall afterwards be dried till constant at the same temperature, and cooled before weighing for not less than 20 minutes in an air-tight desiccator over dry calcium chloride. *Moisture* is the difference between 100 and the percentage of total solids, and *insolubles* the difference between the *total solids* and *total solubles.*

Filtration.—The infusion shall be filtered till optically clear (see below). No correction for absorption is needed for the Berkefeld candle, or for S. & S. 590 paper if a sufficient quantity (250—300 c.c.) is rejected before measuring the quantity for evaporation; and the solution may be passed through repeatedly to obtain a clear filtrate. If other methods of filtration are employed the average correction necessary must be determined in the following manner. About 500 c.c. of the same or a similar tanning solution is filtered perfectly clear, and after thorough mixing 50 c.c. is evaporated to determine 'total soluble No. 1.' The remainder is now filtered in the exact method for which the correction is required (time of contact and volume rejected being kept as constant as possible), and 50 c.c. is evaporated to determine 'total soluble No. 2.' The difference between No. 1 and No. 2 is the correction sought, which must be added to the weight of the total solubles found in analysis. An alternative method of determining correction, which is equally accurate and often more convenient, is to filter a portion of the tanning solution through the Berkefeld candle till optically clear, which can generally be accomplished by rejecting 300 or 400 c.c. and returning the remaining filtrate repeatedly; and at the same time to evaporate 50 c.c. of clear filtrate obtained by the method for which correction is required, when the difference between the residues will be the correction sought.

(Note.—It is obvious that an average correction must be obtained from at least 5 determinations. It will be found that this is approximately constant for all materials, and amounts in the case of S. & S. 605, 150 c.c. being rejected, to about 5 mgr. per 50 c.c. and where 2 grams of kaolin are employed in addition, to 7½ mgr. The kaolin must be previously washed with 75 c.c. of the same liquor, which is allowed to stand 15 minutes and then poured off. Paper 605 has a special absorption for a yellow colouring matter often contained in sulphited extracts.)

The *total solubles* must be determined by the evaporation of a measured quantity of the solution previously filtered till optically clear both by reflected and transmitted light; that is, a bright object such as an electric light filament must be distinctly visible through at least 5 cm. thickness and a layer of 1 cm. deep in a beaker placed in a good light on black glass or black glazed paper must appear dark and free from opalescence when viewed from above.

Hide-powder shall be of woolly texture, thoroughly delimed, preferably with hydrochloric acid, and shall not require more than 5 c.c. or less than 2·5 c.c. of N/10 NaOH or KOH to produce a permanent pink with phenolphthalein on 6½ grams of the dry powder suspended in water. If the acidity does not fall within these limits, it must be corrected by soaking the powder before chroming for 20 minutes in 10–12 times its weight of water to which the requisite calculated quantity of standard alkali or acid has been added. The hide-powder must not swell in chroming to such an extent as to render difficult the necessary squeezing to 70–75 p.c. of water, and must be sufficiently free from soluble organic matter to render it possible in the ordinary washing to reduce the total solubles in a blank experiment with distilled water below 5 mgr. per 100 c.c. The powder when sent out from the makers shall not contain more than 12 p.c. of moisture, and shall be sent out in air-tight tins.

The detannisation shall be carried out in the following manner :—

The moisture in the air-dried powder is determined and the quantity equal to 6·5 grams actual dry hide-powder is calculated, which will be practically constant if the powder be kept in an air-tight vessel. Any multiple of this quantity is taken according to the number of analyses to be made, and moistened with approximately ten times its weight of distilled water.[1] ·2 grams per hundred of dry powder of crystallised chromic chloride $CrCl_3,6H_2O$ [2] is now dissolved in water and made basic with 0·6 gram Na_2CO_3 by the gradual addition of 11·25 c.c. of N/1 solution, thus making the salt correspond to the formula $Cr_2Cl_3(OH)_3$. This solution is added to the powder and the whole churned slowly for 1 hour. In laboratories when analyses are frequently made it is more convenient to use a 10 p.c. stock solution, made by dissolving 100 grams of $CrCl_3,6H_2O$ in a little distilled water in a litre flask, and very slowly adding a solution containing 30 grams of anhydrous sodium carbonate, with constant stirring, finally making up to mark with distilled water and well mixing. Of this solution, 20 c.c. per 100 grams or 1·3 c.c. per 6 5 grams of dry powder should be used.[3]

At the end of one hour, the powder is squeezed in linen to free it as far as possible from the residual liquor, and washed and squeezed repeatedly with distilled water, until on adding to 50 c.c. of the filtrate, 1 drop of 10 p.c. K_2CrO_4 and 4 drops N/10 $AgNO_3$, a brick red colour appears. Four or five squeezings are usually sufficient. Such a filtrate cannot contain more than 0·001 gram of NaCl in 50 c.c.

The powder is then squeezed to contain 70–75 p.c. water, and the whole weighed. The quantity Q containing 6·5 grams dry hide is thus found, weighed out and added immediately to 100 c.c. of the unfiltered tannin infusion along with (26·5–Q) of distilled water. The whole is corked up and agitated for 15 minutes in a rotating bottle at not less than 60 revolutions per minute. It is then squeezed immediately through linen, stirred and filtered through a folded filter of sufficient size to hold the entire filtrate, returning until clear, and 60 c.c. of the filtrate is evaporated and reckoned as 50 c.c. or the residue of 50 c.c. is multiplied by $\frac{6}{5}$. The non-tannin filtrate must give no turbidity with a drop of a 1 p.c. gelatin 10 p.c. salt solution.

One gram of kaolin free from solubles must be used either by mixing it with the hide-powder in the shaking bottle or with the liquid before filtration.

All evaporation shall be rapidly conducted at steam temperature in shallow, flat-bottomed basins of not less than 6·5 cm. diameter to apparent dryness; and shall be subsequently dried between 98·5° and 100° in a water or steam oven until of constant weight, and shall be afterwards cooled in small air-tight desiccators over dry calcium chloride for at least 20 minutes, and then weighed rapidly. Not more than two basins shall be placed in one desiccator, and the basins must not be wiped after removal from the desiccator. The residue is 'non-tannins.' The difference between these and 'total solubles,' is 'tanning matters.'

The Löwenthal method is volumetric, and, as very much weaker infusions can be employed, a larger quantity of water can be used in extraction, or it may be applied to very weak infusions without concentration. It has gone out of use for commercial analysis, but the comparison of its results with the hide-powder method is sometimes useful in the detection of mixtures in extracts; and as a control method in tanning (*cp.* Procter and Hirst, J. Soc. Chem. Ind. 1909, 294).

The method depends on the oxidation of the tannin by permanganate in presence of excess of sulphonated indigo, which serves both as an indicator and regulator of the reaction.

The indigo solution is made by dissolving 5 grams of pure sodium or potassium indigo-sulphonate (Gehe's *Carminum cœrul. op.* answers well) in a litre of distilled water, adding 50 c.c. of concentrated sulphuric acid and filtering; or a solution of 1 gram 'Indigo pure B. A. S. F.' may be dissolved in 25 c.c. of concentrated sulphuric acid, and made up to 1 litre with water and a further 25 c.c. of acid. Samples which give a brownish instead of a pure yellow solution after oxidation are useless. The solutions keep well, but the weak permanganate is best made up as required, by diluting 100 c.c. of a 5 gram per litre solution to 1 litre.

The titration is best carried out in a beaker of 750–1000 c.c. capacity placed on a white tile; and if many titrations are to be made, should be provided with a screw-vaned stirrer driven by a turbine or other motor; but in any case the stirring must be vigorous and constant. 20–25 c.c. of the indigo solution, according to its strength, and 400 c.c. of good water free from organic impurity are introduced into the beaker, and permanganate solution is added from the burette as rapidly as it can be dropped until near the end-point. Uniformity in stirring and in the rate of dropping is of prime importance.

The colour changes first to green, and then to pure yellow, and as it approaches the latter, the flow must be checked and the last drops added very cautiously. The quantity of permanganate used will be that required to oxidise the indigo. If the process be now repeated with the addition of 5 c.c. of the tannin infusion, the excess required to destroy the blue will correspond to that required to oxidise the astringents added, and must not exceed two-thirds of that required for the indigo alone. A second estimation should not differ from the first by more than 0·1 c.c.; and the results added together will correspond to the total astringents in 10 c.c. of the infusion. But as gallic acid and other bodies always present in tanning materials are oxidised like tannin itself, it is necessary to make a second titration after removing the tannin, and estimate by loss.

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[1] Very woolly powders require slightly more than 10 times their weight of water. A powder may be considered 'woolly' if it cannot be poured like sand from a beaker.—H.R.P.

[2] 'Chrom-sesquichlorid cryst,' Kahlbaum.

[3] The solution sometimes changes colour slightly by keeping; but this has been shown to have no influence on results.—H.R.P.

For this purpose hide powder, either white or chromed, may be used as in the previously described process, or to 50 c.c. of the liquor 25 c.c. of a fresh 2 p.c. gelatin solution and 25 c.c. of a saturated solution of salt containing 50 c.c. of concentrated sulphuric acid per litre. The mixture is shaken with a teaspoonful of kaolin for 15 minutes, filtered, and 10 c.c. titrated. The results of the gelatin method in the separation of gallic from gallotannic acid are nearly exact, but probably by a compensation of errors.

As it is impossible to obtain *pure* tannins against which to standardise the results, which can only be compared with others obtained by a precisely similar mode of titration, pure recrystallised gallic acid has been found the most convenient and reliable standard, 5 c.c. of a freshly made solution of 0·1 gram per litre being titrated in place of the tannin solution. If it be desired to calculate from gallic acid to the results of the gravimetric method, the following figures may be employed, but it must be remembered that except in the case of gallotannic acid the comparison is not with a chemical individual, and the results only represent an average. 1 gram gallic acid = 1·34 gram gallotannic acid, 1·65 gram of the tanning matter of chestnut wood, 1·89 gram of that of oak wood, 1·73 gram of myrobalan, 1·69 gram of quebracho, and averaging all ordinary materials 1·76 gram. Further details are given by Procter and Hirst (*l.c.*).

Tannage of sole leather. As this is a simple and typical case of vegetable tanning it may be described in some detail. Knapp, in his classical essay on the Nature and Methods of Tanning (Natur und Wesen der Gerberei, Munich, 1858), adduces reasons for believing that leather is not an actual chemical combination of the gelatinous fibres of the hide with tannin, but rather that the action is a surface one in which they are coated with an insoluble matter which protects and makes them resistant to solvents and decay. Though this conclusion is probably not wholly true, it at least describes a reaction which is specially important in the case of sole leather. Whether the actual conversion of hide fibre into leather is the result of a strictly chemical combination, or of the formation of an adsorption compound, its solidification is certainly largely a case of surface action. It has been said that both acids and alkalis swell the fibrous bundles and split them into finer fibrils, so offering a larger surface and more finely divided texture, and to produce a heavy and solid tannage it is found necessary that this should take place either before or during the tanning process. The English sole-leather tanner usually accomplishes it by the action of lime in depilation; the American, who unhairs by sweating, has to secure it by a separate treatment with sulphuric acid, while in other cases where sulphides or low liming are the agents of depilation, it is partly accomplished by these and partly by the organic acids present in the earlier tanning liquors. The avoidance of stale or old limes is important, as they plump badly and cause serious loss of weight, but sodium sulphide is useful as shortening the process. When a hide swollen with lime is brought into tanning liquors the weak acids present rapidly neutralise the alkali, and the hide, previously plump and firm, becomes soft and flaccid and falls in thickness. If little acid is present in proportion to tannin this action takes place very gradually, and the tannin, which penetrates rapidly in the alkaline state of the hide, fixes the fibre in a swollen condition, and a plump rapid tannage is obtained, which, however, is often deficient in colour from the tendency of the lime to form tannates which darken in drying. If, on the other hand, the hide, comparatively freed from lime, is brought into liquors where acid predominates over tannin, the tissue, at first soft and flaccid, swells gradually and combines with the tannin in an acid condition, again producing a plump leather and of good colour, since lime tannates are easily soluble in the acids present. But if, on the other hand, the unswollen hide comes into liquors which have insufficient acid to plump it, or if, having been swollen by lime, it is allowed to fall back as before described, the tannin will fix it in this fallen condition, and it will be impossible afterwards to plump it or to make thick leather.

(The free acid capable of dissolving lime tannate in a liquor is easily determined directly by adding saturated lime-water from a burette to a measured quantity of liquor, till it forms a permanent cloudiness; 10 c.c. of liquor should require from 5 to 15 c.c. Some of the acids which dissolve lime are too weak to produce any perceptible plumping effect on the pelt.)

For common sole and strap leather the first of these methods may be adopted with satisfactory results, though a previous deliming of the surface with weak solutions of boric, acetic, lactic, or some other weak acid is becoming increasingly common. If this is not done the hides or ‘ butts ’ (from which the bellies and shoulders have been trimmed in the beam-house) are simply suspended in lime water to remove the scud and loosely adhering lime, and are then brought into weak liquors, which have already lost most of their strength in previous use, and which may advantageously contain a considerable proportion of gambier, which has the property of penetrating quickly without much contracting or drawing the grain. These liquors should be contained in deep pits in which the hides may be freely suspended, if possible without touching each other, and in which they may be kept in constant motion, at least for the first day, without exposure to the air, which would darken them by oxidising the alkaline tannates. This is best accomplished by suspension from frames to which an oscillating or traversing motion is given by power, but shaking frequently by hand will answer the same purpose. The butts or hides rapidly colour, and must be moved gradually forward into stronger liquors as the grain becomes set. It is difficult at this stage to state the suitable strength of liquor, since the specific gravity of these old liquors depends more on the impurities than on the tannin present, but they may range from 15° to 20° of the barkometer (sp.gr. 1·015–1·020) or even more in mixed tannage, and the liquor should contain no acids strong enough to redden methyl-orange, but should give a purplish red to litmus paper.

If, on the other hand, it be desired to make a leather of first-rate colour and quality, the hides should be freed as perfectly as possible from lime by scudding and the use of some of the other methods already mentioned, and should come into weak liquors of oak bark, gambier, or other bright coloured materials, which must contain a sufficient proportion of free acid to prevent entirely the rapid colouration which has been mentioned; the butts should colour much more slowly and then take rather a brown than an orange tint. This acidity may be obtained by using in the later parts of the process such materials as ferment and produce acetic and other acids, as for instance light oak bark, and myrobalans, but it will sometimes be difficult to secure sufficient without the direct addition of acetic or other vegetable acid. Mineral acids, such as sulphuric and hydrochloric, must be avoided; but formic, butyric, and lactic acids are suitable, and oxalic acid may be used in small quantities to remove lime and to liberate the natural acids with which it was combined. The goods must gradually be moved into stronger liquors, but care must be taken throughout to keep the acid in excess of the tannin, so that the butts gradually plump up and remain plump, and it must be borne in mind that so far as swelling is concerned, acid and tannin are antagonistic. Putrid or stale liquors (which are often styled 'sour' but contain little or no acid) must be sedulously avoided in every sort of sole-leather tanning.

In the American treatment of 'acid' sweat-leather the sides are usually slightly coloured before plumping in a sweet and moderately strong hemlock liquor, and the acid used with water only, but if the colouring and plumping are done together, a sweet fresh hemlock liquor is used with the vitriol so as to tan the grain before it is much affected by the acid. The butts receive all their plumping in this acid vat, and are then tanned in liquors which contain no vitriol. Good results are not usually attained by adding vitriol in small quantities to the 'handler liquors.'

After the colour is fully set, and the butts by whatever method are fairly plumped in the suspenders, the rest of the process is very simple. The butts are laid flat in 'handler' pits, generally with liquor only, but sometimes with a little solid dusting material as the butts get forward. In these pits the goods are handled once a day or oftener, and the liquors are constantly changed and strengthened. This (or in the early layers) is the stage in which hemlock and other dark-coloured materials can be introduced with least injurious effect. When the butts are coloured quite through, they are placed in 'layers,' with stronger liquor and solid tanning material, such as mimosa bark, myrobalans, and valonia, strewed between them, and they are allowed to remain undisturbed for periods of from 1 to 6 weeks, according to the age and character of the goods and the practice of the tanner. This is repeated till the goods are fully tanned, when they are raised and drained, or sometimes washed from adhering 'dust' and strong liquor in a warm sumach or myrobalans liquor, or are 'vatted.' This process consists in suspension in a strong liquor made with bisulphited or 'bleaching' extract. They are then taken up into the drying lofts, where they customarily receive a slight oiling and are hung up until about half dry. They are then laid in a pile to soften and equalise the moisture ('sammed'), and the grain is struck out either by hand with the 'pin' (a two-handled knife with a triangular blade), or more generally by machine; again slightly oiled, somewhat further dried, and rolled twice and finally dried off in a warm loft. The exact dryness or 'temper' for the different operations is a matter of great importance, but is not easy to describe in writing, and it is besides somewhat influenced by the tannage. It is not uncommon to improve the colour of the grain by washing it with an aniline or other colour in the interval between striking and rolling 'off.'

Dressing leather. Hides intended for 'shaved' hides are generally light, not exceeding 60 lbs. in raw weight; those for 'dressing' or 'common' hides may be somewhat heavier. They are unhaired with lime and bated with hen or pigeon dung, and 'shaved' hides are shaved over the thick parts of the butt with a currier's knife, the edge of which is turned in a peculiar way with a slender steel. They are coloured by frequent handling, or better by the use of a vat agitated by a rotatory paddle wheel, in a sweet liquor sufficiently strong to colour and set the grain in a distended condition, so that, as the inner portions shrink under the further astringent action of the liquor, it becomes wrinkled up into a network of fine furrows. At this stage hides are often split with a reciprocating knife machine for 'grains,' which are finished in various ways, and 'fleshes,' which when good are usually 'waxed.' After this the tannage is conducted similarly to that of sole leather, but with much weaker liquors and tanning materials, selected to produce a soft and pliable leather. Acidity of the liquors which would swell the hide and produce a hard leather must be carefully avoided, while stale and so-called 'sour' liquors will soften and supplement the action of the bate, of course at the cost of a further loss of weight and firmness. In the shed, dressing hides are simply oiled and dried, but it is now more general to curry them wet out of the pits, an operation which is rather mechanical than chemical, but which consists in scouring out the bloom or deposit of ellagic acid which has formed in the surface, shaving down, and treating with oil and tallow. The 'stuffing' or impregnation with fats may be done by coating the moistened leather on one or both sides with 'dubbing,' a pasty mixture of tallow and oil of which the more liquid part is slowly absorbed; but it is now more usual to place the moistened leather in a warmed rotating drum, and run in the melted fats, which are absorbed in about 20 minutes. The mechanical processes are now almost entirely done by machines.

Enamelled, patent, or japanned leather. These names are applied to the various kinds of leather which are finished with a bright waterproof surface similar to the lacquered work of the Japanese, the first generally denoting leather so finished on the grain side, and with a grained surface. The colour is commonly, but not invariably, black. The leather may be tanned with a variety of materials, but must be well scoured and curried with but little oil or degras, and it is necessary that the hides should be well freed from grease by careful scudding before tanning, and frequently by the use of benzene or other solvents in a suitable apparatus. The skins are stretched on boards or frames, and coated with a linseed oil varnish boiled with Prussian blue, and sometimes lampblack, and other pigments. The colour of the japan is not blue, but a brown-black, and the iron of the Prussian blue acts not only as a colouring matter, but as a drier. The frames are then slid into grooves in a sort of closet heated by steam to 70°–80°, and when the coat is dry the process is repeated till the requisite thickness is obtained, each coat being smoothed with pumice before applying the next. In France and Germany the japan is frequently finally hardened in the sun. The American tanners are particularly skilful in treating large thin hides in this way. They are divided by the splitting machine into several thicknesses, and both the grain and flesh splits are frequently enamelled, the flesh split receiving a preliminary coating of thick boiled linseed oil and turpentine to form a sort of artificial grain.

Morocco, when genuine, is produced from goat-skins, but an article of equal quality is made from the rough-haired or 'blue-back' seal, and an inferior description, called 'French morocco,' from sheep-skins. The skins are unhaired by liming, puered with dog-dung, and passed through a bran drench, and are tanned with sumach, first in paddle-tumblers, and then in handlers. With sheep-skins the process is frequently much hastened by sewing them into bags, which are filled with sumach liquor and a little air, and are floated in a sumach bath and then laid on a shelf to drain and press. After a day's treatment they are again filled with a fresh sumach liquor, and this is usually sufficient to complete the tannage. When dried, these are called 'crust-roans.' The dyeing is done either by brushing on a table, or by folding down the back, or pairing, so as to protect the flesh-side as much as possible, and drawing through a dye-bath, which is generally of aniline colours or dye-woods. In more recent times the natural have been almost entirely superseded by artificial (coal-tar) colours, and the dyeing is frequently done in a paddle vat or in a drum. The grain receives a slight glaze of albumen and is polished by glazing machines by friction under agate, glass, or hard wood, and is sometimes impressed with an artificial grain by engraved or electrotyped rollers; the grain being afterwards raised or improved by the operation known as 'boarding.'

Russia leather is tanned with willow, birch, and probably other barks, and is dyed with Brazil wood grounded with stannic chloride. Its peculiar odour is due to the essential oil of birch-bark tar, which is applied during the finishing process. Many imitations made in England and on the Continent are scented by a small proportion applied, mixed with oil, to the flesh-side.

'**Chamois**' or **wash-leather** is a totally different product from those which have been already described. The ordinary article is made from the flesh-splits of sheep-skins, and is thoroughly limed so as to dissolve as much as possible of the cementing substance of the fibres, and so produce softness. The lime is then removed by a short bran-drench, and after the superfluous moisture has been pressed out, the skins are oiled on a table with fish or whale oil, folded in cushions, and worked under fulling stocks for 2 to 3 hours, and then shaken out and hung up for a short time to cool and partially dry. The process is repeated again and again until the water has been entirely replaced by oil, and they are then laid in a pile in a warm place, when a sort of fermentation takes place with a considerable production of heat caused by the oxidation of the oil, and the skins take a yellow colour. The surplus oil is now removed either by pressure ('degras'), or by washing with potash or soda lye, from which 'sod oil' is recovered by neutralisation with sulphuric acid. Though it is not known what chemical change takes place in the fibres, the leather is extraordinarily resistant both to boiling water, acids, and alkalis, and yields no gelatin to the former. It has been supposed that the fibres were merely coated with oxidised oil-products but this is negatived by the fact that the leather is unaffected by alkalis which readily dissolve oxidised oils, and it is more probable that the tannage is due to aldehydic products of the fatty acids and glycerol. Only oils of which the fatty acids have unsaturated double bonds will produce the result, and the most unsaturated are the most effective. Excellent leathers of a chamois type are produced by direct treatment with formaldehyde and some other aldehydes in a solution rendered alkaline by sodium carbonate (Payne and Pullmann's patent, 2872, 1898).

Crown leather (**Preller's**, or **Helvetia leather**). This leather, which is remarkable for its toughness, may be regarded chemically as intermediate between 'chamois' and kid, as it is produced by the action of oils and fats in conjunction with an albuminous 'filling' quite analogous to the egg-yolks and flour which are used in the kid manufacture. As the leather is employed for belting, picker straps, and other mechanical purposes, well flayed hides of medium substance are most suitable. They are unhaired by sulphides or sweating, or by a very short liming hastened by mechanical motion, so as to lessen injury to the fibre. For the sake of appearance they are often grained and coloured by working for 1–2 hours in a paddle tumbler in a moderately strong chestnut, hemlock, or other tanning liquor. They are then swollen (if not unhaired with lime), by paddling for a few hours with about 3½ oz. of sulphuric acid per hide, washed through clean water, and hung up until half dry. They are next spread on a table and covered on the flesh with a layer of tanning paste ¼ inch thick. This may be composed of 7 parts wheat flour, 7 parts horse grease, 1 part salt, and 1–2 parts tallow. (Originally ox-brains were used in the mixture, but are not necessary.) They are then folded in bundles and are placed in a large drum studded with pegs inside, and warmed by the injection of moist air to about 30° or 40°, according to the hardness of the fats employed, in which they are worked for 8–12 hours; at the end of this time they are again partially dried and coated with the fat-mixture, and the process repeated four or five times. The hides are then washed in water, and sometimes with a little soda, and are curried by setting out on both sides, and boarding to raise the grain. The yield is only about 30–40 p.c. of the raw weight of hide.

Calf- and glove-kid. As it is impossible within the limits of this article to give working details where the greatest nicety is required in every stage of manufacture, and as the general outlines are the same in both these products, it must suffice to take them together, briefly indicating how the different qualities of each are produced; especially as calf-kid has been almost entirely superseded for shoe purposes by chrome leathers. In calf-kid considerable firmness is required, together with great pliability, whilst in glove-kid, which is made from actual kid-skins, as well as to a large extent from fine lambskins, not only the greatest softness, but the property of stretching in every direction without tendency to spring back, is essential. This characteristic difference is due partly to the different character of the skins employed, and to the fact that in the latter case special care is taken in the beam-house so to dissolve the cementing matter of the tissue that the separate fibres can move over each other without adherence. Hence the calf-skins are usually unhaired simply by a rather thorough liming, whilst the kids are treated with limes which, in addition, contain realgar (red sulphide of arsenic), which is mixed with the hot slaked lime. In each case the skin is puered, first with a bate of dogs' dung, and then with a bran drench; and in both cases, but especially in the latter, the washing and working on the beam is very thorough, since unless the fat-glands and scud are very completely got rid of, it is impossible to dye the skins uniformly and properly. The tannage is effected in a drum containing a mixture of flour, alum, salt, and egg-yolks, with an addition of olive oil, being in principle a combination of mineral tannage with that of oil and albumen as described under 'crown leather.' After tanning, the goods, whether for shoe or glove purposes, are dried, softened by 'staking' or drawing over a blunt knife, and 'aged' by keeping at least a few weeks in a cool warehouse to fix the tan. Calf-kid is then damped and shaved on the flesh, and dyed black by grounding with a mixture of stale urine, or ammonia and potassium dichromate with logwood, sometimes by brushing, and sometimes by folding grain-side out, and passing through a bath of the dye-liquor, and darkened and fixed by a wash of ferrous sulphate. They are re-egged to restore the egg, &c., removed in washing and dyeing, partially dried, and then grounded with a moon-knife (a round knife with a central handle), rubbed over the grain with a mixture of wax, soap, and gum, and ironed to give them a gloss, hand labour being almost entirely superseded by machines.

In glove-kid the dyeing process is much more complicated, and most of the tannage is washed out with warm water, which necessitates a second feeding in the drum with egg-yolk and salt. The colours are produced by a great variety of dyes and mordants, among which the juices of a variety of berries may be mentioned. Aniline dyes are rarely used alone, but are frequently employed as a final wash to brighten the colour. After dyeing, the skins are wrung out or 'sleeked' out with a brass plate on a beam, dried, and again slightly damped and stretched by drawing over a blunt knife which is fixed on a post; an operation which is called 'staking.'

Mineral tanned leather. It has long been known that not only aluminium salts, but those of iron and chromium of corresponding type were capable of producing leather, and as early as 1858, Knapp described a method of chrome tanning, which is identical with one of the modern processes; but it is only within recent years that it has been realised that such leathers possess valuable properties, and especially as regards their resistance both to hot and cold water, which justify the much greater expense of chrome as compared with aluminium salts. It is quite possible to produce chrome leathers with chrome alum and salt, but practically Knapp's suggestion of forming a basic salt either by addition of sodium carbonate to the solution or in some other way is always employed in 'one-bath' tannage; while the 'two-bath' process of August Schultz, which curiously came into practical use before that of Knapp, actually produced a basic salt in the skin, by treatment with chromic acid and its subsequent reduction with acidified sodium thiosulphate. In either case the salt in the skin afterwards is rendered still more basic by 'neutralisation' with dilute solutions of borax or some other weak alkaline salt, and the leather is afterwards 'fat-liquored' with a thin emulsion of oil and soap, dyed, and subsequently dried out and softened by 'staking' by machine.

Iron leathers have never attained any commercial importance, although Knapp spent time and money in trying to develop them. Titanium and cerium salts have been shown to possess tanning properties, but are still in the experimental stage.

Investigations on chrome tannage have thrown much light on mineral tannages in general. It is now generally admitted that the salts are decomposed by hydrolysis, and the acid and the basic salt are absorbed simultaneously but separately by the skin. The function of common salt is maintained by a physical one, repressing acid swelling, and increasing the fixation of acid, whilst the colloidal basic salt is absorbed chemically or physically by the acidified fibre.

H. R. P.

LEATHER BROWN-YELLOW, CHRYSANILINE, *v.* Acridine dyestuffs.

LECANORIC ACID (*Diorsellinic acid*)

$$C_{16}H_{14}O_7,H_2O$$

was first described by Schunck under the name of 'lecanorin,' and was isolated by him from various species of the *Lecanora* and *Variolaria* lichens. It is also present in some quantity in the *Rocella canariensis*, *R. portentosa*, *R. sinensis*, and *Parmelia perlata*, and, according to Hesse (Annalen, 139, 24), is best isolated by the following method, which is a modification of that originally devised by Schunck. The finely divided lichen is extracted with ether, the extract evaporated, and the greenish-white crystalline residue treated with lime water. The solution, when neutralised with acid, gives a precipitate of lecanoric acid, which is collected and crystallised from alcohol. In case the product is not quite pure it is treated with ether, which dissolves the acid, but not the impurity.

Lecanoric acid crystallises in colourless needles, m.p. 166° (Hesse, Ber. 37, 4693), the solutions of which possess an acid reaction. With alcoholic ferric chloride it gives a dark purple colouration, and with dilute calcium hypochlorite a blood-red liquid, which, according to Hesse, is characteristic, and can be used to distinguish this substance from the known lichen acids.

Dibromolecanoric acid (Hesse, Annalen, 139, 28) $C_{16}H_{12}O_7Br_2$ consists of minute prisms, m.p. 179°, whereas *tetrabromolecanoric acid* $C_{16}H_{10}O_7Br_4$, prisms, melts at 157°.

Potassium lecanorate $C_{16}H_{13}O_7K,H_2O$; *barium lecanorate* $(C_{16}H_{13}O_7)_2Ba,5H_2O$; *calcium lecanorate* $(C_{16}H_{13}O_7)_2Ca,4H_2O$; *silver lecanorate* $C_{16}H_{13}O_7Ag$; *lead lecanorate*

$$(C_{16}H_{13}O_7)_2Pb+PbH_2O_2;$$

and *copper lecanorate* $(C_{16}H_{13}O_7)_2Cu,2H_2O$ have been obtained (J. pr. Chem. [ii.] 57, 264).

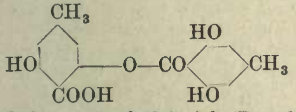
When boiled with water lecanoric acid yields orsellinic acid $C_{16}H_{14}O_7+H_2O=2C_8H_8O_4$; whereas by means of boiling acetic acid or baryta water, orcin, and carbon dioxide are simultaneously produced:

$$C_{16}H_{14}O_7+H_2O=C_8H_8O_4+CO_2+C_7H_8O_2.$$

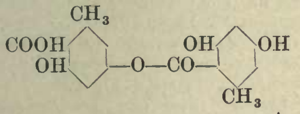
On the other hand, methyl alcohol at 85° gives, in addition to orcin and carbon dioxide, orsellinic acid methyl ester:

$$C_{16}H_{14}O_7+CH_3OH=C_7H_7O_2{\cdot}COOCH_3+C_7H_8O_2+CO_2.$$

The constitution originally assigned to lecanoric acid:



in view of the work of Heinrich (Ber. 37, 1406) on orsellinic acid, is more accurately expressed as follows:



A. G. P.

LECITHIN is a monaminophosphatide widely distributed in the animal and vegetable kingdoms. It is contained in the seeds of cereals, in many plants; in brain, bone-marrow, blood, and in most organs of the animal and human body; in foods, such as milk, butter, wine, in the sugar cane, in various oils and fats, and in the yolk of eggs, but its occurrence in the latter has been denied by Barbieri (Compt. rend. 1910, 151, 405). It is also said to occur in certain soils. It is sometimes spoken of in commerce as '*lecithol.*'

Preparation.—An animal or vegetable substance rich in lecithin may be extracted with volatile esters of fatty acids, the residue, which contains chiefly lecithins and albumins, is extracted with a fatty ester at a higher temperature or with boiling alcohol. The extract on cooling deposits lecithin (Fr. Pat. 390683, 1908); or the first extraction may be carried out with acetone or with acetone mixed with 10–30 p.c. of ether, benzene, chloroform, or similar substance (Fr. Pats. 371391, 1906; 406634, 1908; 333540, 1903).

Lupin or similar seeds freed from skins, may be dried and extracted with hot 96 p.c. alcohol. The extract is evaporated to $\frac{1}{5}$ its bulk and cooled rapidly. On allowing it to stand for a short time, the lecithin separates. It is then boiled with 96 p.c. alcohol until all the lecithin and part of the fat dissolves. On cooling, the fat separates and the solution is decanted and evaporated to obtain pure lecithin (Eng. Pat. 18540, 1909; D. R. PP. 210013, 200253).

Wheat germs are dried and extracted with a suitable solvent to remove oil. They are then extracted with alcohol. The latter is evaporated and the residue, consisting of lecithin, sugar, and albumen, taken up with 50–80 p.c. alcohol, after which the lecithin is precipitated by addition of mineral salts and purified in the ordinary way (Fr. Pat. 364896, 1906; *see* also Schulze, Zeitsch. physiol. Chem. 1908, 55, 338).

Lecithin may also be extracted from the yolk of eggs by means of 96 p.c. alcohol, or a mixture of alcohol and ether. The extract is then precipitated with cadmium chloride at 0°, and the lecithin cadmium chloride salt, suspended in alcohol, is decomposed with lead hydroxide or with moist silver oxide. The lecithin may then be purified by dissolving it in chloroform and reprecipitating with acetone (Ulpiani, Atti. Real. Accad. Lincei. 1901, [v.] 10, i. 368, 421; *see* also Nerking, Biochem. Zeitsch. 1909, 23, 262; Zuelzer, Zeitsch. physiol. Chem. 1899, 27, 254).

Constitution.—The formula usually given to lecithin is

$$RR'O_2:C_3H_5{:}O:P:O(OH)O{\cdot}C_2H_4{\cdot}NMe_3OH,$$

but its exact constitution is not known. It is the choline ester of the palmitic, stearic, or oleic ester of glycerylphosphoric acid, but since the lecithins from various sources, although yielding similar results on elementary analysis, differ in the quantity of choline they form on hydrolysis, it is possible that there is some difference in their constitution; it has therefore been proposed by Winterstein and Hiestand (Zeitsch. physiol. Chem. 1906, 47, 490) to call them by the more general name of *phosphatides.* Various lecithins exist which contain more than one acid radicle in the molecule (*see* also McLean, Bio-Chem. J. 1909, 4, 240; Hunderhagen, J. pr. Chem. [ii.] 28, 219; Gilson, Zeitsch. physiol. Chem. 12, 585; Schulze, *ibid.* 1907, 52, 54; Rollett, *ibid.* 1909, 61, 210; Wintgen and Keller, Arch. Pharm. 1905, 244, 3; Willstätter and Lüdecke, Ber. 1904, 37, 3753; Mayer, Biochem. Zeitsch. 1908, 8, 199; Dezani, Giorn. R. Accad. Med. Torino, 1909, 15; Gobley, Chem. Soc. Trans. 1874, 908; *ibid.* 1875, 92).

Properties.—Lecithin forms a crystalline, wax-like mass, readily soluble in most organic solvents, except acetone or methyl acetate, the solutions being precipitated by salt solutions lying within certain limits of concentration (Porges and Neubauer, Biochem. Zeitsch. 1907, 7, 152; Zeitsch. Chem. Ind. Kolloide, 1909, 5, 193). The alcoholic solution gives characteristic precipitates with cadmium or platinum chlorides (Riedel, Chem. Zentr. 1905, i. 772).

When pure, lecithin should not be transparent, and should form a colourless emulsion with water; to improve its appearance it is often adulterated with solvents and with phosphates and glycerophosphates (Morigi, Chem. Zentr. 1909, ii. 2135). The aqueous emulsion is but slightly affected by light and is very stable with respect to temperature. The emulsion has an acid reaction, but on precipitation with acetone the residue forms a neutral emulsion (Long, J. Amer. Chem. Soc. 1908, 30, 881, 895; *see* also Heubuer, Arch. Exp. Path. Pharm. 1908, 59, 420). When hydrolysed with alkali- or barium hydroxide or with dilute acids, lecithin yields chiefly choline together with palmitic, stearic, oleic, and, probably, linoleic acid (Schulze and Winterstein, Zeitsch. physiol. Chem. 1903, 40, 101; Moruzzi, *ibid.* 1908, 55, 352; McLean, *ibid.* 360; Cousin, Compt. rend. 1903, 137, 68; J. Pharm. Chim. 1906, [vi.] 23, 225; Cariat, Amer. J. Physiol. 1904, 12, 353; D. R. P. 193449; Eng. Pat. 342007, 1904). It is also decomposed readily by the steapsin of the gastric juice and by the pancreatic ferment (Bokay, Bied. Zentr. 1879, 112; Simanowski and Sieber, Zeitsch. physiol. Chem. 1906, 49, 50).

When, in the preparation of lecithin, heat is avoided, the product is dextrorotatory (Ulpiani, *l.c.*).

Ordinary *d*-lecithin when heated in a sealed tube with 10 times its weight of methyl alcohol for 5–6 hours at 90°–100° yields *i*-lecithin which is converted into *l*-lecithin, $[\alpha]_D - 8{\cdot}59°$, by the action of steapsin (Mayer, Chem. Zentr. 1906, ii. 493; Long and Gephart, J. Amer. Chem. Soc. 1908, 30, 1312; McLean, Zeitsch. physiol. Chem. 1908, 57, 296).

Physiological action of lecithin.—Lecithin is said to be a stimulating agent in normal growth (Hatai, Amer. J. Physiol. 1903, 10, 57), and to act favourably on the nutritive processes, being an easily assimilable form of a phosphorus compound (Stassano and Billon, Compt. rend. 1902, 134, 318; Desgrez and Zaky, *ibid.* 1166; Barnard, Chem. Zentr. 1902, i. 854), and it has been recommended as an adjunct to other means of treatment in tuberculosis (Claude and Zaky, Compt. rend. 1901, 133, 486). According to Renshaw and Atkins, lecithins cause a varying retardation in the development of bacteria, but their bactericidal properties are almost negligible for practical purposes (J. Amer. Chem. Soc. 1910, 32, 130).

A great deal of work has been done on the physiological and biological significance of lecithin (*v.* Stoklasa, Ber. 1896, 29, 2761; Zeitsch. physiol. Chem. 1898, 25, 398; Kyes, *ibid.* 1904, 41, 273; Küttner, *ibid.* 1907, 50, 472; Desgrez and Zaky, Compt. rend. 1901, 132, 1512; *ibid.* 1902, 134, 1522; Carrière, *ibid.* 1901, 133, 314; Maxwell, Amer. Chem. J. 15, 185; Slowtzoff, Beitr. Chem. Physiol. Path. 1906, 8, 370; Franchini, Biochem. Zeitsch. 1907, 6, 210; Glikin, *ibid.* 1907, 7, 286; *ibid.* 1909, 19, 270; *ibid.* 1909, 21, 348; Porges and Neubauer, *l.c.*; Usaki, Arch. Exp. Path. Pharm. 1910, 63, 270; Bied. Zentr. 1910, 39, 594).

Addition compounds of lecithin with the halogen hydrides are prepared by saturating an ice-cold solution of lecithin (1 part) in carbon tetrachloride (5 parts) with the required gaseous hydride. It is purified by treating the solution with calcined sodium carbonate, after which it is filtered and evaporated *in vacuô.* The product may then be crystallised from hot alcohol or acetone. The products are yellowish-brown, wax-like masses containing 32 p.c. of iodine or 21 p.c. of bromine. If the treatment with sodium carbonate is omitted, the content of halogen is much higher (Eng. Pat. 28011, 1908).

Bromolecithin is prepared by the action of a chloroform solution of bromine on lecithin, which is capable of combining with 50 p.c. of its weight of halogen (D. R. P. 156110).

An iodo derivative of lecithin has been prepared by shaking 5 kilos. of lecithin dissolved in 3 litres of alcohol, with 10 litres of Hübl's iodine solution at a temperature of 40°–50°. The solution is then cooled, filtered, and evaporated *in vacuô*, when a product containing 20 p.c. of iodine is obtained (D. R. P. 155629).

Lecithin albumin saline preparations may be obtained in the following way: 8 grams of lecithin are emulsified by an aqueous solution of 100 grams of casein and 2 of sodium hydroxide, and the emulsion is then treated successively with solutions of 5 grams sodium phosphate and 3 grams of calcium chloride. The precipitate is finally separated and dried *in vacuô* (D. R. P. 223876).

Lecithin dextrose is probably a solid solution or a molecular combination of the two substances. It readily reduces an alkaline solution of copper, is fermentable and forms an *osazone*, m.p. 205° (Mayer, Chem. Zentr. 1906, ii. 536).

Lecithin glucoses are of variable composition (Baskoff, Zeitsch. physiol. Chem. 1909, 61, 426). Lecithin molybdenum compounds are known (Ehrenfeld, *ibid.* 1908, 56, 89).

Lecithin may be estimated in a variety of ways, but usually the amount of phosphorus or phosphoric acid in the incinerated substance is determined (Nerking and Haensel, Biochem. Zeitsch. 1908, 13, 348; Otolski, *ibid.* 1907, 4, 124; Schulze, Zeitsch. physiol. Chem. 1894, 20, 225; Koch, *ibid.* 1906, 47, 327; Schulze, Chem. Zeit. 1897, 21, 374; *ibid.* 1904, 28, 751; *ibid.* 1908, 32, 186; Heckel and Schlagdenhauffen, Compt. rend. 1886, 103, 388; Bordas and Raczkowski, *ibid.* 1902, 134, 1592; Riedel, *l.c.*; Jäekle, Zeitsch. Nahr. Genussm. 1902, 5, 1062; Riegel, Pharm. Zeit. 1910, 55, 428).

(For further literature on the sources of lecithin, *see* Loew, Pflüger's Arch. Phys. 22, 62; Hoppe-Seyler, Ber. 1879, 12, 702; Schulze and Likiernik, *ibid.* 1891, 24, 71; Shorey, J. Amer. Chem. Soc. 1898, 20, 113; Schlagdenhauffen and Reeb, Compt. rend. 1902, 135, 205; Burow, Zeitsch. physiol. Chem. 1900, 30, 495; Koch, *ibid.* 1902, 36, 134; McLean, *ibid.* 1909, 59, 223; Funaro and Barboni, Chem. Zentr. 1905, i. 552; Rubow, *ibid.* 620; Manasse, *ibid.* 1906, ii. 805; Muraro, Gazz. chim. ital. 1905, 35, i. 314; Fornani, Boll. chim. Farm. 1909, 48, 520; Glikin, Biochem. Zeitsch. 1907, 4, 234; Bolle, *ibid.* 1910, 24, 179.)

LEDITANNIC ACID, LEDIXANTHIN, LEDUM CAMPHOR *v.* LEDUM PALUSTRE (Linn.).

LEDUM PALUSTRE (Linn.). *Marsh tea*; *Wild rosemary. Lédon* (Fr.); *Porsch, Sumpfporst* (Ger.). Marsh tea is a shrub, some 3 feet in height, belonging to the natural order *Ericaceæ*, which inhabits marshes, generally, throughout the northern hemisphere. Its inflorescence consists of umbels of white or pale rose-coloured flowers. The leaves possess acrid narcotic properties, and were formerly made use of in medicine. A strong decoction is now sometimes applied in veterinary practice to destroy cutaneous parasites, and it is also employed to kill vermin in furniture.

The most important constituents of the leaves are volatile oil, camphor, a glucoside and tannin. The *volatile oil* obtained by distilling the leaves with water was examined by Willigk (Sitzungsber. Wien. 9, 305) and Fröhde (J. 1861, 692). It contains a *terpene* $C_{10}H_{16}$, boiling at 160°, an *oxygenated oil* $C_{10}H_{16}O$, perhaps *ericinol*, boiling at 240°–242°, and camphor.

Ledum camphor $C_{15}H_{26}O$, a homologue of common camphor, was examined in 1796 by Rauchfuss (J. Pharm. 3, 1 and 189) and afterwards by Meissner (Berz. J. 13, 170), Grassmann (Rep. Pharm. 38, 53), Buchner (*ibid.* 38, 57; N. Rep. Pharm. 5, 1), Willigk (Sitzungsber. Wien. 9, 302), Rizza (J. Russ. Phys. Chem. Soc. 19, 319), Iwanow (J. 1879, 909), Trapp (Ber. 8, 542), Hjelt and Collan (*ibid.* 15, 2501). The camphor crystallises out abundantly when the volatile oil is placed in a freezing mixture, and may be separated and purified by recrystallisation from alcohol. It sublimes readily in needles, which melt at 104°–105°, and boil at 282°–283°. It is soluble in alcohol, ether, chloroform, and benzene. Heated with acetic anhydride at 150° a sesquiterpene *ledene* $C_{15}H_{24}$ is obtained, which boils at 255°, and at 0° has a sp.gr. 0·9349 (Hjelt, Ber. 28, 308) (*v.* CAMPHORS).

Marsh tea contains small quantities of the glucoside *ericolin* $C_{34}H_{56}O_{31}$ (?) (Rochleder and Schwarz, Sitzungsber. Wien. 9, 308; 11, 371) a compound which occurs generally in ericaceous plants (Kawalier, *ibid.* 9, 297; Thal, J. 1883, 1402). It is an intensely bitter, yellowish-brown, sticky resin (*v.* ERICOLIN). By the action of dilute acids it breaks up into glucose and *ericinol*, $C_{20}H_{26}O$ (?). The latter compound is also a product of the action of dilute acids on pinipicrin, a glucoside occurring in the needles of the Scotch fir (Kawalier, Sitzungsber. Wien. 11, 350; 13, 515). Ericinol is a colourless oil when first obtained, but it soon oxidises and turns brown when exposed to the air.

Leditannic acid $C_{15}H_{20}O_8$ (?) was examined by Willigk (Sitzungsber. Wien. 9, 302), Rochleder and Schwartz (*ibid.* 9, 307), Rochleder (*ibid.* 44, 493), and Thal (J. 1883, 1402). By treatment with dilute acid it is converted into *ledixanthin*, $C_{30}H_{34}O_{13}$ (?), but no sugar is formed. The tannin of the horse-chestnut appears to give the same compound when treated with dilute acids, and is perhaps identical with leditannic acid. Distilled alone leditannic acid yields an oil and *catechol* $C_6H_4(OH)_2$. A. S.

LEEK. *Allium Porrum* (Linn.). The Welsh national plant. The taste and odour are due to the presence of allyl sulphide $(C_3H_5)_2S$.

König gives the following analyses:—

	Water	Protein	Fat	Sugar	Other N-free subst.	Crude fibre	Ash	Organic sulphur
Root and bulb	87·6	2·8	0·3	0·4	6·1	1·5	1·2	0·06
Leaves . .	90·8	2·1	0·4	0·8	3·7	1·3	0·8	0·06

The following shows the composition of the ash:—

	Per cent. of ash in dry substance	K_2O	Na_2O	CaO	MgO	Fe_2O_3	P_2O_5	SO_3	SiO_2	Cl
Root and bulb	6·3	30·7	14·1	10·4	2·9	7·6	16·7	7·4	7·3	3·1
Leaves . .	8·2	40·7	6·9	21·7	4·4	0·6	7·6	4·1	7·3	6·6

H. I.

LEGUMIN. *Vegetable caseïn.* The distinctive protein of the seeds of the *Leguminosæ*, found also in some other seeds; it closely resembles in composition and in some of its properties the casein of milk. It occurs mixed with other proteins in the seeds, and is with difficulty obtained in a pure state.

Different methods of extraction—especially the use of dilute alkalis—cause alterations in the proteins of plants, and hence a good deal of confusion has arisen both as regards the nature and the names of the various proteins.

Legumin was discovered by Einhof in 1805, and has been investigated by Proust, Vogel, Boullay, Braconnot, Liebig, Dumas, and Cahours, and others, and especially by Ritthausen, and later by T. B. Osborne and his fellow-workers.

Ritthausen divided plant caseïn into legumin, conglutin, and gluten-caseïn, which differ a little from each other in their composition and in a few of their properties. The first and third he considered albuminates, and the second a plant globulin.

These three forms of plant casein are, according to Ritthausen, only slightly soluble in water, but easily soluble in dilute alkaline solutions, in solutions of alkaline reacting salts, and in very dilute acids. They are precipitated from alkaline solutions by dilute acids and by rennet. Earlier investigators thought that phosphorus was an essential element. Sp.gr. 1·285–1·36 (Dittmar); specific rotation of legumin in 10 p.c. NaCl $[\alpha]_D$ −44·09° (Osborne and Harris).

Ritthausen obtained legumin from peas, haricots, beans, lentils, vetches, &c., by the following process. The seeds are finely powdered, macerated with about eight times their weight of cold water for 6 hours, the liquid decanted and strained, and the residue again macerated with water. In some cases, notably with beans and lupins, the solution is acid, and in such cases it is desirable to add to the water used in extracting the seed sufficient potassium hydroxide to render the mixture very feebly alkaline, otherwise much less proteïd will be extracted from the seed. The strained extract is allowed to settle for some time at a low temperature, 4°, and when clear, or nearly so, decanted and precipitated with dilute acetic acid (1 : 8), adding only just sufficient acid to complete the precipitation, and keeping the temperature low. The precipitate is collected on a filter washed with 50 p.c. alcohol, which causes it to shrink and separate easily from the filter; the precipitate is then further washed and extracted with dilute alcohol, strong alcohol, and with ether; then pressed, again washed with alcohol, and dried in a vacuum over oil of vitriol.

If the product is still impure it may be purified by dissolving it in the cold in a very dilute solution of potassium hydroxide (0·1–0·2 p.c.), and, after decanting from any insoluble matter, reprecipitating with dilute acetic acid.

Conglutin was obtained in a similar manner from sweet and bitter almonds and from lupins. It contains rather more nitrogen, is more glutinous, and more soluble in acetic acid than legumin, besides being completely soluble in dilute salt solution. Also, its compound with copper oxide differs a little from the legumin copper-oxide compound.

Gluten-caseïn was prepared from the seeds of *gramineæ* in a very similar way.

Ritthausen formed compounds of plant caseïn with copper oxide by dissolving the finely-powdered proteïd in water containing 0·2–0·3 p.c. of potassium hydroxide, largely diluting the solution with water, and adding a solution of blue vitriol and as much caustic potash as is necessary to dissolve the precipitate first formed and give the whole solution a violet colour. The clear solution is then neutralised with dilute sulphuric acid, and the precipitate collected and washed with water till it ceases to give a reaction for sulphates.

Legumin thus treated gives a precipitate containing from 13·5 to 15·5 p.c. of CuO, and the proteïn is unaltered by the treatment.

Conglutin is, to a slight extent, decomposed by the treatment, and yields a compound containing about 11·6 p.c. of CuO.

Gluten-caseïn is but slightly altered by this treatment; but its copper oxide compound is somewhat soluble in water, and contains about 14 p.c. CuO.

The legumin obtained from several sources by Ritthausen was found by him to be partially soluble in dilute solutions of salt; but there was little or no difference in composition between the soluble and insoluble portions. The composition of legumin and its allies, as given by Ritthausen, varies somewhat according to their source. There is no doubt that the use of alkalis in the extraction of the proteins, and also their subsequent precipitation by an acid, led to alterations in composition and properties in the proteins which has led to confusion and some erroneous results.

To T. B. Osborne of the Connecticut Agricultural Experiment Station and his fellow-workers, notably G. F. Campbell, S. H. Clapp, R. D. Gilbert, I. F. Harris, F. W. Heyl, and C. G. Voorhees, we are indebted for more exact knowledge of the composition and nature of legumin and other vegetable proteins. Osborne's researches began about the year 1891, and will be found, for the most part, recorded in the Journal of the American Chemical Society and the American Journal of Physiology from that date onwards. A summary of the results is given in The Vegetable Proteins, by Thos. B. Osborne, 1909, in which is a valuable bibliography of the subject.

Osborne has shown that legumin and its congeners are true globulins; he obtains legumin (and similar proteins) without the aid of alkalis. The finely ground material, peas or vetches, is extracted with petroleum naphtha to remove oil and treated with a strong solution (10–20 p.c.) of common salt. After filtering the liquid is treated with ammonium sulphate, the resulting precipitate redissolved in 10 p.c. sodium chloride solution, and the liquid dialysed free from chlorides when the protein separates in spheroids. It is washed with water and alcohol and dried over sulphuric acid.

Legumin thus prepared is insoluble in water; when freshly prepared and not dried it is readily soluble in a 10 p.c. solution of sodium chloride. After washing with alcohol and drying it becomes less soluble. A solution in 10 p.c. sodium chloride is not precipitated by saturating the solution with magnesium sulphate or with sodium chloride; nor by sodium sulphate at the ordinary temperature, but is precipitated at 34°. Saturation with ammonium sulphate at common temperatures completely precipitates it. In a salt solution, legumin is precipitated by picric, tannic, hydrochloric, nitric, sulphuric, or acetic acids, but not by mercuric chloride. It is readily soluble in dilute alkalis and alkaline carbonates.

The protein described under the name of conglutin by Ritthausen, obtained from almond and peach kernels, has been shown by Osborne to be different in some of its characters from legumin, and he has restored to it the name amandin, first given to it by Proust in 1802.

The name conglutin Osborne retains for the protein of lupins.

The percentage composition of some of the typical and purest preparations is as follows:—

—	Legumin from		Conglutin or amandin from almonds:		Conglutin from lupins.	
	peas and beans. Ritthausen	peas and vetches. Osborne	Ritthausen	Osborne	Ritthausen	Osborne
C .	51·5	52·1	50·4	51·3	50·8	51·0
H .	7·0	7·0	6·9	6·9	6·9	6·9
N .	17·1	18·0	18·1	19·3	18·4	18·0
S .	0·4	0·4	0·4	0·4	0·9	0·4
O .	24·0	22·5	23·7	22·0	23·0	23·7

Globulins have been found in walnuts, hazelnuts, candle-nuts (*Aleurites triloba* [Forst.]), para-nuts (*Bertholletia*), castor-oil beans, cherry kernels, plum and apricot kernels, earth nuts (*Arachis hypogæa* [Linn.]), hemp seed, cotton seed, coconuts, sunflower seeds, and several other seeds.

Ritthausen obtained the following percentages of legumin from different seeds:—French beans 11 p.c., peas 5·4–9·4 p.c., horse beans 10 p.c., Mazagan beans 18·7 p.c., and lentils 5·2 p.c. From sweet almonds he obtained 15 p.c. of conglutin, and from lupins 20 p.c.

The whole of the nitrogenous matter of these seeds is not in the form of legumin; other proteins are present. Thus field beans contain about 23 p.c., and lentils 25 p.c. of nitrogenous matter.

The products of the hydrolysis of legumin with acid and alkalis are those of the proteins generally, the nitrogen being found as ammonia, arginine, and other bases, glycine, alanine, leucine, tyrosine, phenylalanine, aspartic acid, glutamic acid, and other amino acids and tryptophan. Osborne and Harris found, on decomposing with strong hydrochloric acid, that of the total nitrogen 9·3 p.c. was obtained as ammonia, 28·4 p.c. as basic nitrogen, mainly in the forms of arginine, histidine, and lysine, and 61·4 p.c. as non-basic nitrogen.

In China and Japan a kind of vegetable cheese, known in the latter country as *tofu*, is made from the seed of the soy bean (*Glycine hispida* [Maxim.]). This leguminous seed contains about 37–40 p.c. of nitrogenous matter, and about 20 p.c. of fat, being a very concentrated food. Its globulin (glycinin) is very like legumin from peas, but contains rather more sulphur (0·8 p.c.) and rather less nitrogen (17·5 p.c.).

The cheese is made by soaking the beans in water, pounding them, and straining through a sieve, which removes most of the starch, boiling the residue with water, and straining the solution through cotton-cloth and pressing the residue. The strained liquor, containing the nitrogenous matter (legumin, &c.) and fat, is precipitated by the addition of the brine formed on the deliquescence of common sea salt; the precipitate pressed and cut into cakes is ordinary *tofu.* It contains about 89 p.c. of water, the dry matter being nearly two-thirds nitrogenous matter and one-third fat, with small quantities of carbohydrates and ash. A drier product is obtained by freezing these cakes of cheese, and then thawing by exposure to the sun. On thawing, a large quantity of water runs off, leaving a spongy, somewhat horny residue, known as *kori-dofu.*

Analyses of these products gave the following results:—

—	Fresh tofu	Frozen tofu or kori-dofu	Dry matter from frozen tofu
Water . .	89·0	18·8	—
Ash . .	0·5	1·6	2·0
Fat . .	3·2	28·8	35·4
Nitrogenous matter .	6·5	48·8	60·1
Carbohydrates	0·8	2·0	2·5
	100·0	100·0	100·0

E. K.

LEHRBACHITE *v.* SELENIUM.

LEIPSIC YELLOW. *Normal lead chromate* (*v.* CHROMIUM).

LEITHNER'S BLUE. *Cobalt blue* (*v.* PIGMENTS).

LEMNIAN EARTH, *Terra lemnia*, or *Sphragidite.* A red, yellow, or grey earthy substance, somewhat resembling fuller's-earth, and consisting of a hydrated aluminium silicate, with more or less iron. It takes its name from its occurrence at Lemnos, an island in the Grecian Archipelago, where, in consequence of its reputed medicinal virtues, it was formerly regarded as sacred. The earth was dug only once a year, with much ceremony, and, after mixture with goat's blood, was made into small cakes or balls, which were stamped with a seal by the priests, whence it was termed *terra sigillata.*

Lemnian reddle (*Rubrica lemnia*) was a red ochreous earth used as a colouring material.

F. W. R.

LEMON. The fruit of *Citrus medica* (Linn.) [*C. limonum*]. There are many varieties. König gives as the average of 33 analyses—

Mean weight of a fruit	The fruit consists of		
	Skin	Flesh	Seeds
153 grammes	38·5	59·2	2·3

The fruit contains—

Water	Invert sugar	Citric acic	Nitrogenous matter	Ash
82·6	0·4	5·4	0·7	0·6

The juice contains—

Total extract	Invert sugar	Cane sugar	Citric acid	Nitrogenous matter	Ash
10·44	1·42	0·52	5·83	0·32	0·20

The rind of Italian lemons contains—

Water	Nitrogen	Essential oil	Ash
76·38	0·23	1·01	0·52

The ash of lemons (whole fruit) contains—

K_2O	Na_2O	CaO	MgO	Fe_2O_3	Mn_3O_4	P_2O_5	SO_3	SiO_2	Cl
43·2	2·7	30·2	5·1	0·6	0·4	13·6	3·1	0·7	0·5

Boric acid, to the extent of 6 milligrammes per litre, has been detected in lemon juice (Hebebrand, 1902). Lemons are largely used, both in the form of fruit and also for the preparation of citric acid (*q.v.*) and essence of lemon (*q.v.*). Lemon juice, both in its raw and concentrated (5 to 7 times) state, is also an important commercial product. According to the British Pharmacopœia lemon juice should have a sp.gr. of 1·039, and contain 32·5 grains of citric acid per oz., *i.e.* 6·77 grammes per 100 c.c. H. I.

LEMON-GRASS OIL *v. Verbena*, art. OILS, ESSENTIAL.

LEMON, OIL OF, *v.* OILS, ESSENTIAL.

LEMON YELLOW *v.* BARIUM CHROMATE and CHROMIUM.

LENTILS. The seeds of *Lens esculenta* (Moench.) [*Ervum lens*]. These are small in size and are largely used as human food. They are very nutritious, but unless thoroughly cooked are difficult of digestion.

There are many varieties, differing considerably in size and also in composition.

Balland (Compt. rend. 1897, 125, 119) found the following range of variation in composition:—

Weight of 100 seeds. grammes	Water	Protein	Fat	N-free extract	Crude fibre	Ash
2·5	11·7	20·3	0·6	56·1	3·0	2·0
to 6·6	13·5	24·2	1·5	62·4	3·6	2·7

Church (Food Grains of India, 1886 and 1891) gives analyses of husked and whole lentils—

	Water	Protein	Fat	N-free extract	Crude fibre	Ash
Husked .	11·8	25·1	1·3	58·4	1·2	2·2
Unhusked .	11·7	24·9	1·5	56·0	3·6	2·3

König quotes as an analysis of the ash—

Per cent. of ash in dry substance	K_2O	Na_2O	CaO	MgO	Fe_2O_3	P_2O_5	Cl
2·07	34·8	13·5	6·3	2·5	2·0	36·3	4·6

Lentils thrive in temperate climates, and best on a dry calcareous soil; their leaves and stems, when cut in the early stages of growth, furnish nutritious food for cattle and yield a hay which is excellent for dairy cows. H. I.

LENTISCUS or **LENTISK.** The leaves of *Pistacia lentiscus* (Linn.), a small shrub growing wild in Tunis. Contain from 10 to 12 p.c. of tannin and are used in admixture with sumach, the dried leaves of *Rhus coriaria* (Linn.), in tanning. For methods of detecting and estimating lentiscus in Sumach, *v.* Scarlata (J. Soc. Chem. Ind. 1900, 779).

LEPIDINE *v.* QUINOLINE.

LEPIDOLITE *v.* LITHIUM, also MICA.

LEPTANDRA. *Culver's Root.* The rhizome and rootlets of *Veronica* (*Leptandra*) *virginica* (Linn.) contain a resin leptandrin. It is used as a cathartic in biliousness or constipation.

LETHAL *see Spermaceti*, art. WAXES.

LETTUCE. *Lactuca scariola* (Linn.) and other species. Several varieties are known. The leaves are eaten as a salad.

König gives as the average composition of the usual species—

Water	Nitrogenous substances	Fat	N-free extract	Crude fibre	Ash	Organic sulphur
94·3	1·4	0·3	2·2	0·7	1·0	0·01

The ash contains—

K_2O	Na_2O	CaO	MgO	Fe_2O_3	P_2O_5	SO_3	SiO_2	Cl
37·6	7·5	14·7	6·2	5·3	9·2	3·8	8·1	7·6

The juice contains potassium hydrogen citrate.

All lettuces possess slight narcotic properties, and the milky juice of certain species, especially *L. viroŝa* (Linn.), when evaporated, yields a brown, viscid residue which has been used in medicine under the name "lactucarium" (*q.v.*). H. I.

LETTUCE OPIUM *v.* LACTUCARIUM.

LEUCANILINE *v.* TRIPHENYLMETHANE COLOURING MATTERS.

LEUCINE. The name *leucine*, suitably prefixed, is given to the four following monoaminocaproic acids:—

1. *l-Leucine* (*α-amino-γ-methylvaleric acid*)
$(CH_3)_2CH{\cdot}CH_2{\cdot}CH(NH_2)CO_2H$.
2. *d-iso-Leucine* (*α-amino-β-methylvaleric acid*)
$CH_3{\cdot}CH_2{\cdot}CH(CH_3)CH(NH_2)CO_2H$.
3. *n-Leucine* (*α-amino-n-hexoic acid*)
$CH_3[CH_2]_3CH(NH_2)CO_2H$.
4. *ϵ-Leucine* (*ϵ-amino-n-hexoic acid*)
$H_2N{\cdot}CH_2[CH_2]_4CO_2H$.

With the exception of the last they all occur among the degradation products of a great many of the proteins.

***l*-Leucine,** *α-amino-γ-methylvaleric acid*

$$(CH_3)_2CH{\cdot}CH_2{\cdot}CH(NH_2)CO_2H$$

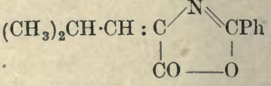
is, next to arginine, the most widespread of the amino acids that occur in proteins. It was discovered by Proust (Ann. Chim. Phys. 1818, [ii.] 10, 40) in decaying cheese and called "oxide-caséux"; Braconnot (*ibid.* 1820 [ii.]. 13, 19) isolated it from the products of the acid hydrolysis of meat, and named it leucine (λευχος) because of the glistening white crystals it forms. Mulder (J. pr. Chem. 1839, 16, 290) established the identity of the two substances and also obtained it by boiling meat with alkali and by the putrefaction of casein.

Leucine occurs in the free state in many of the organs of the animal body, in the tissues of the lung (Cloetta, Annalen, 1854, 92, 289), in the thymoid and thyroid glands and the pancreas (Gorup-Besanez, Annalen, 1856, 98, 7; Radziewsky, Zeitsch. Chem. 1866, 416), in the brain (Müller, Annalen, 1857, 103, 131); it is found in the liver and urine under certain pathological conditions (Frerich and Städeler, J. 1854, 678; 1856, 702; 1858, 550; Salkowsky, J. Thierchem. 1880, 457; Valentiner, J. 1854, 675; Sotnitschwski, Zeitsch. physiol. Chem. 1879, 3, 391). Among the lower animals leucine occurs in the pupæ of butterflies (Schwarzenbach, J. 1857, 538), in spiders and in crayfish. In the vegetable kingdom leucine has been found in the juice of etiolated vetch seedlings (Gorup-Besanez, Ber. 1874, 7, 146; Cossa, Gazz. chim. ital. 1876, 6, 314), also in the young green plants (Schulze, Landw. Versuchs. Stat. 1895, 46, 383); in potatos (Schulze and Barbieri, *ibid.* 24, 167); in young pumpkin plants (Schulze and Barbieri, Ber. 1878, 11, 1233); in fungi (Winterstein, Zeitsch. physiol. Chem. 1899, 26, 438); in the pod of the broad bean (Bourquelot and Hérissey, J. Pharm. Chim. 1898, [vi.] 8, 385); and in beet juice (Erlich, Zeit. Ver. deut. Zuckerind. 1903, 571, 809).

l-Leucine crystallises in glistening white leaves, melts at 280° when rapidly heated (Trans. Guinness Res. Lab. 1903, i. 57), and has sp.gr. 1·293 in absolute alcohol at 18° (Engel and Vilmain, Bull. Soc. chim. 1874, [ii.] 22, 279). It dissolves in 46 parts of water at 18° (Schulze, Zeitsch. physiol. Chem. 1884, 9, 254); in 1040 parts of cold alcohol (96 p.c.) or in 800 parts of hot alcohol (98 p.c.) (Zollikoffer, Annalen, 1852, 82, 176); in 10·9 parts of glacial acetic acid at 16° or 29·23 parts at 117° (Habermann and Ehrenfeld, Zeitsch. physiol. Chem. 1902, 37, 18). The molecular heat of combustion is 854·9 Cal., and the heat of formation 158·4 Cal. (Berthelot and André, Compt. rend. 1890, 110, 884). Natural leucine or *l*-leucine is lævorotatory in aqueous and dextrorotatory in acid or alkali solution (Lewkowitsch, Ber. 1884, 17, 1439), and has $[\alpha]_D+15{\cdot}6°$ in hydrochloric acid solution (Ehrlich and Wendel, Biochem. Zeitsch. 1908, 8, 399); when heated with barium hydroxide solution at 150°–160° for three days it is racemised, and the inactive leucine can be resolved by the action of *Penicillium glaucum*, yielding *d*-leucine, the rotation of which is equal in magnitude and opposite in direction to that of the lævo isomeride (Schulze and Bosshard, Zeitsch. physiol. Chem. 1886, 10, 140).

The constitution of leucine as *α*-amino-*γ*-methylvaleric acid was first established by Schulze and Likiernik (Ber. 1891, 24, 669), who showed that the synthetic *α*-amino*iso*butylacetic acid (*α*-amino-*γ*-methylvaleric acid) prepared by Hüfner (J. pr. Chem. 1870, [ii.] 1, 6) by the action of ammonia and hydrogen cyanide on *iso*valeraldehyde, was identical with the inactive leucine obtained by heating natural *l*-leucine with barium hydroxide. The two compounds have the same solubility in water, 1 part in 105 at 13°; yield the same *d*-leucine when used as a culture medium for *Penicillium glaucum*, and give the same leucic acid (hydroxycaproic acid), m.p. 54·5° on treatment with nitrous acid.

Further syntheses of *r*-leucine are described by (1) Erlenmeyer and Kunlin (Annalen, 1901, 316, 145), who obtained the anhydride



of *α*-benzoylamino-*β*-*iso*propylacrylic acid by condensing hippuric acid and *iso*butyraldehyde in the presence of acetic anhydride; the corresponding acid $(CH_3)_2CH{\cdot}CH{:}C(NH{\cdot}COPh)CO_2H$ when heated with excess of ammonia solution at 150°–170° is hydrolysed, yielding *r*-leucine, *iso*valeric, and benzoic acids. (2) Bouveault and Locquin (Bull. Soc. chim. 1904, [iii.] 31, 1180) from ethyl *α*-oximino*iso*hexoate

$$(CH_3)_2CH{\cdot}CH_2{\cdot}C(NOH)CO_2Et$$

obtained by the action of nitrosyl sulphate on ethyl *iso*butylacetoacetate; this on reduction yielded ethyl α-amino*iso*hexoate

$$(CH_3)_2CH{\cdot}CH_2{\cdot}CH(NH_2)CO_2Et,$$

from which by hydrolysis *r*-leucine was obtained. (3) Fischer and Schmitz (Ber. 1906, 39, 351) who obtained *r*-leucine from ethyl *iso*butylmalonate $(CH_3)_2CH{\cdot}CH_2{\cdot}CH(CO_2Et)_2$ by converting into the bromo derivative

$$(CH_3)_2CH{\cdot}CH_2{\cdot}CBr(CO_2Et)_2,$$

hydrolysing this ester, and converting the *iso*butylbromomalonic acid thus obtained into *iso*butylbromoacetic acid

$$(CH_3)_2CH{\cdot}CH_2{\cdot}CHBr{\cdot}CO_2H$$

by distillation under reduced pressure; this on treatment with ammonia yielded *r*-leucine $(CH_3)_2CH{\cdot}CH_2{\cdot}CH(NH_2)CO_2H$.

r-Leucine has been resolved into *d*- and *l*-leucine by the fractional crystallisation of certain alkaloid salts of the benzoyl and formyl derivatives (*q.v.*) (Fischer, Ber. 1900, 33, 2370; Fischer and Warburg, *ibid.* 1905, 38, 3997).

Derivatives. *Salts.—Mercury salt*

$$(C_6H_{12}O_2N)_2Hg$$

formed by dissolving mercuric oxide in a solution of leucine (Gössmann, Annalen, 1854, 91, 134); *lead salt* $(C_6H_{12}O_2N)_2Pb,H_2O$ crystallises in leaves (Strecker, Annalen, 1849, 72, 90); *copper salt* $(C_6H_{12}O_2N)_2Cu$, small light blue crystals, soluble in 3045 parts of cold or 1460 parts of boiling water (Hofmeister, Annalen, 1877, 189, 16). The salts with acids are readily soluble; the two *hydrochlorides* $C_6H_{12}O_2N,HCl$ and $(C_6H_{12}O_2N)_2,HCl$ are described (Laurent and Gerhardt, Ann. Chim. Phys. [iii.] 34, 321; Schwanert, Annalen, 1857, 102, 222); the *nitrate* $C_6H_{12}O_2N,HNO_3$ (Laurent and Gerhardt); the *platinichloride* $(C_6H_{12}O_2N)_2,H_2PtCl_6$ forms a yellow crystalline precipitate.

Anhydride $(C_6H_{12}ON)_2O$ obtained together with its *dibenzoyl* derivative $(C_6H_{11}ON{\cdot}C_7H_5O)_2O$, m.p. 80°, by the action of benzoyl chloride on leucine at 100° (Destrem, Compt. rend. 1878, 86, 484). *The potassium salt of trimethylleucine iodide*

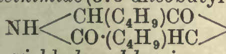
$$C_5H_{10}(NMe_3I)CO_2K$$

hygroscopic slender needles obtained by the action of methyl iodide and potassium hydroxide on leucine; the corresponding *chloro* compound forms a yellow *aurichloride*

$$C_6H_{11}O_2NMe_3Cl{\cdot}AuCl_3,$$

m.p. 163°, and an orange-yellow *platinichloride* $(C_6H_{11}O_2NMe_3Cl)_2PtCl_4$ (Koener and Menozzi Gazz. chim. ital. 1883, 13, 351).

Leucinimide (3:6-di*iso*butyl-2:5-diketopiperazine)



$$NH{<}\genfrac{}{}{0pt}{}{CH(C_4H_9)CO}{CO{\cdot}(C_4H_9)HC}{>}NH,$$

m.p. 271° (corr.), yields *leucyl-leucine*

$$NH_2{\cdot}CH(C_4H_9)CO{\cdot}NH{\cdot}CH(C_4H_9)CO_2H$$

on hydrolysis, this crystallises with $1\frac{1}{2}H_2O$, and melts slightly above 270° (Cohn, Zeitsch. physiol. Chem. 1900, 29, 283; Fischer, Ber. 1900, 33, 2370; 1902, 35, 1095; Salaskin, Zeitsch. physiol. Chem. 1901, 32, 592). *Ethyl ester* of *r-leucine* has b.p. 83·5°/12 mm., sp.gr. 0·929 at 17°; the *picrate* has m.p. 136° (corr.), and the *d-tartarte*, m.p. 145° (corr.); the *ethyl ester* of *l-leucine* has $[\alpha]_D^{20°} + 13{\cdot}1°$, and is not racemised on hydrolysis; it forms a *picrate*, m.p. 129·5° (corr.) (Fischer, Ber. 1901, 34, 433; *cf.* Röhmann, *ibid.* 1897, 30, 1978). When the ethyl ester of *r*-leucine is left in contact with water and crude pancreatin, it undergoes asymmetric hydrolysis, that is, the *l*-ester is hydrolysed, whilst the *d*-ester is not (Warburg, Ber. 1905, 38, 187). *n-Propyl ester* of *leucine* has b.p. 95°–96°/12 mm. (Warburg, Zeitsch. physiol. Chem. 1906, 48, 205).

r-Leucinamide $C_6H_{14}ON_2$, m.p. 106°–107° (corr.), is prepared by the action of liquid ammonia on the ethyl ester; the *β-naphthalene sulphonyl derivative* has m.p. 176°–178° (corr.); and *carbethoxy-dl-leucinamide* $C_9H_{18}O_3N_2$, m.p. 108°, readily yields *β-iso*butylhydantoin by shaking with sodium hydroxide (Koenigs and Mylo, Ber. 1908, 41, 4427).

The *ethyl ester* of *l-leucinecarbimide*

$$CO : N{\cdot}CH(CO_2Et)CH_2{\cdot}CHMe_2,$$

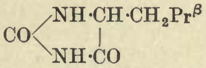
b.p. 120°–130°/18 mm. is formed together with *diethyl leucinecarbimide*

$$CO[NH{\cdot}CH(CO_2Et)CH_2{\cdot}CHMe_2]),$$

b.p. 180°–190°/18 mm. by the action of carbonyl chloride on the ethyl ester of leucine; *isobutylhydantoic acid*

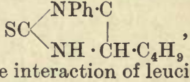
$$NH_2{\cdot}CO{\cdot}NH{\cdot}CH(CH_2Pr^\beta)CO_2H,$$

m.p. 200°–210° (with decomposition) is obtained by dissolving leucine in excess of carbamide at 130°–135°, and yields *isobutylhydantoin*



$$CO{<}\genfrac{}{}{0pt}{}{NH{\cdot}CH{\cdot}CH_2Pr^\beta}{NH{\cdot}CO}$$

m.p. 200°–210°, when heated at 150°; the *ethyl ester* of *isobutylhydantoic acid* is obtained by the action of ammonia on the ethyl ester of *l*-leucinecarbimide, and this on hydrolysis yields the free acid identical with the substance obtained by the action of carbamide on leucine; when aniline is substituted for ammonia the *acid* $NHPh{\cdot}CO{\cdot}NH{\cdot}CH(CH_2Pr^\beta)CO_2H$ is obtained, m.p. 115° (Hugounenq and Morel, Compt. rend. 1905, 140, 150, 505, 859). *Leucine phenylthiohydantoin*



$$SC{<}\genfrac{}{}{0pt}{}{NPh{\cdot}C}{NH{\cdot}CH{\cdot}C_4H_9},$$

m.p. 178°, is formed by the interaction of leucine and phenyl mustard oil in the presence of potassium hydroxide, and its formation affords a convenient method of isolating leucine from the crude material obtained by hydrolysing proteids (Röhman, Ber. 1898, 31, 2188).

Phthalylaminocaproic acid $C_{14}H_{15}O_4N$, prepared by fusing a mixture of phthalic anhydride and leucine, has m.p. 115°–116°; it is lævorotatory, and is converted into the racemic isomeride on dry distillation; the *platodiammonium salt* $Pt(NH_3{\cdot}NH_3C_{14}H_{15}ON)_2$ of the active acid contains $3H_2O$, that of the inactive acid $3\frac{1}{2}H_2O$. *Leucinephthaloic acid*

$$CO_2H{\cdot}C_6H_4{\cdot}CO{\cdot}NH{\cdot}CH(CO_2H)CH_2{\cdot}CHMe_2$$

is obtained by the partial hydrolysis of the preceding compound, the active acid melts and decomposes at 130°–137°, forming phthalylaminocaproic acid; the *potassium salt*

$$K_2C_{14}H_{15}O_5N$$

is crystalline and readily soluble; the *sodium salt* is amorphous; the *barium salt* is crystalline and sparingly soluble; the *platodiammonium salt* forms soluble rhombic plates; the amorphous *copper salt* is soluble in alcohol; the inactive *leucinephthaloic acid* has m.p. 152°–153°, and forms a crystalline *potassium* and an amorphous *silver salt* (Reese, Annalen, 1887, 242, 1; Ber. 1888, 21, 277). The *benzene sulphonic* derivative

$$SO_2Ph{\cdot}HN{\cdot}C_5H_{10}{\cdot}CO_2H$$

of *r*-leucine sinters at 140°, melts at 146° (corr.), and forms soluble crystalline alkali salts, and sparingly soluble lead and silver salts; the corresponding derivative of *d*-leucine crystallises in needles, m.p. 119°–120° (corr.), and has $[\alpha]_D^{20}-39°$ (Fischer, Ber. 1900, 33, 2370; 1901, 34, 449).

Benzoyl-r-leucine

$$(CH_3)_2CH{\cdot}CH_2{\cdot}CH(NH{\cdot}COPh)CO_2H,$$

m.p. 137°–141° (corr.), can be resolved by means of its alkaloid salts, the cinchonine salt of the *d*- and the quinidine salt of the *l*-isomeride being sparingly soluble. *Benzoyl-d-leucine* melts at 105°–107° (corr.), dissolves in 120 parts of boiling water and has $[\alpha]_D^{20}$ $-6{\cdot}39$ in sodium hydroxide solution. *Benzoyl-l-leucine* melts at 105°–107° (corr.), has $[\alpha]_D^{20}+6{\cdot}59$ (Fischer, Ber. 1900, 33, 2370).

Formyl-r-leucine

$$(CH_3)_2CH{\cdot}CH_2{\cdot}CH(NH{\cdot}CHO)CO_2H$$

forms octahedra, m.p. 115°–116° (corr.); *formyl leucylchloride* $C_4H_9{\cdot}CH(NH{\cdot}CHO)COCl$ is a crystalline powder. The *brucine* salt of formyl-*d*-leucine is sparingly soluble, and yields on decomposition *formyl-d-leucine*, crystallising in long thin prisms, m.p. 141°–144° (corr.), $[\alpha]_D^{20}$ $+18{\cdot}8°$ in 10 p.c. alcoholic solution. *Formyl-l-leucine* obtained from the more soluble leucine salt has the same melting-point as the *d*- compound and $[\alpha]_D^{20}-18{\cdot}5°$. For a description of the numerous *polypeptides* containing the leucyl radicle, *see* Fischer and Bargell, Ber. 1903, 36, 2592; Fischer and Brunner, Annalen, 1905, 340, 142; Fischer and Warburg, *ibid.* 152; Fischer and Koelker, *ibid.* 172; Fischer, Ber. 1905, 38, 2914; 1906, 39, 2893; Fischer and Steingroever, Annalen, 1909, 365, 167; Fischer and Gerngross, Ber. 1909, 42, 1485; Fischer and Gluud, Annalen, 1909, 369, 247; Fischer and Fielder, *ibid.* 1910, 375, 181; Abderhalden and Hirszowski, Ber. 1908, 41, 2840; Abderhalden, *ibid.* 1909, 42, 2331; Abderhalden, Hirsch, and Schuler, *ibid.* 1909, 42, 3394; 1910, 43, 907; Abderhalden and Weber, *ibid.* 1910, 43, 2429; Hans Fischer, *ibid.* 1909, 42, 4320; Krause, Monatsh. 1908, 29, 1119; Hopwood and Weizmann, Chem. Soc. Trans. 1911, 99, 574, 1579).

Decomposition.—Experiments conducted on dogs show that leucine, like other amino acids, can replace ammonium salts in the formation of urea (Salaskin, Zeitsch. physiol. Chem. 1898, 25, 128). Leucine as well as tyrosine is assimilated by certain plants such as *Algæ* (Loew and Bokorny, J. pr. Chem. 1887 [ii.] 36, 279; Schulze, Landw. Versuchs. Stat. 1901, 56, 97), *Cucumis* species *Aspergillus niger*, *A. repens*, *Penicillium glaucum* (Lutz, Compt. rend. 1905, 140, 380). Yeast poor in nitrogen develops rapidly in a sugar solution containing leucine; when racemic leucine is employed the fermentation proceeds at the expense of both optical isomerides, but the natural *l*-leucine is destroyed much more rapidly than the *d*-leucine, which can thus be recovered to the extent of 76 p.c. of the theoretical quantity at the end of the reaction (Ehrlich, Zeit. Ver. deut. Zuckerind, 1906, 608, 840). The degradation of amino acids in the plant and animal economy appears to be deamidisation and oxidation of the terminal carbon atom (Sachs, Biochem. Zeitsch. 1910, 27, 27), this would lead in the case of leucine to the formation of ammonia and amyl alcohol; and Ehrlich (Ber. 1906, 40, 1027) is of opinion that the occurrence of fusel oil during alcoholic fermentation is due to the hydrolysis of *l*-leucine and *d*-*iso*leucine according to the equations:

$$CHMe_2{\cdot}CH_2{\cdot}CH(NH_2)CO_2H+H_2O$$
$$=CHMe_2{\cdot}CH_2{\cdot}CH_2{\cdot}OH+CO_2+NH_3$$
$$CHMeEt{\cdot}CH(NH_2)CO_2H+H_2O$$
$$=CHMeEt{\cdot}CH_2{\cdot}OH+CO_2+NH_3$$

On oxidation with hydrogen peroxide leucine yields *iso*valeraldehyde, *iso*valeric acid, ammonia and carbon dioxide; on further oxidation acetone is formed from *iso*valeric acid, the reaction closely resembling several biochemical reactions in which leucine takes part (Dakin, J. Biol. Chem. 1908, 4, 63).

By the action of nitrous acid leucine is converted into leucic acid (α-hydroxycaproic acid) (Strecker, Annalen, 1848, 68, 55); and on reduction with hydriodic acid yields caproic acid and ammonia (Hüfner, Zeitsch. Chem. 1868, 391).

Separation and *detection.*—A mixture of leucine and tyrosine is readily separated by the aid of boiling glacial acetic acid in which the leucine is fairly (29·23 at 117°) and the tyrosine very sparingly soluble (0·18 at 117°) (Habermann and Ehrenfeld, Zeitsch. physiol. Chem. 1902, 37, 18). To separate tyrosine, leucine, and valine, Levene and Jacobs (Biochem. Zeitsch. 1908, 9, 231) recommend the following method. The mixture is treated with bromine, and the bromo derivative of the tyrosine removed by means of amyl alcohol; the valine and leucine are crystallised from the mother liquor, redissolved, and the leucine precipitated by lead acetate and ammonia. On decomposing the lead precipitate with sulphuretted hydrogen, leucine and *iso*leucine are obtained and can be separated by extracting the copper salts with methyl alcohol in which the copper derivative of *iso*leucine is soluble. Glutamic acid and leucine can be separated by saturating the solution with hydrogen chloride when the insoluble hydrochloride of glutamic acid is precipitated (Étard, Compt. rend. 1901, 133, 1231).

*d-iso***Leucine,** *α-amino-β-methylvaleric acid* $CH_3{\cdot}CH_2{\cdot}CH(CH_3)CH(NH_2)CO_2H$ was discovered by Ehrlich (Zeit. Ver. deut. Zuckerind. 1903, 571, 809; Ber. 1904, 37, 1809) in the mother liquor of the beet sugar manufacture to which the strontia desaccharification process had been applied; it is separated from the *r*- and *l*-leucine that occur with it by the aid of its copper salt which dissolves freely in methyl alcohol, the corresponding salt of leucine being only sparingly soluble. *iso*Leucine has also been isolated from the products of hydrolysis obtained by digesting blood fibrin with pancreatic juice, from the hydrolytic products of ovalbumin, from the crude leucine obtained by the putrefaction of beef (Ehrlich, *l.c.*); and from the products of hydrolysis of casein (Weitzenböck, Monatsh. 1906, 27, 831). It is probable indeed that *d-iso*leucine occurs invariably along with *l*-leucine as a primary product of proteid hydrolysis (Ehrlich, *l.c.*; Ehrlich and Wendell, Biochem. Zeitsch. 1908, 8, 399).

*d-iso*Leucine crystallises in shining rods or leaflets, which melt and decompose at 280° when heated in a closed tube; it has $[\alpha]^{20}_{D}+9{\cdot}74$ in aqueous, $+36{\cdot}80$ in 20 p.c. hydrochloric acid, or $+11{\cdot}1°$ in alkaline solution, and dissolves in 25·84 parts of water at 15·5°, the solution having a bitter taste. It is completely racemised and partially converted into *alloisoleucine* after heating for 20 hours at 180° with barium hydroxide solution (Ehrlich, Ber. 1904, 37, 1809).

Locquin (Bull. Soc. chim. 1907, [iv.] 1, 595, 601) finds slightly different physical constants for the synthetic *d*- and *l-iso*leucine; both compounds crystallise from water in brilliant spangles, and have m.p. 280°–290°; *l-iso*leucine has $[\alpha]^{20}_{D}-10{\cdot}55$ in aqueous, $-31{\cdot}37°$ in dilute or $-40{\cdot}86°$ in concentrated hydrochloric acid solution, and *d-iso*leucine has $[\alpha]^{20}_{D}+11{\cdot}29$ in aqueous or $+40{\cdot}61°$ in concentrated hydrochloric acid solution.

When *d-iso*leucine is subjected to dry distillation it yields partially racemised *d*-amylamine $CH_3{\cdot}CH_2{\cdot}CH(CH_3)CH_2{\cdot}NH_2$, together with *iso*leucinimide; and it is decomposed by yeast growing in a sugar solution to form *d*-amylalcohol

$$CH_3{\cdot}CH_2{\cdot}CH(CH_3)CH(NH_2)CO_2H+H_2O$$
$$=CH_3{\cdot}CH_2{\cdot}CH(CH_3)CH_2{\cdot}OH+NH_3+CO_2$$

It follows, therefore, that *iso*leucine is α-amino-β-methylvaleric acid, and this view of its constitution is confirmed by various synthetic preparations. (1) Bouveault and Locquin (Compt. rend. 1905, 141, 115) prepared an inactive leucine from ethyl *sec*butylacetoacetate

$$CHMeEt{\cdot}CHAc{\cdot}CO_2Et,$$

this yields ethyl α-oximino-*sec*butylacetate (α-oximino-β-methylvalerate)

$$CHMeEt{\cdot}C(NOH){\cdot}CO_2Et$$

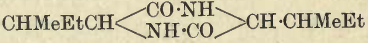
by the action of nitrosylsulphate, which on reduction is converted into the inactive leucine $CHMeEt{\cdot}CH(NH_2)CO_2H$. On resolving this compound by the fractional crystallisation of the leucine salt of its formyl derivative, *d-iso*leucine was obtained, identical with Ehrlich's natural product (Locquin, Bull. Soc. chim. 1907, [iv.] 1, 595, 601). (2) Ehrlich (Ber. 1907, 40, 2538) synthesised *iso*leucine from *d*-amylalcohol $CHMeEt{\cdot}CH_2{\cdot}OH$, by the following series of reactions, the *d*-amylalcohol was oxidised to *d*-valeraldehyde $CHMeEt{\cdot}CHO$, which was converted by the action of ammonia and hydrogen cyanide into aminovaleronitrile $CHMeEt{\cdot}CH(NH_2)CN$, and this, on hydrolysis, gave a mixture of *d-iso*leucine and *alloisoleucine* $CHMeEt{\cdot}CH(NH_2)CO_2H$. Allo*iso*leucine is a stereoisomide of *iso*leucine, which contains two asymmetric carbon atoms; it closely resembles *iso*leucine in its external appearance, and in the properties of its derivatives; it has, however, a sweet taste, is lævorotatory, $[\alpha]^{20}_{D}-14{\cdot}4$ in aqueous and $-36{\cdot}95$ in hydrochloric acid solution; and it dissolves in 34·2 parts of water at 20°. (3) Using Fischer's method (Ber. 1906, 39, 351), Ehrlich (*ibid.* 1908, 41, 1453) has synthesised racemic *iso*leucine from secondary butyl iodide and ethyl malonate; on hydrolysing the condensation product of these two compounds, Rombурgh's *sec*butylmalonic acid is obtained; this on bromination yields bromo-*sec*butylmalonic acid $CHMeEt{\cdot}CBr(CO_2H)_2$, which decomposes when distilled under reduced pressure yielding α-bromo-β-methylvaleric acid

$$CHMeEt{\cdot}CBr{\cdot}CO_2H,$$

on treating this compound with ammonium hydroxide it is converted into racemic *iso*leucine, m.p. 275° in a closed tube. The same synthesis was made by Brasch and Friedmann (Beitr. Chem. Physiol. Path. 1908, 11, 376).

Derivatives. *Salts.*—*d*-iso*Leucine-hydrochloride* forms stellate needles; the *copper salt* $C_{12}H_{22}O_4N_2Cu$ is deep blue and crystalline, dissolves in 278 parts of water at 17°, in 476 parts of 99 p.c. alcohol, and in 55 parts of methyl alcohol at 17°; the *silver salt* is white flocculent and crystalline; the *lead salt* is strongly lævorotatory.

Acyl derivatives of (1) *r-iso*leucine, the *formyl* derivative has m.p. 121°–122°; the *benzoyl* derivative has m.p. 79°, and b.p. 211°/15 mm.; the *benzenesulphonyl* derivative has m.p. 169°; and the *p-toluenesulphonyl* derivative has m.p. 139°. (2) *d-iso*Leucine, *formyl* derivative forms fine translucent crystals from water, m.p. 156°–157°, $[\alpha]^{20}_{D}+28{\cdot}26$; *benzoyl* derivative, m.p. 116°–117°, $[\alpha]^{20}_{D}+26{\cdot}36°$ in alkaline solution; *benzenesulphonyl* derivative, m.p. 149°–150°, $[\alpha]^{20}_{D}-12{\cdot}04°$ in alkaline solution; the *phenylisocyanate*, m.p. 119°–120°, $[\alpha]^{20}_{D}+14{\cdot}92$ in alkaline solution; the *phenylhydantoin* has m.p. 78°–79°; *leucinimide* (*iso*-2 : 5-*diketo*-3 : 6-*diisobutylpiperazine*)



$$CHMeEtCH\left\langle\begin{matrix}CO{\cdot}NH\\NH{\cdot}CO\end{matrix}\right\rangle CH{\cdot}CHMeEt$$

forms slender needles, m.p. 280°–281°, and is slightly dextrorotatory in alcoholic solution. (3) *l-iso*Leucine, *formyl* derivative has m.p. 156°–157°, and has $[\alpha]^{20}_{D}-27{\cdot}76°$ in alcoholic solution; the *benzoyl* derivative has m.p. 118° and $[\alpha]^{20}_{D}-26{\cdot}03$ in *N*/2 sodium hydroxide. For the description of *polypeptides* containing the *iso*leucine radicle, *see* Abderhalden, Hirsch, and Schuler, Ber. 1909, 42, 3394; 1910, 43, 907.

n-**Leucine**, *α-amino-n-hexoic acid*

$$CH_3[CH_2]_3CH(NH_2)CO_2H$$

has not been isolated from the products of hydrolysis of proteins, but *n*-valeric acid is formed when casein is oxidised by bromine (Skraup and Witt, Monatsh. 1906, 27, 663), and this suggests the presence of *n*-leucine in casein. Further evidence in favour of this suggestion was obtained by Heckel (Monatsh. 1908, 29, 15), who found that by oxidising with potassium permanganate that fraction of the leucine esters from casein least soluble in hydrochloric acid, a mixture of acids was obtained about one half of which was *n*-valeric acid. Samee (Monatsh. 1908, 29, 55) also obtained a similar result, using the leucine obtained from the neck band of the ox. Kudielka (Monatsh. 1908, 29, 351) has prepared *n*-leucine by Fischer's method (Ber. 1900, 33, 2320) from both natural and synthetic *n*-hexoic acid, using Kahlbaum's preparation; 100 parts of the former gave 37 parts of *n*-leucine, whilst 100 parts of the latter gave only 6 parts. Racemic *n*-leucine melts at 290° (corr.) in a closed tube. The *copper* salt forms pale blue leaflets, the *nickel* salt is greenish-blue, the *cobalt* salt crystallises in red leaflets; the methylated base yields a yellow *aurichloride* $C_9H_{19}O_2N,HAuCl_4$, m.p. 142°.

The resolution of racemic *n*-leucine has been effected by Fischer and Hagenbach (Ber. 1901, 34, 3764) by the fractional crystallisation of the cinchonine salt of the benzoyl derivative. The *benzoyl* derivative of racemic *n*-leucine has m.p. 134° (corr.); l-*benzoyl*-n-*leucine* crystallises with $\frac{1}{2}H_2O$, has m.p. 53° (corr.), and $[\alpha]_D^{20°}-21{\cdot}9$ in aqueous solution; lævo n-*leucine* prepared from this has $[\alpha]_D-22{\cdot}4$; *d-benzoyl*-n-*leucine* has $[\alpha]_D+21{\cdot}4°$, and dextro n-*leucine* has $[\alpha]_D+21{\cdot}3°$.

Marko (Annalen, 1908, 362, 333) has similarly separated *d*- and *l*- *n*-leucine from the racemic compound by crystallising the brucine salt of the formyl derivative of the racemic compound. *r-Formyl*-n-*leucine* has m.p. 113°–115° (corr.); *l-formyl*-n-*leucine* has m.p. 115°–118·5° (corr.), and $[\alpha]_D^{20}-17{\cdot}56°$; *lævo* n-*leucine* has $[\alpha]_D^{20}-22{\cdot}99°$, *d-formyl*-n-*leucine* has $[\alpha]_D^{20}+17{\cdot}63$, and yields *dextro* n-*leucine* $[\alpha]_D^{20}+23{\cdot}14°$. M. A. W.

LEUCITE. A volcanic mineral consisting of potassium aluminium silicate $KAl(SiO_3)_2$, found as grey crystals with the external form of the cubic icositetrahedron (211). Optical examination of the crystals in thin sections shows them to be birefringent and to consist of a complex intergrowth of twin-lamellæ. At a temperature of 714° the material is optically isotropic and truly cubic, and in the red-hot lavas it, no doubt, grew as a cubic crystal. Sp.gr. 2·47; H. 5½. The mineral occurs abundantly as embedded crystals in the alkali-rich lavas of certain districts, *e.g.* Vesuvius, Rome, and the Eifel. It is decomposed by hydrochloric acid, and is readily affected by weathering processes. Containing a considerable amount of potash (K_2O, 21·5 p.c.), attempts have been made to employ this mineral as a source of potassium salts and as a fertiliser. L. J. S.

LEUCOMAÏNES *v.* PTOMAÏNES.

LEVANT SAPOTOXIN *v.* GLUCOSIDES.

LEVIGATION. Levigation is the mechanical process by which hard substances are reduced to a very fine powder by grinding them with water. The process is used principally in the preparation of pigments. On a small scale the substance is ground with a 'muller.' The muller is a piece of hard stone, convenient in shape and size to hold in the hand, and carefully flattened and polished on one side. The pigment to be ground is mixed with water on a large square slab of stone, preferably marble, and then ground with the muller. The finest artists' colours are ground in this way. On the large scale the pigment is first thoroughly mixed with water in a pug-mill. It is then ground between millstones similar to those used for flour, or under edge runners. Sometimes the millstones are replaced by three horizontal granite rollers, between which the pigment is ground. A mill with stones 2 feet in diameter will grind 15 cwt. of paint in 11 hours.

LEVULIN *v.* DANDELION ROOT.

LEVULOSE, LÆVULOSE *v.* CARBOHYDRATES.

LEVURETIN, LEVURINOSE *v.* SYNTHETIC DRUGS.

LIBAVIUS, FUMING LIQUOR OF. *Stannic chloride* $SnCl_4$ (*v.* TIN).

LICHENIN *v.* GUMS.

LICHENS. According to modern ideas these curious and interesting plants are of a compound character, and are considered to be algæ upon which fungi are supported. Many species have been employed from the earliest times in medicine, dyeing, and as foodstuffs (Mémoires sur l'utilité des lichens, par Hoffmann, Amoreux et Willemet, Lyon, 1787). From about the year 1300 certain species have been employed for the production of the purple dyestuff 'archil' or 'orchil,' since, as shown by modern researches, they contain colourless principles, derivatives of orcin, which under the influence of ammonia and atmospheric oxygen yield the purple colouring matters known as orcein (*v.* ARCHIL). Under the name of *Crottle* or *Crotal*, with various descriptive prefixes, several species have been, and still are to a very limited extent, directly applied in dyeing buff and brown colours on homespun yarn in the Highlands of Scotland, Wales, &c. Those lichens, *e.g.* Iceland moss (*Cetraria islandica*, Ach.), which serve as foodstuffs, contain a starch-like substance termed *lichenin*, which is capable of conversion into glucose.

Our earlier chemical knowledge of the constituents of many of these lichens is mainly due to the work of Knop, Rochleder, Heldt, Schunck, Schmidt, Stenhouse, Stenhouse and Groves, and Weppen, whereas for the later very numerous investigations we are chiefly indebted to the chemists Oswald Hesse and Wilhelm Zopf. As a result, a very large number of new compounds have been isolated and described, the constitutions of which in most cases, however, are as yet undecided. On the other hand, considerable advance has been made as regards the exact structure of some of the more common constituents, viz. atranorin (atranoric acid), barbatic acid, evernic acid, erythrin (erythric acid), lecanoric acid, and ramalic acid, and the chemistry of these substances is dealt with under their special headings.

As the work of Hesse (H.) is mainly to be found in the Journal für praktische Chemie, and that of Zopf (Z.) in the Annalen, to avoid frequent repetition the year only of the papers published in the journals is noted below.

Trachylia tigillaris, Fr. (*Acolium tigillare*; *Calicium tigillare*, *Cyphelium tigillare*), rhizocarpic acid $C_{28}H_{20}O_7$ (H.), m.p. 177°–178°, and acolic acid (H. 1900).

Acarospora chlorophana, rhizocarpic acid, pleosidic acid $C_{17}H_{28}O_4$, m.p. 131°–132° (Z. 1903).

Alectoria implexa, Nyl. (*A. cana*), zeorin, salazinic acid (Z. 1898). *A. ochroleuca*, usnic acid $C_{18}H_{16}O_7$, and barbatic acid (Z. 1899). *A. sarmentosa*, usnic acid (Z. 1900). *A. jubata*, var. *implexa*, salazinic acid, alectoric acid $C_{28}H_{24}O_{15}$, m.p. 186°. *A. articulata*, *d*-usnic acid, usnaric acid

$C_{30}H_{22}O_{15}$, m.p. 240°–260°. *A. canariensis*, *d*-usnic acid, usnaric acid (H. 1902). *A. implexa*, atranorin (H. 1906).

Anaptychia ciliaris, atranoric acid (atranorin). *A. speciosa*, atranorin, zeorin $C_{52}H_{88}O_{4}$ (Z. 1895–1897).

Aspicilia calcarea, erythric acid, oxalic acid, aspicilin, m.p. 178·5° (H. 1900). *A. gibbosa*, aspicilic acid, m.p. 150° (H. 1904).

Baeomyces roseus, an acid, m.p. 180° (H. 1898).

Biatora lucida, rhizocarpic acid $C_{28}H_{20}O_7$, atranorin (Z. 1897; H. 1907); no usnic acid (*cp.* Knop, 1843). *B. mollis*, diffusic acid (Z. 1905). *B. Lightfootii*, *l*-usnic acid (Z. 1906). *B. grandulosa*, gyrophoric acid $C_{16}H_{14}O_7$ (Z. 1906).

Blastenia arenaria (*Callopisma erythrocarpa*), phytosterol, blasterin, m.p. 170° (H. 1898). *B. arenaria*, atranorin, gyrophoric acid $C_{16}H_{14}O_7$ (H. 1898). *B. Jungermanniæ*, parietin (Z. 1906).

Calycium crysocephalum, vulpic acid (H. 1898; Z. 1895). *C. chlorinum* or *chlorellum*, vulpic acid (Z. 1895); pulvic acid and traces of leprarin $C_{19}H_8O_9$ (Kassner, Arch. Pharm. 239, 44; H. 1900). *C. flavum*, chyrsocetraric acid $C_{19}H_{14}O_6$ (H. 1900). *C. Stenhammari*, calycin $C_{18}H_{12}O_5$ (Z. 1895).

Callopisma flavovirescens, chrysophanic acid, physcion $C_{16}H_{12}O_5$ (H. 1902). *C. vitellinum*, calycin (Z. 1895); callopismic acid and mannitol (Z. 1897).

Rhizocarpon oreïtes, A. Zahlbr. (*Catocarpus oreïtes*), rhizocarpic acid $C_{28}H_{20}O_7$, psoromic (parellic) acid, $C_{21}H_{16}O_9$ (Z. 1905).

Cetraria cucullata (*Platysma cucullatum*), protolichesteric acid $C_{18}H_{32}O_5$ (Z. 1902). *C. chlorphylla*, protolichesteric acid and atranorin (Z. 1902). *C. complicata*, protocetraric acid $C_{30}H_{22}O_{15}$, *l*-usnic acid, and atranorin.

Cetraria islandica contains starch not deposited in granules, but uniformly distributed among the cells (lichenin). The lichenin, which is convertible into sugar, is present in such large quantity that this lichen can be used for food (Schmidt, Annalen, 51, 29). There is also said to be present cetraric acid, lichenstearic acid (Knop and Schaedermann, Annalen, 55, 114), protocetraric acid, and proto-*a*-lichesteric acid Z. 1902; H. 1903 and 1904), *a*-lichenostearic acid $C_{18}H_{30}O_5$ (m.p. 122°–123°), *β*-lichenostearic acid $C_{18}H_{20}O_5$ (m.p. 121°), *γ*-lichenostearic acid $C_{18}H_{30}O_5$ or $C_{19}H_{32}O_5$ (m.p. 121°–122°), paralichenostearic acid $C_{20}H_{34}O_5$, dilichenostearic acid $C_{36}H_{60}O_{10}$, and cetraric acid $C_{26}H_{20}O_{12}$ (H. 1898).

C. nivalis, usnic acid (Z. 1904). *C. stuppea* protolichesteric acid (Z. 1904). *C. aculeata* or *Cornicularia aculeata*, protolichesteric acid (Z. 1904); lichenin and lichenic (fumaric) acid. *C. pinastri*, pinastric acid $C_{10}H_8O_3$ (Z. 1895). *C. glauca* (*Platysma glaucum*), lichenin (Berzelius). *C. juniperina*, chrysocetraric acid $C_{19}H_{14}O_6$, usnic and vulpic acids (H. 1898). *C. pinastri*, chrysocetraric, usnic and vulpic acids (H. 1898; Z. 1899). *C. fahlunensis*, cetraric acid (Z. 1898).

Candelaria concolor, callopismic acid or ethylpulvic acid $C_{20}H_{16}O_5$, dipulvic acid $C_{32}H_{22}O_9$ (Z.); calycin, and stictaurin $C_{18}H_{12}O_5$ (H.; Z. 1899). According to Hesse, 1898, dipulvic acid is a mixture of calycin and pulvic anhydride. *C. vitellina*, stictaurin (Z. 1899), calycin and pulvic anhydride (Z. 1899).

Cladina silvatica, usnic acid and cetraric acid (Z. 1898). *C. alpestris*, usnic acid (Z. 1898). *C. rangiferina*, cetraric acid and atranorin (Z. 1898) and usnic acid (H. 1898). *C. pyxidata*, parellic acid (H. 1898). *C. coccifera*, cocellic acid $C_{20}H_{22}O_7$ (H. 1898). *C. uncialis*, *d*-usnic and thamnolic acids $C_{20}H_{18}O_{11}$ (Z. 1902).

Cladonia amaurocraea, usnic acid (Z. 1898). *C. alcicornis*, usnic acid (H. 1902). *C. deformis*, usnic acid (Z. 1900). *C. cyanipes*, usnic acid (Z. 1900). *C. Floerkeana*, cocellic and thamnolic acids (H. 1900). *C. rangiformis*, atranorin, rangiformic acid $C_{20}H_{33}O_5{\cdot}OMe$ (H. 1898). *C. uncinata* (no usnic acid, see Knop, Annalen, 1844, 49, 120); but uncinatic acid $C_{23}H_{28}O_9$ (H. 1900). *C. destricta* (*C. uncialis*), usnic acid and starch (Knop, Annalen, 49, 119); *l*-usnic acid (Salkowski, Annalen, 1901, 319, 391). *C. incrassata*, *l*-usnic acid (S.). *C. glauca*, squamatic acid (Z. 1902). *C. strepsilis*, thamnolic acid and strepsilin (Z. 1903). *C. thamnolis*, thamnolic acid $C_{20}H_{18}O_{11}$, and strepsilin. *C. destricta*, *l*-usnic acid (Z. 1903); *l*-usnic and squamatic acids and cladestin (H. 1904). *C. macilenta*, usnic acid and starch (Knop, *l.c.*); rhizonic acid (Z. 1903). *C. squamosa*, var. *ventricosa*, squamatic acid (Z. 1904). *C. squamosa*, var. *denticollis*, squamatic acid (Z. 1907). *C. fimbriata*, var. *simplex*, fumaroprotocetraric acid and fimbriatic acid (Z. 1907). *C. fimbriata*, var. *cornuto-radiata*, fumaroprotocetraric acid (Z. 1907). *C. pityrea*, var. *cladomorpha*, fumaroprotocetraric acid (Z. 1907). *C. silvatica*, var. *condensata*, *l*-usnic acid (Z. 1907). *C. verticillata*, var. *subcervicornis*, fumaroprotocetraric acid (Z. 1907), atranorin and cervicornin. *C. chlorophæa*, fumaroprotocetraric acid. *C. gracilis*, var. *chordalis*, fumaroprotocetraric acid (Z. 1907). *C. crispata*, var. *gracilescens*, squamatic acid (Z. 1907). *C. coccifera*, cocellic acid $C_{20}H_{22}O_7$ (H. 1895). *C. incrassata*, *l*-usnic acid (Z. 1905). *C. rangiferina* usnic acid (Rochleder and Heldt, Annalen, 48, 2); lichenin (Schmidt, *ibid.* 51, 29); cladonic acid (*β*-usnic acid) $C_{18}H_{18}O_7$ (Stenhouse, *ibid.* 155, 58); *d*-usnic acid (no *l*-usnic) and silvatic acid $CO_2Me{\cdot}C_{18}H_{34}O_3{\cdot}COOH$ (H. 1907); atranorin and fumaroprotocetraric acid (Z. 1906). *C. rangiferina*, var. *vulgaris*, atranorin and protocetraric acid (H. 1898). *C. rangiferina*, var. *silvatica*, *d*-usnic acid (Z. 1906); usnic and protocetraric acids (H. 1898). *C. pyxidata*, lichenin (Schmidt, Annalen, 51, 29); emulsin (Hérissey, J. Pharm. Chim. 1898, [vi.] 7, 577).

Cornicularia aculeata, rangiformic acid (H. 1902).

Chiodecton sanguineum (*C. rubrocinctum*), chiodectonic acid $C_{14}H_{18}O_5$.

Cyphelium trichiale, var. *candelare*, calycin (Z. 1906).

Darbishirella gracillima, parellic acid (H. 1898).

Dendographa leucophæa, protocetraric acid (H. 1898); erythrin and orcinol (Ronceray, Bull. Soc. chim. 1904, [iii.] 31, 1097).

Dimelaena oreina, zeorin and usnic acid (Z. 1897).

Diploicia canescens (*Catolechia canescens*), diploicin, m.p. 225°, catolechin, m.p. 214°–215°, and atranorin (Z. 1904).

Diploschistes scruposa, diploschistessic acid $C_{15}H_{16}O_7$ (Z. 1906).

Endocarpon miniatum (α) *vulgare*, phytosterol and an acid (H. 1898).

Evernia divaricata, divaricatic acid (H. 1900) $C_{21}H_{23}O_6{\cdot}OMe$, and usnic acid (Z. 1897); no usnic acid (H.). *E. furfuracea*, usnic acid (Rochleder and Heldt, Annalen, 48, 9); no usnic acid, but erythric acid (Z. 1897), or rather olivetoric acid $C_{27}H_{36}O_8$ (Z. 1900), physodic acid, physodylic acid $C_{23}H_{26}O_8$, and furevernic acid (H. 1907); atranorin, evernuric acid $C_{22}H_{24}O_8$, and furevernic acid, but no erythric or olivetoric acids (H. 1906); emulsin (Hérissey, J. Pharm. Chim. 1898, [v.] 7, 577). *E. prunastri*, evernic acid, atranorin (Z. 1897); evernic acid, usnic acid, and atranorin, and chrysocetraric acid (H. Annalen, 1895) $C_{19}H_{14}O_6$. *E. thamnodes*, divaricatic acid, usnic acid (Z. 1897; H. 1900). *E. vulpina*, vulpic acid and atranorin (H). *E. illyrica* (Dalmatia), divaricatic acid and atranorin (Z. 1904). *E ochroleuca*, usnic acid (Knop, Annalen, 49, 122).

Everniopsis Trulla, salazinic acid and atranorin (Z. 1897).

Gasparrinia medians (*Physcia medians*) calycin, rhizocarpic acid (H. 1898); pulvic lactone (H. 1903). *G. sympagea*, parietin (Z. 1905). *G. elegans* (*Physcia elegans*), physcion (H. 1898). *G. murorum*, physcion (H. 1898). *G. decipiens* physcion (H. 1898). *G. cirrhochroa*, chrysophanic acid (Z. 1897).

Graphis scripta, salazinic acid (H. 1900).

Gyalolechia aurella, calycin (Z. 1895), callopismic acid (Z. 1897), stictaurin (Z. 1899).

Umbilicaria pustulata (Hoffm.) (*Gyrophora pustulata*), gyrophoric acid $C_{36}H_{36}O_{15}$ (Stenhouse, Annalen, 70, 218) $C_{16}H_{14}O_7$ (H.). *G. hirsuta*, gyrophoric acid (Z. 1898). *G. deusta*, gyrophoric acid (Z. 1898). *G. polyphylla*, umbilicaric acid $C_{25}H_{22}O_{10}$ (Z. 1898); umbilicaric acid and gyrophoric acid (H. 1898, 1901). *G. hyperborea*, umbilicaric acid (Z. 1898). *G. deusta*, umbilicaric acid (Z. 1898). *G. vellea*, gyrophoric acid and gyrophorin, m.p. 189° (Z. 1899). *G. spodochroa*, var. *depressa*, gyrophoric acid (Z. 1900). *G. polyrrhiza*, umbilicaric acid, lecanoric acid, gyrophoric acid (Z. 1905).

Hæmatomma ventosum, divaricatic acid $C_{22}H_{26}O_7$, m.p. 149° (Z. 1898); *d*-usnic acid, divaricatic acid, and an acid resembling alectoric acid (H. 1900). *H. coccineum*, var. *leiphæmum*, leiphæmin, m.p. 193°, atranorin, zeorin (Z. 1902). *H. coccineum*, var. *abortivum*, coccic acid $C_{12}H_{16}O_{10},3H_2O$, m.p. 262°–264°, atranorin, hæmattomin $C_{10}H_{16}O$ or $C_{20}H_{32}O_2$, m.p. 143°–144°, and hæmatommidin, m.p. 194°–196° (Z. 1903); no zeorin (H. 1907). *H. coccineum*, var. (?), lecanoric acid (H. 1907). *H. coccineum*, var. (?) (from Wildbad), coccic acid, atranorin, zeorin, hydrohæmatommin $C_{10}H_{18}O$, m.p. 101° (H. 1906). *H. coccineum*, *l*-usnic acid, zeorin, atranorin, porphyrillic acid, hymenorhodin, and leiphæmin (Z. 1906). *H. leiphæmum*, atranorin, zeorin, leiphæmin, leiphæmic acid $C_{22}H_{46}O_5$, m.p. 114°–115° (Z. 1903). *H. porphyrium*, atranorin, zeorin, porphyrilic acid, leiphæmin, hymenorhodin (Z. 1906).

Pertusaria dealbata, Nyl. f. *corallina*, Cromb. (*Isidium corallinum*) ('white crottle'), calcium oxalate (Braconnot, Ann. Chim. Phys. [ii.] 28, 319).

Lecanora atra, atranoric acid (atranorin) $C_{19}H_{18}O_8$, and a yellow crystalline substance (Paternò and Oghaloro, Gazz. chim. ital. 1877, 7). Hesse (Ber. 10, 1324) considers the atranoric acid to be hydrocarbonusnic acid, and the yellow substance to be cladonic acid. Obtained from certain districts it contains lecanorol (Z. 1897) $C_{27}H_{30}O_9,H_2O$. *L. varia*, psoromic acid and *l*-usnic acid (Z. 1905). *L. grumosa*, atranorin and lecanorol (Z. 1897). *L. cenisea*, atranorin and roccellic acid $C_{17}H_{32}O_4$ (*cp.* Schunck and Hesse, *Roccella tinctoria*). *L. sordida*, atranorin, zeoric acid (Z. 1897). *L. sordida*, var. *glaucoma*, atranorin and parellic acid (H. 1898). *L. sordida*, var. *Swartzii*, atranorin, thiophanic acid $C_{12}H_6O_{12}{\cdot}H_2O$, m.p. 242°, roccellic acid, lecasteric acid $C_{10}H_{20}O_4$, m.p. 116°, and lecasteride $C_{10}H_8O_5$, m.p. 105° (H. 1898). *L. campestris*, atranorin (Z. 1897). *L. badia*, stereocaulic acid (Z. 1897). *L. effusa*, atranorin and usnic acid (Z. 1897). *L. subfusca*, atranorin (Z. 1897; H. 1900). *L. epanora*, zeorin and lepanorin, m.p. 131°–132° (Z. 1900). *L. glaucoma* (*L. sordida* α-*glaucoma*) (from Tyrol), atranorin, thiophanic acid, roccellic acid (Z. 1903). *L. sulphurea*, usnic acid (Z. 1903). *L. parella* ('light crottle'), parellic acid, lecanoric acid (Schunck, Annalen, 54, 257, 274; 41, 161). *L. tartarea* (Linn.) (*Patellaria tartarea*, *Parmelia tartarea*), erythric acid, synonymous with Nees. v. Esenbeck's 'remarkable resin' (Brandes' Archiv. Apoth. 16, 135), with Heeren's erythrin, and with Kane's erythrilin (Schweigger's, J. Ch. Phys. 59, 313). Schunck found crustaceous lichens belonging to *Lecanora*, &c., collected on the basalt rocks of the Vogelsberg in Upper Hessia to contain lecanoric and erythric acids (Annalen, 41, 157). In a specimen from Norway, Stenhouse (*ibid.* 70, 218) found gyrophoric acid. *L. ventosa*, usnic acid (Knops, *ibid.* 49, 122).

Rhizocarpon geographicum, Dl. (*Lecidea geographica*) usnic acid (Knop, *l.c.*). *Lecidea candida* (*Psora candida*), calcium oxalate (Braconnot, Ann. Chim. Phys. [ii.] 28, 319). *L. cineroatra*, lecidic acid $C_{22}H_{27}O_4{\cdot}COOMe$, m.p. 147°, and lecidol, m.p. 93° (H. 1898). *L. sudetica*, salazinic acid (Z. 1899). *L. confluens*, confluetin, m.p. 147°–148° (Z. 1899). *L. grisella*, gyrophoric acid (H. 1900). *L. aglæotera* (*L. armeniaca*, var. *lutescens*), roccellic and cetraric acids (Z. 1904).

Lepraria latebrarum, leprarin, m.p. 155°, roccellic acid (Z. 1897), and atranorin (Z. 1900); *d*-usnic, hydroroccellic, lepraric, and talebraic acids (m.p. 208°) and atranorin (H. 1903). *L. flava*, calycin, pinastric acid, calyciarin (Z. 1905). *L. xanthina* (from Vorarlberg), physcion (H. 1906). *L. latebrarum* (Baden-Baden), atranorin, leprariaic acid, oxyroccellic acid, and neobraic acid (H. 1906). *L. candelaris*, calycin (Z. 1906). *L. chlorina*, calycin (Z. 1895).

Lepra candelaris (*Lepraria flava*), calycin

$$C_{18}H_{11}O_4{\cdot}OH,$$

m.p. 240°–242° (H. 1898).

Leprantha impolita (*Arthonia pruinosa*), lecanoric acid, lepranthin $C_{25}H_{40}O_{10}$, m.p. 183°, lepranthaic acid $C_{20}H_{32}O_2$, m.p. 111°–112° (Z. 1904).

Mycoblastus sanguinarius, caperatic acid and atranorin (Z. 1899).

Menegazzia pertusa (*Parmelia pertusa*), atranorin and farinacic acid (capraric and pysodic acids absent) (H. 1907).

Nephroma arcticum, zeorin, nephrin, and *d*-usnic acid (Z. 1909). *N. antarcticum*, zeorin and *d*-usnic acid (Z. 1909). *N. parile*, zeorin and mannitol (Z. 1909). *N. resupinatum*, mannitol (Z. 1909). *N. lævigatum*, mannitol (Z. 1909). *Nephromium lævigatum*, usnic acid and nephrin $C_{20}H_{32},H_2O$, m.p. 168° (H. 1898). *N. tommentosum*, usnic acid and nephrin (H. 1898). *N. lusitanicum*, nephrin and nephromin $C_{16}H_{12}O_6$, m.p. 196° (H. 1898).

Ochrolechia androgyna (*Lecanora subtartarea*), gyrophoric acid and calyciarin (Z. 1905). *O. pallescens* var. *parella* (from Auvergne), parellic acid and ochrolechiasic acid $C_{22}H_{14}O_9$, m.p. 282° (H. 1906); but no lecanoric acid (*see* Schunck, Annalen, 1845, 54, 274) (Z. 1898). *O. tartarea*, gyrophoric acid (Z. 1898)

Pannaria lanuginosa, hydroxyroccellic acid $C_{17}H_{32}O_5$, m.p. 128°, and pannaric acid $C_9H_8O_4$, m.p. 224° (H. 1901).

Parmelia aleurities, atranorin (Z. 1897). *P. tiliacea*, atranorin and parmelialic acid, m.p. 165° (Z. 1897); the latter is in reality lecanoric acid (H. 1898 and 1900). *P. perlata*, atranorin and hæmatommic acid (Z. 1897); usnic acid, lecanoric acid, and perlatin (H. 1900); imbricaric acid (Z. 1902); no lecanoric acid (H. 1903); atranorin and perlatic acid $C_{27}H_{27}O_9\cdot OMe,2H_2O$ (H. 1904). *P. perlata* from certain sources: (*a*) atranorin, (*b*) atranorin, usnic, and vulpic acids, (*c*) atranorin and lecanoric acid, (*d*) atranorin and perlatin $C_{19}H_{14}O_5(OMe)_2$ (H. 1898). *P. saxatilis*, var. *sulcata*, atranorin and stereocaulic acid (Z. 1897); protocetraric acid only (H. 1900), not protocetraric but pannatic acid (H. 1904); usnic acid (Schmidt, Annalen, 51, 29). *P. saxatilis*, var. *panniformis*, atranorin, protocetraric acid, and usnetic acid $C_{24}H_{26}O_8$ (not $C_9H_{10}O_3$), m.p. 192° (H. 1900). *P. saxatilis retiruga*, atranorin, protocetraric acid, and saxatic acid $C_{25}H_{40}O_8$, m.p. 115° (H. 1903). *P. physodes* (or *P. ceratophylla*, var. *physodes*) is known as 'dark crottle,' and is employed for dyeing a brown colour on homespun woollen yarn. Contains physodin and two colourless substances (Gerding, Brandes, Arch. Pharm. [ii.] 87, 1), ceratophyllin (H. Annalen, 119, 365); atranorin, physodalic acid, and physodalin (Z. 1897 and 1898); evernuric acid, physodylic acid, capraric acid, and atranorin (H. 1907). *P. parietina*, chrysophanic acid (Rochleder and Heldt, 48, 12); identical with Thomson's (Edin. New. Phil. Jour. 37, 187), parietin, also (H. 1895) physcion $C_{16}H_{12}O_5$, physcianin $C_{10}H_{12}O_4$, m.p. 143°, and physciol $C_7H_8O_3$, m.p. 107°. A variety of *P. parietina* growing on sandstone rock and not on trees like that of Rochleder and Heldt, contained vulpic acid (chrysopicrin) Stein (J. pr. Chem. [i.] 93, 366). *P. caperata* ('stone crottle'), emulsin (Hérissey, J. Pharm. [vi.] 7, 577); capraric acid $C_{22}H_{18}O_8(COOH)_2$, m.p. 240°, usnic acid, caperatic acid $COOMe,C_{18}H_{33}O_2(COOH)_2$, m.p. 132°, and caperin $C_{36}H_{60}O_3$, m.p. 243° (H. 1898), *d*-usnic acid (H. 1900). *P. caperata* from *Castanea vesca*, usnic, capraric and caperatic acids (H. 1904). *P. conspersa*, usnic acid, zeorin, and atranorin (Z. 1898); usnic acid and salazinic acid (H. 1898); *d*-usnic acid and conspersaic acid, m.p. 252° (H. 1903). *P. acetabulum*, atranorin (Z. 1898); atranorin and salazinic acid (H. 1901). *P. excrescens*, zeorin and atranorin (Z. 1898). *P. perlata*, var. *exrescens*, atranorin (Z. 1898). *P. Nilgherrensis*, atranorin (Z. 1898). *P. perforata*, zeorin and atranorin (Z. 1898); lecanoric acid (H. 1900). *P. olivetorum*, atranorin (Z. 1898); lecanoric acid, but no erythric acid (H. 1900); olivetoric acid $C_{27}H_{34}O_8$, m.p. 141°-142° (Z. 1902); atranorin, olivetorin, m.p. 143°, and olivetoric acid $C_{21}H_{26}O_7$ (H. 1903). *P. pertusa*, physodalic acid (Z. 1898). *P. fuliginosa*, atranorin and lecanoric acid (H. 1898). *P. fuliginosa*, var. *ferruginascens*, lecanoric acid (Z. 1899). *P. pulverulenta*, unknown acid (H. 1898). *P. ciliaris*, everninic acid and atranorin (?) (H. 1898). *P. omphalodes* (*P. saxatilis*, var. *omphalodes*). Under the name of 'black crottle' this lichen is employed for dyeing a brown colour in the outer Hebrides (Lewis and Harris); contains stereocaulic acid (Z. 1899). *P. tiliacea*, var. *scortea*, lecanoric acid (Z. 1899). *P. verruculifera*, lecanoric acid (Z. 1899). *P. glomellifera*, glomelliferin, m.p. 143°-144° (Z. 1899 and 1902). *P. incurva*, usnic acid (Z. 1900). *P. Borreri*, lecanoric acid (Z. 1900). *P. sorediata*, diffusin (Z. 1900); lecanoric acid (H. 1900). *P. tinctorum*, atranorin (H. 1900). *P. tinctorum* (E. Africa), atranorin and lecanoric acid (H. 1906). *P. tinctorum* (Madras cinchona bark), atranorin and lecanoric acid (H. 1904). *P. glabra*, lecanoric acid (H. 1902). *P. lacarnensis*, imbricaric acid (Z. 1902). *P. sinuosa*, *d*-usnic and usnaric acids (Z. 1902).

Parmelia cetrata (Java cinchona bark), cetrataic acid $C_{29}H_{24}O_{14}$, m.p. 178°-180° (H. 1903). *P. olivacea*, oliveacein $C_{17}H_{22}O_6\cdot H_2O$, m.p. 156°, and oliveaceic acid $C_{16}H_{19}O_5\cdot OMe$, m.p. 138° (H. 1903). *P. revoluta*, atranorin and gyrophoric acid (Z. 1905). *P. pilosella*, atranorin and pilosellic acid, m.p. 245° (Z. 1905). *P. Mougeotti*, *d*-usnic acid (H. 1906).

Peltigera apthosa, peltigerin $C_{21}H_{20}O_8$ (or $C_{16}H_{16}O_6$), m.p. 170°-180°, and mannitol (Z. 1909). *P. malacea*, peltigerin, zeorin, and mannitol (Z. 1909). *P. horizontalis*, peltigerin, zeorin, and mannitol (Z. 1909). *P. polydactyla*, peltigerin, mannitol, polydactylin, m.p. 178°-180°, and peltidactylin, m.p. 237°-240°. *P. venosa*, peltigerin. *P. scabrosa*, peltigerin. *P. propagulifera*, peltigerin and zeorin. *P. lepidophora*, peltigerin. *P. praetextata*, mannitol. *P. rufescens*, mannitol. *P. spuria*, mannitol. *P. canina*, caninin (Z. 1909); emulsin (Hérissey, J. Pharm. Chim. [vi.] 7, 577).

Pertusaria amara (*P. communis β-variolosa*, *Variolaria amara*), emulsin (Hérissey, *l.c.*); cetraric acid, pertusaric acid $C_{24}H_{38}O_6$, m.p. 103°, pertusarin $C_{30}H_{50}O_2$, m.p. 235°, pertusarene $C_{60}H_{100}$, m.p. 286°, and pertusaridin (H. 1898); salazinic acid and picrolichenin (Z. 1900); orbiculatic acid $C_{22}H_{36}O_7$ (H. 1901). *P. lactea*, lecanoric acid and variolaric acid, m.p. 285° (Z. 1902). *P. lactea* (sterile Auvergne), lecanoric acid and ochrolechiasic acid (H. 1906). *P. corralina* (*P. ocellata β-coralline*), ocellatic acid $C_{20}H_{15}O_{11}\cdot OMe$, m.p. 208° (H. 1901). *P. rupestris* (*P. communis β-areolata*), areolatin $C_{11}H_7O_6\cdot OMe$, m.p. 270°, areolin, m.p. 243°, and gyrophoric acid $C_{16}H_{14}O_7$ (H. 1903). *P. glomerata* (Wildbad), porin $C_{42}H_{67}O_9OMe$, m.p. 166°, and porinic acid $2[C_{11}H_{12}O_4],H_2O$, m.p. 218° (H. 1903). *P. Wulfenii* (*P. sulfurea*, *P. sulphurella*, *P. fallax*), thiophanic acid (Z. 1904). *P. lutescens*, thiophanic acid (Z. 1904).

Placodium gypsaceum, squamaric acid and usnic acid (Z. 1898); parellic acid, but no usnic acid (H. 1901). *P. chrysoleŭcŭm*, usnic acid (Z. 1898). *P. saxicolum*, var. *vulgare*, usnic acid and zeorin (Paternò, Atti. R. Accad. Lincei, 1876, [ii.] 3); zeorin, but no atranorin (H. 1898), *d*-usnic acid (H. 1900). *P. saxicolum*, var. *compactum*, atranorin (H. 1901). *P. melanaspis*, atranorin (Z. 1898). *P. Lagascœ*, psoromic and usnic acids (Z. 1897).

Placodium crassum, atranorin (trace), *l*-usnic acid (H. 1901). *P. circinatum* (*a*) *radiosum*, salazinic acid (H. 1902).

Physcia ciliaris, emulsin (Hérissey, J. Pharm. Chim. [vi.] 7, 577). *P. endococcina*, zeorin and atranorin (Z. 1895), rhodophyscin and endococcin (Z. 1905). *P. caesia*, zeorin and atranorin (Z. 1895); atranorin and zeorin (H. 1902). *P. stellaris*, *f. adscendens*, atranorin (Z. 1895). *P. parietina*, atranorin and placodin, m.p. 245° (H. 1899). *P. medians*, vulpic acid and calycin (Z. 1895), calycin and callopismic acid (Z. 1897). *P. pulverulenta*, var. *β-pityrea*, atranorin (Z. 1895).

Physcia tenella, atranorin (Z. 1895). *P. aipolia*, atranorin (Z. 1895).

Cetraria glauca (*Platysma glaucum*) atranorin and caperatic acid (Z. 1899). *Cetraria cucullata* (*P. cŭcŭllatum*), lichenostearic acid and usnic acid (Z. 1899). *P. diffusum*, diffusin, m.p. 135°–136°, and usnic acid (Z. 1899).

Pleopsidium chlorophanum, rhizocarpic acid (Z. 1895).

Pseudevernia ericetorum, atranorin, physodalin (Z. 1905).

Psora ostreata, lecanoric acid (Z. 1899).

Pulveraria chlorina, calycin, vulpic acid, and lepraric acid, m.p. 228° (H. 1898). *P. latebrarum*, atranorin, parellic acid, latebride, m.p. 128°, and pulverin, m.p. 262° (H. 1898). *P. farinosa*, oxyroccellic acid, and pulveraric acid, m.p. 234° (H. 1898).

Raphiospora flavovirescens, rhizocarpic acid (Z. 1895).

Ramalina calicaris, var. *fastigiata*, contains large quantities of starch (lichenin) and a small quantity of saccharic acid (Berzelius, Scherer's Annalen, 3, 97), usnic acid (Rochleder and Heldt, *ibid.* 48, 9). *R. calicaris*, var. *fraxinea*, lichenin and usnic acid (R. and H. *l.c.*); *a*-usnic acid (Hesse, Annalen, 117, 297). *R. ceruchis*, usnic acid and usnaric acid (H. 1898). *R. armorica*, atranorin, armoricaic acid, m.p. 240°–260°, armoric acid $C_{18}H_{18}O_7,H_2O$, m.p. 226°–228° (H. 1907). *R. cuspidata*, cuspidatic acid $C_{16}H_{20}O_{10}$, m.p. 218° (H. 1900). *R. farinacea*, *d*-usnic acid and ramalic acid $C_{30}H_{26}O_{15}$, m.p. 240°–245° (H. 1903). *R. subfarinacea*, *d*-usnic acid and salazinic acid (Z. 1907). *R. minuscula*, *d*-usnic acid (Z. 1907). *R. Kullensis*, *d*-usnic acid, kullensisic acid $C_{22}H_{18}O_{12}$ (Z. 1907). *R. obtusata*, *d*-usnic acid, ramalinellic acid, m.p. 169°, and obtusatic acid (Z. 1907). *R. Landroënsis*, *d*-usnic acid and landroënsin (Z. 1907). *R. pollinaria*, ramalic acid $C_{16}H_{13}O_3OMe$ and evernic acid (Z. 1897); usnic acid, atranorin, evernic acid, and ramalic acid (H. 1898). *R. fastigiata*, emulsin (Hérissey, J. Pharm. Chim. 1898, [vi.] 5, 577). *R. fraxinea*, emulsin (Hérissey, *ibid.*). *R. polymorpha*, usnic acid (Z. 1897). *R. scopulorum* (*see* Thomson, Annalen, 53, 252), *d*-usnic acid, scopuloric acid $C_{19}H_{16}O_9$, m.p. 260° (Z. 1907). *R. thraŭsta*, usnic acid (Z. 1900). *R. yemensis*, *d*-usnic acid (H. 1902).

Reinkella birellina, roccellic and oxyroccellic acids (H. 1898).

Rhizocarpon geographicum f. contiguum, parellic acid, rhizonic acid $C_{19}H_{20}O_7$, m.p. 185°, rhizocarpic acid $C_{28}H_{22}O_7$ (H. Ber. 1898, 31, 663), rhizonic acid is $OMe{\cdot}C_{17}H_{14}O_2(OH)_2COOH$ (H.). *R. geographicum f. lecanorinum*, rhizocarpic acid (Z. 1895); parellic acid, rhizocarpinic acid, m.p. 156°, rhizocarpic acid

$$COOH{\cdot}C_{24}H_{16}O_3{\cdot}COOEt,$$

m.p. 177°–178°. Parellic acid

$$COOMe{\cdot}C_{17}H_{11}O_3(COOH)_2,$$

m.p. 262°–265°, is the same as Zopf's psoromic acid, and the squamaric acid and zeoric acid of other writers (H.). *R. geographicum f. geronticum*, parellic and rhizocarpic acids, but not rhizocarpinic acid (H. 1909).

Rhizoplaca opaca (*Lecanora chrysoleuca*, *β-opaca*, *Parmelia rubina β-opaca*, *Squamaria chrysoleuca β-opaca*), usnic acid, placiodilic acid (previously termed placiodĭlin), and rhizoplacic acid $C_{21}H_{40}O_5$, m.p. 94°–95° (Z. 1905), usnic acid and placiodilic acid $C_{17}H_{18}O_7$, m.p. 156°–157° (Z. 1906).

Roccella fuciformis (*R. tinctoria*, var. *fuciformis*). This well-known 'orchella weed' is imported from Angola, Zanzibar, Madagascar, Ceylon, and Lima for the purpose of manufacturing archil and cudbear. It contains erythric acid (Heeren's erythrin, Kane's erythrilin) and roccellic acid (Schunck, Pharm. J. [iii.] 39, 164; Annalen, 61, 64; Kane, Trans. Roy. Soc. 1840, 273; Heeren and Schweiggers, J. Pharm. Chim. 59, 346). Stenhouse (Annalen, 149, 288) examined a Lima weed in 1848, and found it to contain lecanoric acid, but this was probably *R. tinctoria* and not identical with the *R. fuciformis* examined by him in 1869, and in which he found erythric acid. Compare Hesse (Annalen, 117, 329, and 139, 22) who found Lima weed to contain erythric acid, but not lecanoric acid. Stenhouse considers the *R. Montagnei* from Angola, in which he found erythric acid to be identical with *R. tinctoria*, var. *fuciformis*, examined by Schunck. A stunted variety of *R. fuciformis*, examined by Menschutkin and Lamparter, contained *β*-erythrin. In a better growing specimen erythrin was obtained (Lamparter, Annalen, 134, 243). A variety of *R. fuciformis*, probably from the west coast of Africa, contained erythric acid and a bitter substance picroroccellin (Stenhouse and Groves, *ibid.* 185, 14). More recently Hesse (1898) has found the weed to contain erythric acid and oxyroccellic acid.

Roccella Montagnei, erythric acid and oxyroccellic acid (H. 1898); orcinol (Ronceray, Bull. Soc. chim. 1904, iii. 1097). *R. fruticosa*, eyrthric acid (erythrin) (H. Ber. 1904, 37, 4693). *R. phycopsis* (Crete), erythrin, oxyroccellic acid, oxalic acid, and erythritol (H. 1906). *R. peruensis* (*R. fructectosa* and *R. cacticola*), erythrin, oxyroccellic, and roccellic acids (H. 1898), erythrin, erythritol, and oxalic acid (H. 1906). *R. portentosa*, lecanoric acid (H. 1898). *R. decipiens*, lecanoric acid (H. 1898). *R. sinensis*, lecanoric acid (H. 1898).

Roccella tinctoria. This lichen used largely for the manufacture of orchil and cudbear, is imported from the Cape of Good Hope, the Cape Verd Islands, and Chile (Valparaiso Weed). Formerly it seems to have been imported also from Lima (Stenhouse). It contains lecanoric acid (Stenhouse's α- and β-orsellic acid) and roccellinin. The latter is, however, probably a decomposition product of the former (Stenhouse, Annalen, 68, 55; 149, 288; Phil. Mag. [iii.] 32, 300). According to Hesse (1898) it contains erythrin, oxyroccellic acid, roccellic acid, and lecanoric acid, whereas Ronceray (Bull. Soc. chim. 1904, [iii.] 31, 1097) detected in this lichen the presence of lecanoric acid and orcinol (*cp.* Hesse, Ber. 1904, 37, 4693).

Roccellaria intricata, zeorin and roccellaric acid, m.p. 110° (H. 1898).

Squamaria elegans (*Gasparrinia elegans*), chrysophanic acid (Thomson, Phil. Mag. [iii.] 25, 39); physcion (H.).

Solorina crocea, soloric acid, m.p. 199°–201° (Z. 1895).

Sphærophorus fragilis, sphærophorin, m.p. 138°–139°, and fragilin (Z. 1898), sphærophorin $(C_{14}H_{16}O_4)_n$, or $C_{28}H_{34}O_8$, sphærophoric acid, m.p. 206°–207 , and fragilin (Z. 1905).

Sphyridium placophyllum, atranorin (Z. 1898).

Stereocaulon alpinum atranorin, and stereocaulic acid, m.p. 200°–201° (Z. 1895). *S. corallöides*, atranorin and psoromic acid (Z. 1895), usnetic acid, atranorin, and an acid not psoromic acid. Zopf's stereocaulic acid from *S. alpinum* is usnetic acid (H. 1900). *S. incrustatum*, atranorin and psoromic acid (Z. 1895). *S. vesuvianum*, psoromic acid (Z. 1895). *S. denudatum*, var. *genuinum* atranorin (Z. 1895). *S. tomentosum*, atranorin (Z. 1895). *S. pileatum*, atranorin and stereocaulic acid (Z. 1895 and 1899). *S. condensatum*, atranorin (Z. 1895). *S. paschale*, atranorin (Z. 1895). *S. virgatum* f. *primaria*, atranorin (Z. 1895). *S. ramulosum*, atranorin (Z. 1895). *S. salazinum*, salazinic acid, which blackens at 260°–262° (H. 1900).

Sticta fuliginosa, trimethylamine (Z. 1897). *S. aurata*, stictaurin a derivative of pulvic acid (Z. 1899). Stictaurin has the formula $C_{18}H_{12}O_5$ (H. 1900). *S. desfontainii*, calycin and ethylpulvic acid (H. 1900). *S. pulmonaria*, stictaic acid $C_{18}H_{11}O_8(OMe.)$, m.p. 264°, stictinic acid, (Knop and Schnedermann, J. pr. Chem. 1846, 39, 365), and not protocetraric acid (H. 1900). This lichen is known as 'hazel crottle.'

Stictina gilva, stictinin, m.p. 160°–161° (Z. 1905).

Thamnolia vermicularis, thamnolic acid, m.p. 202°–204° (Z., Chem. Zentr. 1893, ii. 54). According to Hesse this has the formula $C_{19}H_{15}O_{10}\cdot OMe$ (1898 and 1900).

Thallœdema candidum, probably lecanoric acid (H. 1898).

Thalloschistes flavicans, parietin (Z. 1905) (Brittany); physcion and acromelin (H. 1907).

Tornabenia chrysophthalma, physcion (H. 1907). *T. flavicans*, var. *crocea*, physcion (H. 1907). *T. flavicans*, var. *acromela* (*Physcia acromela*), acromelin $C_{17}H_{16}O_9$, m.p. 242°, and acromelidin $C_{17}H_{20}O_9$, m.p. 162° (H. 1907). *T. flavicans*, var. *cinerascens*, physcion and acromelin (H. 1907).

Umbilicaria pustulata (*Gyrophora pustulata*), gyrophoric acid $C_{18}H_{18}O_7$ (?) (Stenhouse, Annalen, 70, 218; Z. 1898; H. 1898).

Urceolaria lichens, collected from the basalt rock of the Vogelsberg in Upper Hessia, contain lecanoric and erythric acids (Schunck, Mem. Chem. Soc. 1, 71).

Urceolaria scruposa, var. *vulgaris*, atranorin and lecanoric acid (H. 1898, 1904, 1907); patellaric acid (Z. 1902). *U. cretacea* (*U. scruposa*, var. *gypsacea*), lecanoric acid, but no atranorin, zeorin, or parmelialic acid (H. 1898; *cp.* Zopf, 1897).

Usnea barbata (*Lichen barbatus*, *Parmelia barbata*), usnic acid (Rochleder and Heldt, Annalen, 48, 8; Stenhouse, *ibid.* 155, 51) and lichenin (Berzelius, Scherer's Annalen, 3, 205; Hesse, Annalen, 137, 241; Ber. 10, 1324), usnic and barbatic acids (H. 1898); emulsin (Hérissey, J. Pharm. Chim. [vi.] 7, 577). *U. barbata* f. *dasypoga*, usnic acid and usnaric acid $C_{30}H_{22}O_{15}$, m.p. 240°–260° (H. 1898), *d*-usnic, usnaric, and alectoric acids (H. 1900); barbatic, usnic, and usnaric acids, but no alectoric acid (Z. 1902); alectoric acid (H. 1903). *U. barbata*, var, *ceratina*, usnic acid $C_{18}H_{16}O_7$, m.p. 195°–196°, and barbatin (H. Annalen, 1895, 284, 157). *U. barbata α-florida*, *d*-usnic, usnaric, and parellic acids, and usnarin (H. 1902). *U. ceratina*, usnic acid, barbatic acid and barbatin (H. 1898). *U. ceratina* (Black Forest), barbatic and usnic acids (Z. 1902), *d*-usnic acid, barbatic acid, and barbatin (H. 1903) (Java cinchona bark), *d*-usnic, usnaric, and parellic acids and ceratin (H. 1903). *U. ceratina β-hirta*, Bolivian, *d*-usnic, usnaric, plicatic, and barbatic acids (H. 1903). *U. barbata* (β·) *hirta*, *d*-usnic, usnaric, and barbatic acids, and usnarin (H. 1902), atranorin (H. 1906). *U. barbata* (β-) *hirta*, (St. Thomas), *d*-usnic and usnaric acids, and santhomic acid $C_{11}H_{14}O_4$, m.p. 166° (H. 1902). *U. hirta*, usnic acid (Knop, Annalen, 49, 103), usnic acid, alectoric acid, hirtic acid, m.p. 98°, and hirtellic acid (m.p. 215° decomp.) (Z. 1903). *U. cornuta*, *d*-usnic and usnaric acids (Z. 1902). *U. longissima*, barbatic and usnic acids (Z. 1897; H. 1898). *U. longissima* (from Amani), ramalic acid, *d*-usnic acid, and dirhizonic acid $C_{18}H_{16}O_5(OMe)_2$, m.p. 189° (H. 1906). *U. florida*, usnic acid (Knop, Annalen, 49, 103); usnic acid and hirtellic acid (Z. 1904). *U. schraderi*, *d*-usnic acid and usnaric acid (Z. 1905). *U. microcarpa*, *d*-usnic acid and usnaric acid (Z. 1905). *U. articulata*, var. *intestiniformis* (Indian cinchona bark), *d*-usnic acid, barbatic acid, and articulatic acid $C_{18}H_{16}O_{10}$ (?) (H. 1907). *U. plicata*, *d*-usnic acid, usnaric acid, usnarin, and plicatic acid $C_{20}H_{33}O_8(OMe)$, m.p. 133° (H. 1900). *U. scrŭposa*, atranorin and lecanoric acid (Z. 1902).

Pertusaria dealbata, Nyl. (*Variolaria dealbata*, *Lichen dealbatus*), variolarin (Robiquet, Annalen, 42, 236; 58, 320). Schunck found crustaceous *Variolaria* collected on the basalt rocks of the Vogelsberg in Upper Hessia, to contain lecanoric and erythric acids.

Xanthoria parietina (*Parmelia parietina*, *Physcia parietina*), atranorin and physcion (H. 1898). *X. lychnea*, physcion (H. 1898). *X. candelaria* (*X. controversa*, *X. lychnea*, var. *pygmœa* *X. parietina*, var. *lychnea*), parietin, m.p. 202° (Z. 1904). A. G. P.

LICKNER'S BLUE. A silicate of cobalt and potassium. A variety of smalt COBALT.

LIDDITE *v.* EXPLOSIVES.

LIEBERMANN'S REACTION *v.* PHENOL AND ITS HOMOLOGUES.

LIEBIGITE. *Calcium uranium carbonate* v. Uranium.

LIÈGE BLACK. *Blue black* v. Pigments.

LIEN, LIENADEN v. Synthetic drugs.

LIGHT CARBURETTED HYDROGEN. *Marsh gas* v. Methyl.

LIGNIN DYNAMITE v. Explosives.

LIGNITE v. Fuel.

LIGNOCERIC ACID $C_{23}H_{47}COOH$, m.p., 80·5° is found in the solid paraffin obtained from beechwood tar (Hell and Hermanns, Ber. 1880, 1713) and in earth nut oil (Kreiling, *ibid.* 1888, 880).

LIGNUM COLUBRINUM v. Nux vomica.

LIMA WOOD. A variety of Brazil wood (*q.v.*).

LIME v. Calcium; also Cements.

LIME, BISULPHITE OF, v. Calcium.

LIME BURNING v. Calcium.

LIME, HYDRAULIC, v. Cements.

LIME, SUPERPHOSPHATE OF, v. Calcium; also Fertilisers.

LIME-OIL v. Oils, essential.

LIMESTONE (*Kalkstein*, Ger.; *Calcaire*, Fr.). A rock composed essentially of calcium carbonate ($CaCO_3$) in the form of the mineral calcite. Owing, however, to the frequent presence of mechanically admixed impurities and to variations in texture, the rocks of this class exhibit wide differences in character (v. Marble, Chalk, Lithographic stone, Marl). A snow-white crystalline limestone—*i.e.* a statuary marble—is quite compact, and is pure calcium carbonate, consisting, in fact, of a granular aggregate of calcite. With the admixture of clayey material there may be a gradual passage through argillaceous limestone to calcareous mudstone or to an incoherent marl. Other limestones, containing mechanically admixed impurities of various kinds, are described as silicious, sandy, carbonaceous, bituminous, ferruginous, and phosphatic limestones. In dolomitic or magnesian limestones there is an isomorphous replacement of lime by varying amounts of magnesia. The majority of limestones are bedded rocks of sedimentary origin, and are composed of the calcareous remains of marine organisms. As a general rule the compactness of a limestone is a measure of its geological age; the harder and more compact varieties belonging to the Silurian and Carboniferous Systems, whilst those of the Jurassic, Cretaceous and Eocene Systems are less coherent. Although limestones often resemble some other kinds of rocks in their appearance, they can always readily be recognised by the fact that they easily yield to the knife and effervesce with cold dilute acid (those containing much magnesium effervesce only with hot acid). In addition to their extensive application as building stones, limestones are much used for making lime in the manufacture of mortars and cements of various kinds (v. Cements); as fluxes in smelting; and as fertilisers, either in the powdered form or burnt as lime.

References.—G. P. Merrill, Stones for Building and Decoration, 3rd ed., New York, 1903; A. Harker, Petrology for Students, 4th ed., 1908; for British Limestones v. J. A. Howe, Geology of Building Stones, 1910. On economic questions much has been written in the geological survey publications of the United States. L. J. S.

LIMESTONE, MAGNESIAN, v. Calcium, Magnesium, and Dolomite.

LIMNITE (λιμνή, a marsh). A hydrated ferric oxide, perhaps $Fe_2O_3,3H_2O$, but passing into limonite (*q.v.*).

LIMOGES ENAMELS v. Enamels.

LIMONITE or **Brown Iron-Ore.** A hydrated ferric oxide $2Fe_2O_3,3H_2O$ of importance as an ore of iron (Fe, 59·9 p.c.). It is not crystallised, and often occurs as rounded, stalactitic, or mamillated forms with an internal radially fibrous structure. The surface of such masses is sometimes black and lustrous (German, Glaskopf), but here, as in all other instances, the streak of the mineral is of a very characteristic brownish-yellow colour. Concretionary (pisolitic) and earthy or ochreous masses are also of common occurrence. The sp.gr. varies from 3·6 to 4·0, reaching the higher value in the compact, fibrous material. Limonite is of abundant occurrence in nature as the final product of weathering of all iron-bearing minerals. Pseudomorphs of limonite after crystals of iron-pyrites and other minerals are well known. As an earthy ochreous deposit it separates from the waters of chalybeate springs, and in peat-bogs and at the bottom of pools and lakes. Such deposits are known as bog-iron-ore (*q.v.*), lake-ore, &c., and the name limonite (from λειμών, a meadow) means, in fact, meadow-ore. The brown iron-ores extensively mined in Northamptonshire, the north of Spain, Luxemburg, Lorraine, and western Germany (here a pisolitic or bean-ore known as 'minette'), and many other places, occur as beds in sedimentary rocks. Ochreous limonite is used for making paint, and in the manufacture of linoleum, brown paper, &c. L. J. S.

LINADIN v. Synthetic drugs.

LINAMARIN v. Glucosides.

LINARIN. A glucoside found in the flowers and leaves of *Linaria Vulgaris* (Mill.) (Klobb, Compt rend. 1907, 145, 331).

LINNÆITE. Native cobalt sulphide Co_3S_4.

LINOLENIC ACID, LINOLIC ACID v. Oils, Fixed, and Fats.

LINSEED. The seeds of *Linum usitatissimum* (Linn.). There are two chief varieties, with white and blue flowers respectively. The plant requires moist heat, but is not suited to great heat and drought or to frosty conditions. It therefore does best on the seacoast or plains and hills where the rainfall is abundant or dews and fogs frequent, and in damp soils rather than in dry ones. It is grown in many countries, but the chief sources of the linseed of commerce are Russia and India.

The average composition, as given by König, as the mean of 61 analyses, is—

Water	Protein	Fat	Nitrogen free substances	Crude fibre	Ash
9·0	22·8	34·4	22·8	6·8	4·2

All the constituents are liable to considerable variation, *e.g.* protein 16–31 p.c., fat 22–40 p.c. The 'protein' of linseed is almost wholly albuminoid in nature, not more than 2–4 p.c. of it being in other forms (a small portion as a glucoside). Linseed contains a characteristic mucilage (about 6 p.c. of its weight), which exists mainly in the membranes of the outer cells and causes the seeds when macerated with water to swell up so much as to burst the cell-walls. When linseed is boiled with water, the mixture thickens owing to the solution of this mucilage.

Linseed is very largely consumed, being used as a food for young calves (as a partial substitute for milk), and in enormous quantities in the preparation of linseed oil, so important in the preparation of varnishes, paints, and linoleum, the by-product linseed cake or linseed meal, also forming an important cattle food, valuable not only for its nutritive value, but also on account of its richness in the manurial substances, nitrogen, phosphoric acid, and potash.

The ash of linseed contains—

K_2O	Na_2O	CaO	MgO	Fe_2O_3	P_2O_5	SO_3	SiO_2	Cl
30·2	2·1	8·1	14·3	1·1	40·5	2·3	1·2	0·2

Of pure linseed cakes there are two types, viz. those from which the oil has been *expressed*, and those from which the oil has been *extracted* by the use of volatile solvents; the former are richer in fat and more digestible, the latter richer in albuminoids and ash. The following average compositions are given by Kellner—

	Water	Protein	Fat	*N*-free extract	Crude fibre	Ash
Expressed cake	11·0	33·5	8·6	31·7	8·7	6·5
Extracted ,,	10·2	37·4	3·8	32·7	9·1	6·8

It was shown by Jorissen (Bull. Acad. Roy. Belg., 1883, 3, 5, 750) that linseed contains a cyanogenetic glucoside. This glucoside, named *linamarin* by Jorissen, has been shown to be identical with *phaseolunatin* (*a*-dextrose ether of acetone cyanohydrin) which occurs in the beans of *Phaseolus lunatus* (Linn.) (Dunstan, Auld and Henry, Proc. Roy. Soc., 1906, B. 78, 145). This substance is present in young linseed plants, in linseed, and also in linseed cake. In the latter, to the extent of yielding 0·03 to 0·04 per cent. of hydrocyanic acid, but the enzyme which hydrolyses the glucoside, and which is present in the seed, is destroyed by the high temperature employed in expressing the oil, and is therefore absent from the cake (Dunstan and Auld, J. Soc. Chem. Ind., 1908, 428). Pure linseed cake is therefore not *likely* to act as a poison, but *might* do so if prepared by cold pressure, or if fed along with any foodstuff containing the enzyme necessary for the hydrolysis of the glucoside. H.I.

LINSEED GUM *v.* Gum.

LINSEED OIL, flax seed oil, is obtained from the seeds of the flax plant, *Linum usitatissimum* (Linn.), a native of Central Asia. The principal countries where it is grown in considerable quantities to yield oil seed are the Argentine, India, the United States, Canada, and Russia. Notable quantities of seed are also produced in Morocco. Attempts are being made to grow linseed oil in Australia and in the Transvaal Colony.

Two qualities of Russian seed are recognised in the trade, known, according to their source, as Baltic and Black Sea seed; hence the terms 'Baltic linseed oil' and 'Black Sea linseed oil.' The oil expressed from Indian seed is known as 'East India oil.' The Baltic linseed yields the best drying oil; this is explained by the fact that the Baltic seed is the purest, whereas in Black Sea seed 5 p.c. (and more) of hemp seed and (or) ravison seed are usually present. Indian seed is always mixed with mustard, rape, and cameline seed, owing to the plants yielding the latter being grown along with the flax plant. It has been proved that when the Indian linseed is carefully separated from the foreign seeds and then expressed, the oil possesses as good drying properties as does best Russian oil. During latter years, more attention having been paid in India to this growing industry, the quality of seed has improved. Argentine seed, yielding the (River) Plate oil (La Plata oil), being badly harvested, contains much chaff and admixed fibres; if more care were exercised, La Plata oil also would more regularly approach Baltic oil in drying properties. The United States, who until recently had been importing East Indian seed, have so considerably increased the home production that they rank occasionally (*i.e.* when the harvest is plentiful) amongst the exporting countries. Canada also is exporting considerable quantities of linseed.

The proportion of linseed oil in the seed varies with the origin of the seed and also with the seasons. It may be accepted that linseed contains from 32 to 42 p.c. of oil, according to the origin. On a large scale the quantity of linseed oil obtained from good seed does not exceed 35 p.c.

On cold-pressing, a golden-yellow coloured oil is obtained, having a pleasant taste, so that it can be used as an edible oil. Considerable quantities are being expressed for this purpose in Russia, Hungary, Germany, and India. In some parts of Germany the oil is used either as such, or (as 'Leinoelschmalz') in admixture with tallow or (and) lard for edible purposes. By far the largest quantities of oil are, however, employed in the arts. In that case the seed is crushed between rollers and then heated to about 160°F. in the mixing kettle; subsequently the seed is expressed while still warm. The oil so obtained has a yellowish-brown hue, and is somewhat turbid, due to traces of moisture and mucilaginous matter. The press cakes retain about 10 p.c. of oil; they are used as one of the most valuable and wholesome cattle foods.

On storing the oil, the moisture and the mucilaginous matter gradually settle out, and the oil hereby acquires a higher value, especially for some technical uses, as in the making of varnish. Such oil, sometimes kept for years, is known as 'tanked oil.' The suitability for varnish-making purposes is ascertained by heating rapidly the linseed oil in a test tube. Oil from which gelatinous matter separates is considered unsuitable. Seed pressed in a comparatively fresh ('green') state yields oil containing larger quantities of 'mucilage' than seed three to six months old. The gelatinous matter ('mucilage' or 'spawn' or 'break') contains phosphates and traces of sulphates.

The bulk of linseed oil is at present produced by expression. The main reason for this is that the hot-pressed cake is valuable as cattle food, whilst linseed meal obtained by extraction with solvents could only be used as manure, at any rate in this country. Occasionally linseed has been extracted with solvents, as it was thought that the oil so obtained, being richer in unsaturated acids, and containing less of the mucilaginous matter, would be more suitable for the paint and varnish trades. This has, however, not been borne out in practice, extracted oil having been found unsuitable as a paint oil. Moreover, the oil obtained by extracting with carbon disulphide, light petroleum, &c., possesses an inferior colour and a more unpleasant smell than expressed oil. Therefore it would only be profitable to extract damaged seed, which cannot be used for proper cattle food.

A rapid method for removing the impurities in the crude oil is to refine it, which is done on a large scale by treating crude linseed oil with 1–2 p.c. of a somewhat concentrated sulphuric acid. The charred mass carries down with it the bulk of impurities contained in the crude oil. For the manufacture of the best and finest kinds of linseed oil ('artists' oil'), the refined oil is subjected to 'sun-bleaching,' by exposure in shallow zinc trays under glass to the action of sunlight. Powdered lead placed in the trays accelerates the bleaching process. Recently a proposal has been made to bleach linseed oil by exposure to the Cooper-Hewitt mercury lamp. Dark linseed oils intended for soft soap are usually bleached in the soap works by treatment with a small amount of caustic potash. The soap which is formed carries down with it the colouring matters.

The chemical composition of linseed oil is not yet fully known. It may, however, be stated broadly that linseed oil contains about 10 p.c. of solid fatty acids, amongst which palmitic acid and arachidic acid have been identified. In addition thereto the oil contains a high proportion of linolenic acid and linolic acid. The proportion of oleic acid which Hazura gave as amounting to about 5 p.c., may possibly, according to later statements, have to be raised to 15 p.c. The '*iso*linolenic acid,' which Hazura stated to occur in linseed oil does not appear to be a chemical individual (according to the researches of Rollett, who doubts the existence of a β-linolenic acid, which Erdmann and Bedford state is obtainable from linolenic acid).

Linseed oil has a higher specific gravity than any fatty oil that would be used to adulterate it, with the exception of tung oil. Hence, in the trade a specific gravity lower than 0·93 is considered to indicate adulteration with other fatty oils or mineral oils.

The higher the specific gravity of a linseed oil, the more suitable it is for the purposes of the paint and varnish manufacturer. This is also expressed in a general way by the magnitude of the iodine value. Linseed oil has, with the exception of perilla oil, the highest value of all known fatty oils. Hence the iodine test is the most characteristic one for identifying a sample. The iodine value of linseed oil should not fall below 170 (La Plata and North American oils), although much higher iodine values reaching as high a figure as 205 have been recorded. Thus Indian oils usually absorb from 183 to 192 p.c., and Baltic oil from 190 to 200 p.c.

When the price of linseed oil is high adulteration is practised to a very considerable extent. For the methods devised for detecting these adulterants the reader is referred to Lewkowitsch's Chemical Technology, vol. ii. 50–60.

Linseed oil (provided its price is not excessively high) is very extensively used as stock material for soft soaps; for this purpose those oils are especially employed which have a comparatively low iodine value. The presence of mucilage forms no objection in the soapery.

A further important application of linseed oil is found in the manufacture of boiled oil for paints, varnishes, lithographic varnishes, and for the manufacture of linoleum. No other drying oil approaches the properties of linseed oil, the drying oil *par excellence*. Hence linseed oil is also the best oil for making putty. Linseed oil is further largely used in the preparation of plastic masses.

Boiled oil is obtained by heating linseed oil with driers to a temperature of about 150°C. The process is carried out by introducing the oil into a cylindrical vessel provided with a heating coil and agitating gear, so as to produce an intimate intermixture between oil and drier while they are heated to the desired temperature.

According to the quality and the amount of drier added, and the length of time during which the oil is heated ('boiled'), pale or dark oils are produced. The former are known in commerce as 'pale boiled oils,' the latter as 'double boiled oils.' The temperature of 'boiling' can be reduced even to 120°C. when 'liquid driers' (solutions of lead linoleate, &c., in linseed oil) are used. They are merely dissolved in the oil and the operation is assisted, if required, by a current of air.

This last process yields somewhat inferior drying oils to those obtained by boiling at 150°C. with lead oxide, &c. It has, however, been inferred therefrom that in order to obtain a quickly drying oil it suffices to prepare a solution of metallic salts in oil. This view has even led to the preparation of 'boiled oils' in the cold, by merely adding to linseed oil a solution of lead linoleate or manganese linoleate, and carefully intermixing it with the oil. (An oil having the properties of a 'boiled' oil can also be prepared by carefully grinding linseed oil with manganese borate in the cold.) These 'boiled oils' are, therefore, identical with the product which painters used to prepare themselves from raw linseed oil by grinding it with a drier. Such oils naturally do not dry so rapidly as do the oils prepared at a higher temperature; they behave more nearly like raw linseed oil as regards the time required to 'dry.'

With regard to the employment of other oils in the manufacture of boiled oils and the adulterants of boiled oils (*cp.* Lewkowitsch, Chemical Technology, vol. ii. 109 *et seq.*).

Linseed oil is also used in the manufacture of 'vulcanised oils,' and for extracting indiarubber from 'waste rubber.' By heating linseed oil with sulphur, the official *oleum lini sulf.* is prepared. J. L.

LIPASE, the enzyme which hydrolyses fats to glycerol and fatty acids, is of considerable importance in animal physiology and in germinating seeds. It is used industrially in the manufacture of glycerol and fatty acids, and is concerned in the phenomenon of rancidity. The knowledge of it, however, is still in a somewhat fragmentary state. It was first discovered by Reynolds Green (Proc. Roy. Soc. 1890, 48, 370) in the germinating seed of *Ricinus communis*

(Linn.), and has since been found in many other seeds, usually in the germinating rather than in the resting stage; it also occurs in mould fungi and in yeast. Lipoclastic enzymes are present in most animal tissues, the liver being the most active. The enzyme appears to cling to the solid particles of tissue cells.

Vegetable lipase is very sparingly soluble in water, and it is doubtful whether active filtered extracts of the enzyme can be obtained. It has been shown by Connstein and others (*see* summary in Asher and Spiro's Ergebnisse der Physiologie, 1904, 3, 194) that *Ricinus* lipase is effective only in the presence of acid, and that it acts preferentially on the natural fats, other ethereal salts being but little attacked by it.

Animal lipase, on the other hand, is quite active in hydrolysing simple esters and acts on the natural fats with difficulty, though this is perhaps due to the difficulty of securing a satisfactory emulsion (*cp.* H. E. Armstrong, Proc. Roy. Soc. 1905, 76B, 606; 1906, 78B, 376; Kastle and Loevenhart, Amer. Chem. J. 1900, 24, 491).

According to Tanaka (Chem. Soc. Abstr. 1910, i. 800) lipase is present in castor oil seeds in the form of an insoluble zymogen which is readily converted by dilute acid into the insoluble enzyme, the acid acting merely to liberate the enzyme which, when once liberated, is active in a neutral medium. It is inactive in alkaline solution.

The action of lipase is accelerated by manganese sulphate and by bile salts. All acids are effective in activating the enzyme, action depending on the amount rather than on the concentration of the acid.

Animal lipase may be separated by dialysis, or filtering, into two substances which are inactive singly, but the original activity is restored when they are mixed; the activity of the filtrate is not destroyed by boiling (Magnus, Zeitsch. physiol. Chem. 1904, 42, 149; Rosenheim and Shaw-Mackenzie, J. physiol. 1910, 40). Lipase also exercises synthetic activity (Kastle and Loevenhart, Amer. Chem. J. 1900, 24, 491; Hanriot, Compt. rend. 1901, 132, 212).

The ferment process is used for the preparation of soap-stock fatty acids (Connstein, Eng. Pat. 22111, 1902). The ground seeds were made into an emulsion with oils and dilute acetic acid, but the original process was abandoned on account of the losses due to the formation of a middle layer between the fatty and aqueous layers. According to Lewkowitsch (Chemical Technology of Oils, Fats, and Waxes, 1909, 3) it is now customary to prepare a 'ferment' by grinding decorticated seeds with a large quantity of water and filtering. The creamy liquor is allowed to ferment spontaneously when a creamy emulsion containing the active enzyme rises to the top. The oil is emulsified by air currents in lead-lined vessels with 40 p.c. of water, 5–8 p.c. of the ferment and 0·2 p.c. manganese sulphate, the last substance serving to accelerate the change (Eng. Pat. 25680, 1905). After several days the mixture is warmed to 80°C., and 0·3–0·45 p.c. sulphuric acid (50 p.c.) is added; it is then allowed to settle. Three layers are formed—a bottom aqueous layer containing glycerol, an upper fatty layer and a middle layer consisting of an emulsion, which is allowed to accumulate, and on renewed treatment separates into three layers. The temperature of hydrolysis is maintained above 20°C. and below 42°C.; it should be slightly above the melting-point of a fat. The products so obtained are much lighter in colour than those given by the older processes of hydrolysis.

Rancidity.—The presence of lipase in oily seeds leads to the formation of small quantities of fatty acids, particularly in presence of moisture. Commercial fats of both vegetable and animal origin, if they have not been submitted to a sufficiently high temperature to kill the enzyme during their manufacture, are likely to contain traces of lipase, and this in presence of moisture may cause the formation of free fatty acids. When the fatty acids are further exposed to oxidation, particularly in presence of light, rancidity takes place (*see* further on this point, Lewkowitsch, *l.c.* 1, 35) (*v.* FERMENTATION).

E. F. A.

LIQUATION. 'When an ore or metallic mixture containing ingredients differing sensibly in fusibility is exposed to a degree of heat sufficient only to melt the most fusible which may flow away from the unmelted mass, this process is termed liquation' (Percy's Metallurgy). In certain cases a mixture of two metals can be roughly separated in this way. For instance, if an alloy of lead and copper be heated to a temperature a little above the melting-point of lead, the lead trickles out, leaving a porous mass behind. The lead contains 2–3 p.c. of copper. The copper contains 25 p.c. of lead. This process is used commercially to separate antimony sulphide from the ore, by heating in earthenware pots with a hole in the bottom, through which the melted sulphide flows.

At the Schemnitz silver works impure lead is purified by melting it on the bed of a furnace, the lower end of which is connected with a large iron pot, heated independently, and into which the lead trickles. Fresh lead is thrown into the furnace from time to time; the melted lead flows into the pot and leaves less fusible alloys behind. The lead in the pot is then made hot, skimmed and poled. The purification of a metal by this means depends upon the formation of less fusible alloys between the metal and the foreign metals present. Pattinson's process (*v.* LEAD) for desilverising lead depends on the formation of such alloys, but in that case the solidified alloys are fished out of the melted lead by a ladle, instead of allowing the lead to flow away from them.

LIQUEFACTION OF GASES. The readiness with which many liquids can be converted into vapours similar in many respects to ordinary gases, suggests the possibility of an intimate relationship between the gaseous and liquid states of matter. Van Helmont, to whom we owe the introduction of the term 'gas,' in the latter part of the 16th century, distinguished between 'gases' and 'vapours,' saying that only the latter could be reduced to the liquid state. Boerhaave (1731) in his Elements of Chemistry (Eng. ed., 249), comments on the impossibility of liquefying air either in the sharpest frost or under pressure. Dalton clearly foresaw the result of subjecting gases to low temperatures and high pressures when he said: 'There can scarcely be a doubt entertained respecting the reducibility of all elastic fluids of whatever kind into liquids; and we ought not to despair of effecting it in low temperatures and by strong pressures exerted upon the unmixed gases.'

The statement in Fourcroy's Chemistry, 2, 74, that Monge and Clouet liquefied sulphur dioxide is one of the earliest recorded references to the liquefaction of a substance commonly recognised as a gas. Shortly afterwards, in 1805-1806, Northmore (Nicholson's Journal, 1805, 12, 368; 1806, 13, 233) succeeded in liquefying chlorine, hydrogen chloride, and sulphur dioxide, by compressing the gases into a strong glass receiver. These results, however, did not attract much attention, and no further work on the liquefaction of gases appeared until 1823.

The discovery of the production of liquid chlorine by heating chlorine hydrate in a closed glass tube, led Faraday to undertake a systematic study of the liquefaction of gases. The method employed in his first series of experiments (Phil. Trans. 1823, 113, 189) was simple. Into the sealed limb of a bent glass tube were placed materials for generating the gas. The other limb of the tube was then sealed and cooled in a freezing mixture of ice and salt. The end containing the reacting substances was heated to generate the gas; the pressure steadily increased as the gas was produced, and ultimately the gas liquefied in the cold limb. In this manner Faraday succeeded in liquefying sulphur dioxide, hydrogen sulphide, 'euchlorine,' cyanogen, ammonia, carbon dioxide, and nitrous oxide, the experiments on the last two gases being often accompanied by violent explosions.

The first experimenter to utilise the evaporation of a liquid under reduced pressure in order to produce low temperatures was Bussy (Ann. Chim. Phys. 1824, 26, 63). By the rapid evaporation of liquid sulphur dioxide he reached temperatures sufficiently low to liquefy chlorine, ammonia, and cyanogen. This method of producing low temperatures soon came into general use.

In 1834 Thilorier (Ann. Chim. Phys. 1835, 60, 427, 432; Annalen, 1839, 30, 122) prepared liquid carbon dioxide on a large scale by what was essentially the method of Faraday, using, however, a wrought iron generator and receiver connected by a copper tube. Moreover, he succeeded in freezing this liquid by allowing it to escape through a jet into a specially constructed drum-shaped box. Solid carbon dioxide has proved of service to subsequent experimenters. A mixture of solid carbon dioxide and ether, often called *Thilorier's mixture*, is even to-day a very valuable refrigerant; by evaporating it under reduced pressure, temperatures as low as −110°C. can be obtained.

In Faraday's second research on the liquefaction of gases (Phil. Trans. 1845, 135, 155) the gases were subjected to the simultaneous influence of high pressure and low temperature. The former was applied by means of two air pumps, and the latter was produced by means of a cooling bath of Thilorier's mixture boiling under diminished pressure. The gases were condensed in suitably shaped tubes of green bottle-glass, the pressures were measured by means of small air gauges inserted in the tubes, and temperatures were recorded by an alcohol thermometer. In these experiments, ethylene, silicon fluoride, phosphine, and boron trifluoride were liquefied, and hydrogen bromide, hydrogen iodide, sulphur dioxide, 'euchlorine,' hydrogen sulphide, ammonia, cyanogen, and nitrous oxide were solidified. Faraday was, however, unable to liquefy hydrogen, nitrogen, oxygen, nitric oxide, or carbon monoxide, although he predicted that, if the temperature could be sufficiently reduced, these gases would pass into the liquid state.

The work of Natterer (J. pr. Chem. 1844, 31, 375; 1845, 35, 169; 1852, 56, 127; Pogg. Ann. 1844, 62, 132; 1855, 94, 436; Wien. Ber. 1850, 5, 351; 1851, 6, 557, 570; 1854, 12, 199), which began in 1844 and extended over several years, placed at the disposal of experimenters a method for obtaining extremely high pressures. Natterer was the first observer to prepare liquid nitrous oxide in quantity. He repeatedly endeavoured to liquefy hydrogen, oxygen, nitrogen, and carbon monoxide, modifying his apparatus from time to time until the gases were subjected to the enormous pressure of 3600 atmospheres. Even the application of Thilorier's mixture to the gases at this pressure failed to effect their liquefaction.

Critical phenomena and the relation between the liquid and gaseous states.—The classical work of Andrews (Phil. Trans. 1869, ii. 575; also *ibid.* 1876, ii. 421) marks an era in the development of the subject of the liquefaction of gases. The relative values of temperature and pressure in effecting liquefaction had, up to that date, not been understood. As early as 1822, Cagniard de la Tour (Ann. Chim. Phys. 1822, 21, 127; 1823, 22, 411) had performed a series of experiments on heating volatile liquids in closed glass vessels. He showed that such a liquid as ether could be converted wholly into vapour, notwithstanding the existence of an enormous pressure, in a volume less than twice the volume of the liquid from which it was produced. He also observed that there was a definite temperature, independent of the actual amount of ether present, above which the liquid meniscus could not be observed, an indication that ether cannot exist as liquid above a certain temperature. Similar results were obtained with a number of other liquids, but their significance was not generally recognised at the time. Faraday, however, realised that the reason why he was unable to liquefy certain gases was that they were probably in the same condition as the ether vapour in Cagniard de la Tour's experiments when heated above the temperature at which the liquid meniscus disappeared, in which case he added that 'no compression, without the conjoint application of a degree of cold below that we have as yet obtained, can be expected to take from them their gaseous state.' It is curious, therefore, that Faraday made no attempt to realise the Cagniard de la Tour's state with any of the gases he had succeeded in liquefying.

Andrews found that on compressing carbon dioxide in a glass capillary tube at temperatures below 30·9°C., the volume diminished more rapidly than would be indicated by Boyle's Law, until at a certain pressure, depending on the temperature, liquefaction commenced. The pressure then remained constant while the volume was being diminished, until liquefaction was complete. After this, a large increase in pressure again became necessary in order to diminish the volume further. At temperatures above 30·9°C., however, he could obtain no indications of liquefaction at all, whatever pressure was applied. On partially liquefying carbon dioxide, and slowly raising the temperature, the surface of demarcation between the liquid and gas became fainter, lost its curvature, and finally disappeared at 30·9°C. 'The space was then occupied by a homogeneous fluid which exhibited, when the pressure was suddenly diminished or the temperature slightly lowered, a peculiar appearance of moving or flickering striæ throughout the entire mass.'

From these results on carbon dioxide and from analogous results for nitrous oxide, Andrews concluded that there is a perfect continuity between the gaseous and liquid states, and that for each gas there is a definite temperature above which it cannot be condensed to the liquid state. This temperature he called its *critical temperature.* The 'Cagniard de la Tour point,' to which Faraday frequently referred, and the 'absolute boiling-point' of Mendeleeff, correspond to the same temperature. The pressure required to effect liquefaction at the critical temperature is called its *critical pressure.*

Andrews was able from his results to draw a rational distinction between a 'vapour' and a 'gas' by defining them as gaseous substances respectively below and above their critical temperatures.

As a result of the work of Andrews it is clear that the general nature of the isothermals for a gas over a range of temperature, including the critical point, is similar to that shown in Fig. 1. Each isothermal below the critical point consists of three distinct parts, the middle portion being horizontal. The abscissæ of its extremities, *e.g.* v_v and v_l on the T_0 isothermal, represent the specific volumes of the substance, if the diagram refers to unit mass, as saturated vapour and as liquid under its own vapour pressure at T_0 respectively; intermediate volumes correspond to mixtures of liquid and vapour.

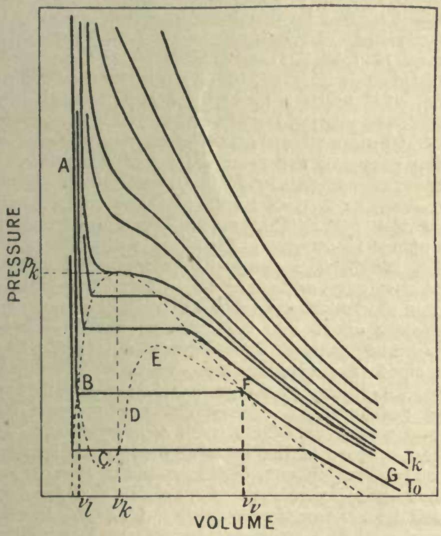


Fig. 1.

The theory of Andrews, that the change from gas to liquid is continuous, and that there is no essential difference between the two states, was adopted by Van der Waals, who, in 1879, put forward an equation to represent the behaviour of any fluid that does not change its molecular complexity on passing from the gaseous to the liquid state (Van der Waals, Die Continuität des gasformigen und flüssigen Zustandes).

The characteristic equation for a perfect gas

$$pv=RT$$

(where p, v, and T denote pressure, volume: and absolute temperature respectively, and R is a constant) represents the behaviour of ordinary gases accurately only over a small range of pressure, and at temperatures sufficiently removed from the critical point. As p increases, at constant temperature, from atmospheric pressure to one or two hundred atmospheres, the compressibility is initially greater than Boyle's Law indicates, the product pv diminishing as p increases (Regnault, Mém. de l'Acad. 21, 329; Amagat, Ann. Chim. Phys. 1880, [v.] 19, 345; 1881, [v.] 22, 353; 1883, [v.] 28, 456, 464; 1893, [vi.] 29, 68). The value of pv reaches a minimum, and afterwards increases with increase of pressure, so that at extremely high pressures all gases are much less compressible than is expressed by Boyle's Law (Natterer, *l.c.*; Amagat, *l.c.*). The initial diminution in the value of pv for a gas becomes less marked with rise of temperature, and at a sufficiently high temperature it is not observed. In the cases of hydrogen, helium and neon, this temperature, although considerably above the critical point, is much below the ordinary temperature, and the values of pv for these gases at this temperature steadily increase with rise of pressure from atmospheric pressure upwards (Regnault, Amagat, *l.c.*; Wroblewski, Monatsh. 1888, 9, 1067; Witkowski, Bull. Acad. Sci. Cracow, 1905, 6, 305; Kamerlingh Onnes and Braak, Comm. Phys. Lab. Leiden, 1907, No. 97; Burt, Trans. Faraday Soc. 1910, 6, 19).

These results can be represented fairly accurately by the equation of Van der Waals,

$$(p+\frac{a}{v^2})(v-b)=RT$$

the magnitudes of the (small) constants a and b (which may be deduced from the experimental values for p, v, and T) depending respectively upon the extent to which the molecules of the gas attract one another and upon their actual volume. This equation, besides representing the behaviour of compressed gases fairly accurately, also gives some account of the relationship between the liquid and gaseous states.

The equation represents the isothermals of a gas over a range of temperature including the critical point as being of the form shown in Fig. 1, with this difference, that those isothermals below the critical isothermal have the horizontal portions replaced by wavy curves, as indicated in the diagram by BCDEF on the isothermal for T_0°. The passage from vapour to liquid is thus represented as a continuous process. The portions BC and EF of the curve correspond with the conditions of superheated liquid and supersaturated vapour respectively, but the portion CDE of the curve, where p and v increase or decrease together, cannot be experimentally realised. At the critical point the specific volumes of vapour and liquid are identical, and the wavy portion of the curve therefore vanishes. Therefore the tangent at the critical point is horizontal, *i.e.* $dp/dv=0$. Since, moreover, the curvature of the critical isothermal changes sign at the critical temperature, $d^2p/dv^2=0$. These two relations give

$$2av_k^{-3}=\mathrm{RT}_k(v_k-b)^{-2} \text{ and } 3av_k^{-4}=\mathrm{RT}_k(v_k-b)^{-3}$$

the suffixes denoting critical values; whence

$$v_k=3b \text{ and } \mathrm{T}_k=8a/27b\mathrm{R}.$$

Substituting in the original equation, $p_k=a/27b^2$. The critical constants for carbon dioxide, calculated by Van der Waals from these formulæ, were $\mathrm{T}_k=32{\cdot}5$°C., $v_k=0{\cdot}0069$, $p_k=61$ atmos., in good agreement with the experimental values 30·9°C., 0·0066 and 70 atmos. respectively. The critical constants for hydrogen were determined by Wroblewski (Monatsh. 1888, 9, 1067) in a similar manner from his observations on the compressibility of the gas at low temperatures; his results agree remarkably well with the experimental values (Dewar, Chem. News. 1900, 81, 136) and afford a good instance of the utility of Van der Waals' theory. For further information concerning Van der Waals' equation, see Nernst's Theoretical Chemistry.

Liquefaction of the so-called 'permanent gases.'—The liquefaction of the five or six gases which Faraday and others had been unable to liquefy, and which had been called the 'permanent gases,' was, in the light of Andrews' researches, seen to depend upon the production of extremely low temperatures, since the lowest temperatures previously obtained had been above their critical points.

The first successful attempts to effect their liquefaction were made in 1877. On December 24th of that year, at the meeting of the French Academy, it was announced that Louis Cailletet of Chatillon-sur-Seine had liquefied both oxygen and carbon monoxide, whilst Raoul Pictet of Geneva had succeeded in liquefying oxygen (Compt. rend. 1877, 85, 1214, 1217, 1220).

The method used by Pictet (Compt. rend. 1877, 85, 1214; Ann. Chim. Phys. 1878, [v.] 13, 145; Arch. des Sci. Phys. et Nat. 1878) is essentially that devised by Faraday. Oxygen was generated by heating potassium chlorate in a wrought-iron flask. A long steel tube, provided at one end with a stop-cock, was attached to the flask. The accumulation of oxygen in the retort and tube created a pressure of 500 atmospheres. The tube was cooled to −120° to −140°, which is below the critical temperature of oxygen, by surrounding it with a copper cylinder through which liquid carbon dioxide, boiling under reduced pressure, was circulated. The liquid carbon dioxide was obtained by compressing the gas to 4–6 atmospheres, and cooling it externally by means of liquid sulphur dioxide, boiling under diminished pressure at −65°C. The elaborate apparatus employed was so designed that both sulphur dioxide and carbon dioxide could be liquefied, evaporated and re-liquefied repeatedly, so as to produce *continuous cooling*. The oxygen liquefied in the cooled tube, and when the stop-cock was opened, issued as a liquid jet with great violence, since the pressure employed was far in excess of that actually necessary for liquefaction.

The simple apparatus employed by Cailletet (Ann. Chim. Phys. 1878, [v.] 15, 132) is shown in Fig. 2. The gas is introduced into a glass tube, TTP, the narrow end of which consists of a stout capillary tube. By means of a metal collar, A, and the nut E′, the tube is screwed into a strong steel cylinder, B, partially filled with mercury. To compress the gas, water is forced into the steel cylinder by a hydraulic pump, through the copper tube U, which is fastened by the screws R and E into the apparatus; a pressure of several hundred atmospheres can thus be applied. A glass jacket M, and a bell-jar C, supported on the plate S, surround the capillary tube. The tap r serves to run off any liquid refrigerant in the jacket M.

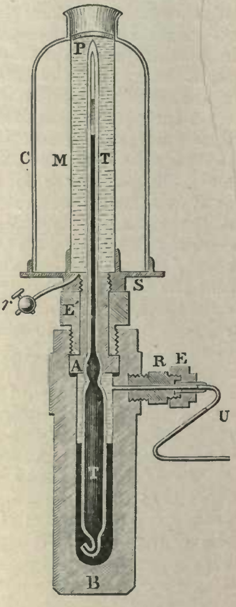


FIG. 2.

With this apparatus Cailletet liquefied acetylene (Compt. rend. 1877, 85, 851) and nitric oxide (*ibid.* 85, 1016), the latter condensing at −11° under a pressure of 104 atmospheres. Methane was not liquefied at 7° under a pressure of 180 atmospheres; but by suddenly releasing the pressure, the temperature of the gas was reduced sufficiently for liquefaction to occur, and a fine mist of liquid methane was formed in the tube. This method was successfully applied to oxygen and carbon monoxide (*ibid.* 85, 1213). The gases were compressed to 300 atmospheres, and cooled to −29°. The pressure was then suddenly released, when the resultant cooling effect was sufficient in both cases to produce partial liquefaction, a mist being formed of minute liquid droplets.

The theory of the process is simple. When a gas expands against external pressure, it performs work. This work is accomplished at the expense of the internal energy of the gas, and a diminution in the internal energy means a fall in temperature. To obtain the greatest fall in temperature possible, it is essential to perform the expansion with great rapidity in order that there may be no appreciable time for the gas to acquire heat from its surroundings. The fall in temperature experienced by a perfect gas when it expands adiabatically from an initial pressure p_1, at absolute temperature T_1, to a final pressure p_2, is given by $T_1 - T_2$, where

$$\frac{T_1}{T_2} = \left(\frac{p_1}{p_2}\right)^{\frac{k-1}{k}}$$

(k denoting the ratio of the specific heats of the gas). In the case of air, where $k=1\cdot41$, if p_1, p_2, and T_1 were 100 atmospheres, 1 atmosphere, and 273° abs. respectively, the final temperature T_2 should be 71·5° abs., or −201·5°C. Although this numerical result is necessarily somewhat inacccurate, owing to the fact that air under the above conditions deviates considerably from the laws of a perfect gas, it is sufficient to indicate that the adiabatic expansion of a gas is capable of producing extremely low temperatures. In Cailletet's experiments, expansion occurred practically under adiabatic conditions.

By this method Cailletet also succeeded in liquefying air and nitrogen, and obtained indications of the liquefaction of hydrogen (Compt. rend. 1877, 85, 1270). He also prepared liquid ethylene, first obtained by Faraday, in large quantities, and recommended its use as a refrigerant (Compt. rend. 1882, 94, 1224; 1883, 97, 1115; Ann. Chim. Phys. 1883, [v.] 29, 153). By cooling compressed methane and oxygen with this reagent boiling under diminished pressure, Cailletet obtained liquid methane and oxygen in the static form (Compt. rend. 1884, 98, 1565; 1885, 100, 1033).

A period of great activity in connection with the liquefaction of gases followed the publication of the successful pioneering experiments of Pictet and Cailletet, the subject being taken up by Wroblewski and Olszewski in Cracow, by Dewar at the Royal Institution in London, and by Kamerlingh-Onnes at Leyden. The Polish physicists occupied themselves mainly in determining the physical constants of liquefied gases. To obtain low temperatures, they acted upon Cailletet's suggestion, and employed liquid ethylene, which boils at −102°C., as a refrigerant. They compressed oxygen, nitrogen, and carbon monoxide in a stout glass tube by means of a modified Cailletet pump and cooled the gases to −136° by the rapid evaporation under diminished pressure of liquid ethylene, previously cooled with Thilorier's mixture. Under a pressure of 22·5 atmospheres, oxygen readily liquefied. The liquefaction of the other two gases was only effected by compressing them to 150 atmospheres at −136°, and then slowly reducing the pressure, when a further cooling effect was obtained. In each case a transparent liquid, with a well-defined meniscus, was obtained (Wied. Ann. 1883, 20, 243; Compt. rend. 1883, 96, 1140, 1225; Monatsh. 1883, 4, 415). The later work of these investigators was published separately. Wroblewski, who reached the temperature of −152°C. by rapidly evaporating liquid ethylene, obtained considerable quantities of liquid oxygen; he solidified nitrogen and carbon monoxide, and obtained temperatures below −200° by the rapid evaporation of the corresponding liquids; studied the utility of liquid methane as a refrigerant; obtained indications of the liquefaction of hydrogen; and at the time of his death was engaged in a study of the compressibility of hydrogen over a wide range of pressure and at very low temperatures (Wroblewski, Compt. rend, 1883, 97, 166, 309, 1553; 1884, 98, 149, 304, 982; 99, 136; 1885, 100, 979; 1886, 102, 1010; Wied. Ann. 1883, 20, 860; 1885, 25, 371; 1885, 26, 134; 1886, 29, 428; Monatsh. 1885, 6, 204).

The independent investigations of Olszewski, in which he solidified ethylene, carbon monoxide, nitrogen, and methane; liquefied oxygen in quantity and used the liquid as a refrigerant; obtained indications of the liquefaction of hydrogen and determined the physical constants of these and other gases, were summarised by himself in 1895 (Phil. Mag. 1895, [v.] 39, 188; 40, 202; *cf.* Compt. rend. 1884, 98, 365, 913; 1884, 99, 133, 184, 706; 1885, 100, 350, 940; 1885, 101, 238; Monatsh. 1884, 5, 124, 127; 1886, 7, 371; 1887, 8, 69; Ann. Phys. Chim. 1889, [ii.] 37, 337; 1895, [ii.] 56, 133).

The work of Dewar at the Royal Institution, from 1880 to 1895, led to the production of liquid air, oxygen, &c., in large quantities by using a liquefying plant constructed of metal and utilising liquid ethylene as refrigerant (Proc. Roy. Inst. 1886, 550; *cf. ibid.* 1884, 148; Phil. Mag. 1884, [v.] 18, 210). Dewar commenced a study of the properties of matter in general at low temperatures, and in this connection he made a most valuable contribution towards the manipulation of liquefied gases by introducing a vessel in which they could be kept with the minimum of loss by evaporation. The *Dewar flask* (Fig. 3) is simply a double-walled flask of convenient shape, from the space between the walls of which the air has been exhausted. The contained liquid is thereby separated from the atmosphere by a vacuum-jacket except at the mouth of the flask. Evaporation of liquid air and similar liquids in these flasks takes place only very slowly, since the heat radiated across the vacuous space is only one-seventh of the total heat which would reach the inner vessel were the jacket to contain air. If desired, the flasks may be silvered on the inside, thus increasing their efficiency.

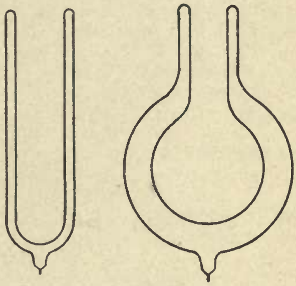


FIG. 3.

The method of self-intensive refrigeration (*so-called regenerative process*).—The experiments of Wroblewski, Olszewski, and Dewar on the production of low temperatures, previously described, involved no new principle; the 'cascade' method of lowering the temperature by stages, originated by Pictet, had been employed, and at times combined with Cailletet's expansion method. In 1895 a new principle, that of producing cold by self-intensive refrigeration, was introduced almost simultaneously by

Hampson and Linde. Briefly, it consists in continuously supplying the gas to be liquefied to an apparatus in which it may be cooled by expansion, and utilising each portion of gas, after it has been expanded and cooled, in lowering the initial temperature of the gas about to be expanded, until the cumulative effect of the cooling process is sufficient to produce liquefaction. For this purpose, the highly compressed gas at the ordinary temperature is passed downwards through a long copper spiral tube, expanded through a throttle valve, and the issuing gas passed upwards over the exterior of the copper tube.

For a description of Linde's liquefying plant *v.* the Engineer, October 4, 1895; J. Soc. of Arts, 1897, 1091; *cf.* also Eng. Pat. 12528, 1895; Ann. Phys. Chem. 1895, [ii.] 57, 328; Ber. 1899, 32, 925).

The general arrangement of Hampson's air-liquefying plant is indicated in Fig. 4. Air is drawn into the compressor through the large purifier, containing slaked lime to absorb carbon dioxide, and compressed in two stages to 150–200 atmospheres. The compressor is water-cooled to remove the heat generated by compressing the air. The air is then forced through a separating vessel, in which most of the water used as lubricant separates out, and afterwards through the high-pressure purifier containing potassium hydroxide, in which the remaining water and carbon dioxide are completely absorbed. The purified air then enters the liquefier; that which passes out is usually returned through the low-pressure purifier to the compressor, and used again. The purifiers do not then have to be very often refilled.

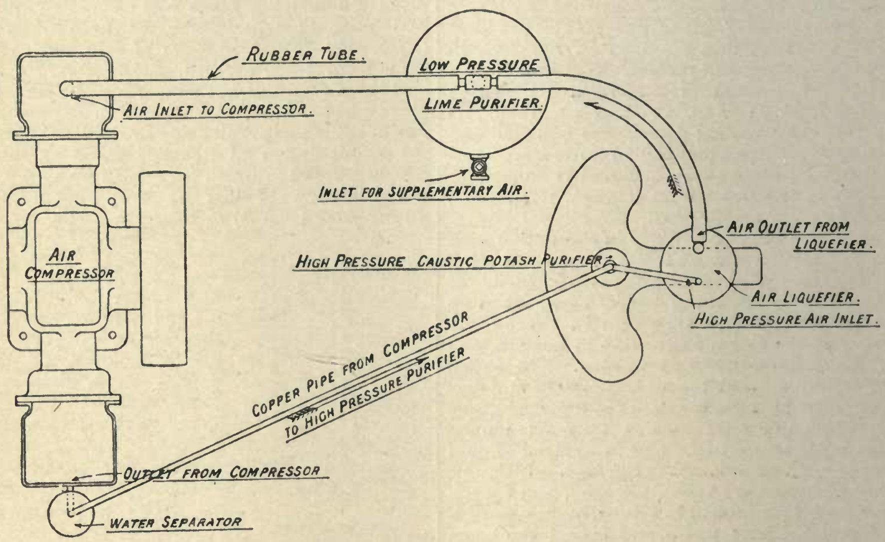


FIG. 4.

The Hampson liquefier, manufactured by the British Oxygen Co. (Eng. Pat. 10165, 1895; 7773, 1898; J. Soc. Chem. Ind. 1898, 17, 411), is shown in section in Fig. 5. In designing it, the following points were kept in view: the necessity for having a large, exposed surface of material of high thermal conductivity between the compressed and expanded air, the thickness of the material being diminished as far as possible; the desirability of having both compressed and expanded air in small masses in close contact with the conducting material, and of reducing the total mass and volume of this heat interchanger to the smallest possible amount, in order to minimise the mass of metal to be cooled down with the gas, and prevent, as far as possible, any access of heat from the surroundings. The liquefier consists of four copper coils, B, wound co-axially about a spindle, D, and joined at their lower ends to a valve, C, which may be opened or closed by turning the hand wheel E attached to the top of the spindle. A metal chamber, G, soldered directly to the casing of the coils, serves to collect the liquid air. The whole is enclosed in a metal chamber and the space between this jacket and the casing of the coils is filled with non-conducting material.

The purified air, the pressure of which is indicated by the gauge O, enters the liquefier through A, travels down the coils and is allowed to escape through the valve C. The released air immediately expands down to approximately atmospheric pressure, and travels back over the exterior of the coils B, finally passing back into the compressor or directly into the atmosphere. The expanded air acts with a self-intensifying cooling effect on the compressed air which is passing down through the coils, and in from 6 to 10 minutes part of the air begins to liquefy and collect in G. This receiver is emptied by turning the wheel T, which opens the valve P, when the liquid flows down the hollow spindle R into a vacuum receiver. A gauge H, connected by the tube J with the receiver G, indicates the amount of liquid in G. About 1½ litres of liquid air per hour can be obtained with an ordinary Hampson apparatus, and no auxiliary refrigerant is required. The interchanger acts so perfectly that the air which leaves the apparatus is only about 1° colder than that which enters it. About 5 p.c. of the air passing through the apparatus is liquefied.

In the liquefying machines of Hampson and Linde, the work done against atmospheric pressure as the gas flows along after expansion is not performed by the gas at the expense of its internal energy; the necessary energy is continuously supplied by the compression pump. A steady stream of gas at high pressure is pumped continuously into the coils of the liquefier, and after passing through the valve, is converted into a steady stream of gas at low pressure. There is a slight thermal effect due to the performance of external work, but its magnitude only depends upon the extent to which Boyle's Law is in error in representing the compressibility of the gas. It may be calculated from a knowledge of the specific heat of the gas and its compressibility, and at ordinary temperatures amounts to a slight cooling effect with all gases except hydrogen, helium, and neon. The main thermal change, however, is due to free expansion of the gas, and work is done in increasing the mean distance between the molecules of the gas in opposition to the forces of molecular attraction. This is performed at the expense of the internal energy of the gas. The subject was studied experimentally by Joule and Thomson (Phil. Trans. 1853, 143, 357; 1854, 144, 321; 1862, 152, 579) for a number of gases, and a slight cooling effect was found to be the net result in each case at ordinary temperatures except for hydrogen. The fall in temperature was proportional to the fall in pressure (up to 6 atmospheres), and varied approximately as the inverse square of the absolute temperature. At 17·1°C. the fall in temperature for air is 0·255°C. per atmosphere.

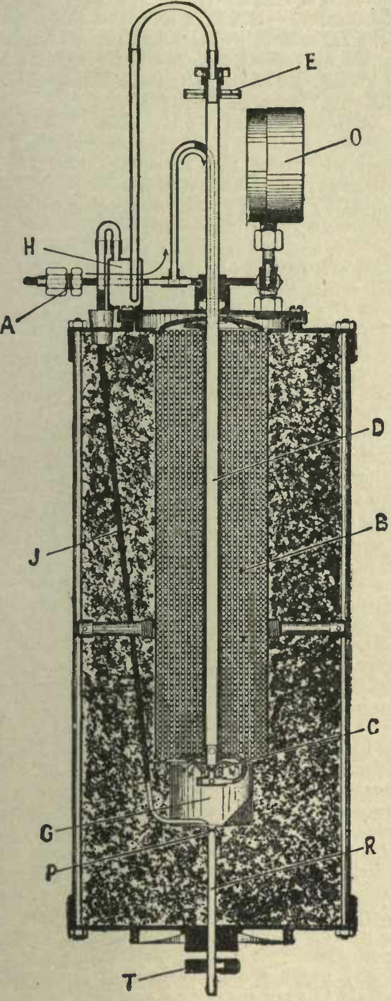


Fig. 5.

There is a temperature at which the thermal effect produced by free expansion (the Joule-Thomson effect) is zero. According to Olszewski (Phil. Mag. 1902, [vi.] 3, 535) this is −80·5°C. for hydrogen, and below this temperature hydrogen is also cooled by free expansion. The 'inversion temperatures' in the case of air and nitrogen are considerably higher than ordinary temperatures, and appear to vary with the initial pressure of the gas (Olszewski, Bull. Acad. Sci. Cracow. 1906, 792).

To liquefy hydrogen (and helium) it is therefore necessary to cool the gas strongly before applying the self-intensive cooling process. It was by this means that Dewar (Chem. News, 1900, 81, 136) first succeeded in collecting liquid hydrogen. Travers (Phil. Mag. 1901, [vi.] 1, 411) and Olszewski (Bull. Acad. Sci. Cracow, 1902, 619; 1903, 241) have since described modified Hampson liquefiers for preparing liquid hydrogen, in which the hydrogen is cooled by liquid air and then allowed to expand through a specially constructed valve. By cooling helium to the temperature of liquid hydrogen and then applying the self-intensifying process, Kamerlingh-Onnes (Compt. rend. 1908, 147, 421; Proc. K. Acad. Wetensch. Amsterdam, 1908, 11, 168) succeeded in obtaining helium in the liquid state.

The hydrogen liquefier designed by Travers and manufactured by the British Oxygen Company, is shown in Fig. 6. Pure dry hydrogen at 150–200 atmospheres pressure, enters the lower end of the coils A and is cooled by the cold hydrogen returning to the gas-holder. It then passes into the top of the coils in the chamber B, which is filled with liquid air, and by the time it has reached the bottom of the coils it is cooled to −190°C. The cold gas has its temperature lowered to below −200°C. as it passes through the coils in chamber C, which is connected by the pipe D to a vacuum pump, and in which liquid air is boiled under diminished pressure. The hydrogen then expands through the valve F at the end of the regenerator-coil E. The cooling-effect is self-intensified in the usual way, the cooled gas passing upwards over the coils E, and the outsides of the chambers B and C, finally cooling the coil A as it passes out of the apparatus. The coils B, C, and E are enclosed in a large, silvered vacuum-jacket. Liquid hydrogen collects in the vacuum vessel K, which is enclosed in a special box, hinged at LL to the supporting column and provided with glass windows.

Claude's process for liquefying gases.—The cooling effect produced when a gas expands with the performance of external work is much greater than that which is produced by the free expansion of the compressed gas. Mechanical difficulties for many years prevented this cooling effect from being intensified by rendering the process continuous, but it has now been effected by Claude. The process, as worked by Claude for the liquefaction of air, consists in compressing the air to 40 or 50 atmospheres and dividing it into two portions. One of these is expanded in a cylinder to 4 or 5 atmospheres, performing external work and thereby becoming cooled, and this cold air is then used to cool the other part, which can be thereby liquefied. This method, when applied on a large scale, needs less power than the Linde process; moreover, it may be used as a means of producing a low temperature preparatory to applying the ordinary self-intensive refrigeration method (Claude, Compt. rend. 1900, 131, 500; 1902, 134, 1568; 1905, 141, 762, 823; Eng. Pat. 27658, 1902; Fr. Pat. 322107, 1902; Linde, J. Soc. Chem. Ind. 1911, 30, 744). For further information concerning Linde and Claude's processes, *v.* OXYGEN.

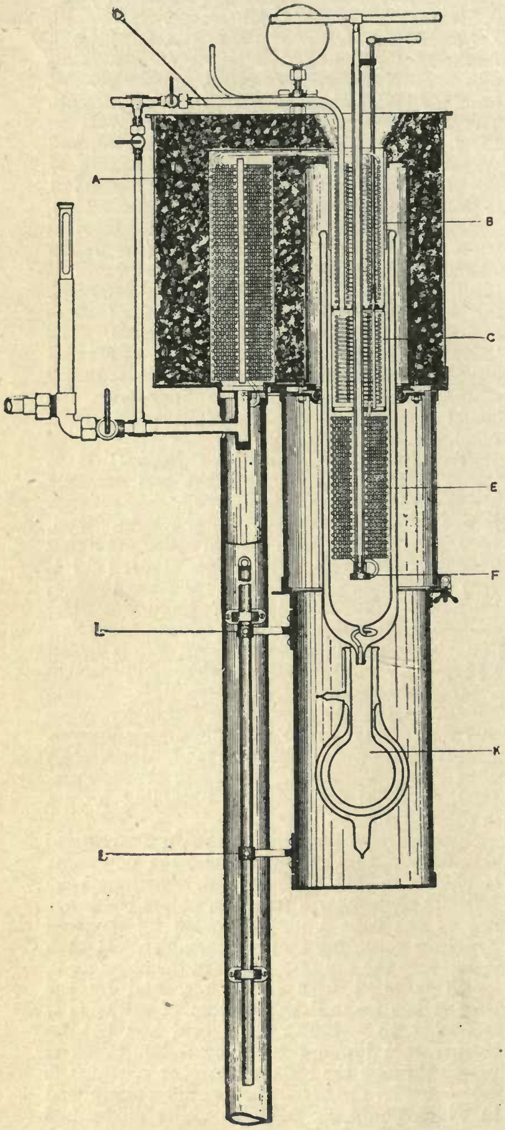


FIG. 6.

Literature.—Hardin's Rise and Development of the Liquefaction of Gases; Sloane's Liquid Air and the Liquefaction of Gases; Ewing's Mechanical Production of Cold; Travers' Study of Gases; Preston's Theory of Heat; &c.

LIQUEURS and **CORDIALS.** The general characters of these beverages have already been described under the heading CORDIALS AND LIQUEURS (vol. II.), the former term being usually applied to British preparations and to such as have only one characteristic flavouring ingredient, and the latter to the foreign varieties which are usually of a more complex character. The term *liqueur* is also applied to certain wines and spirits remarkable for their bouquet as 'Tokay,' 'Liqueur brandy,' &c. *Bitters* are generally classed commercially with liqueurs and cordials, and contain one or more ingredients supposed to possess tonic and medicinal properties.

In ancient times, liqueurs consisted merely of wine flavoured with spices (as cinnamon) and sweetened with honey, and in the Middle Ages various aromatic herbs (as absinth, hyssop, &c.) were employed in a similar manner, the product being known as 'wine of herbs.' The 'liquori' of Italy were, however, the true prototypes of the modern liqueur, as the Italians were the first to extract the aromatic principles of the roots, leaves, flowers, fruit, and seeds of plants by means of spirit. Sometimes gold or silver leaf in a finely divided state was added to the liqueur, not only to give lustre, but also because of certain medicinal virtues these metals were supposed to possess.

At the present time, France is *par excellence* the home of the liqueur, and some of the most celebrated varieties have originated at certain monasteries which formerly derived considerable revenues from their manufacture and sale, *e.g.* *Benedictine*, *Chartreuse*, *Trappistine*, &c. Other countries have their special preparations as *Anisette d'Hollande* and *Crême de Genièvre* (Holland), *Allasch* and *Kümmel* (Russia), *Alkermes* (Italy), *Maraschino* (Dalmatia), and the various *Cocktails* of the United States of America.

The number and variety of liqueurs and cordials is very great but the best known are comprised in the following list:—

Absinth
Advocaat
Alkermes
Allasch
Angostura (bitters)
Anisette
Benedictine
Brandy (cherry, &c.)
Chartreuse
Clove cordial
Cocktails (American)
Crême de Menthe
Curaçoa
Gin (sloe, &c.)
Kirsch
Kümmel
Maraschino
Noyau
Parfait Amour
Peppermint cordial
Ratafias
Trappistine
Vermouth
Whiskey (cherry, &c.)

In the manufacture of liqueurs, the purity and good quality of all the ingredients used is a matter of the first importance. The spirits should be highly rectified spirits of wine as free as possible from fusel oil and free acid; the sugar of the finest white crystals or sugar-candy made into a clear syrup with distilled or pure soft water; glycerol (when employed) should be highly refined and colourless; and all the flavouring ingredients (*e.g.* flowers, fruits, rinds, roots, seeds, &c.) should be sound and well-dried.

The simplest method of manufacture, adopted for the commoner kinds of liqueurs, is that of merely adding essential oils to the spirit, and then the necessary amount of sugar syrup or glycerol.

The essential oils should be recently distilled and dissolved in from 5 to 10 times their weight of alcohol before being added. The particular flavour required can thus be better attained and cloudiness or milkiness of the finished liqueur avoided.

The finer qualities, however, are made by macerating the flavouring ingredients in spirit of about 85° to 90° alcohol by volume and distilling the infusion. The distillation was formerly conducted in copper stills heated by direct fire, then double-bottomed coppers were employed, and subsequently a water-bath added, but now steam-jacketed stills only are used in the largest liqueur factories. The middle portion of the distillate is used for the finest liqueurs, the first fractions being rough and the last inferior in character. Syrup is added and sometimes glucose or glycerol to give density and impart a 'velvety' character to the liqueur, and the whole is heated, well mixed and diluted with water, after which filtration and 'fining' may be found necessary.

Liqueurs are often classified in France according to the proportions of spirit and sugar used, *e.g.* 'crêmes,' 'huiles,' or 'baumes,' which are heavily sweetened to a thick oily consistency, and 'eaux,' 'elixirs,' and 'extraits,' which are perfectly limpid and less highly sweetened. As a rule, the same proportions are employed for the same quality of liqueur. The following grades may be taken as typical:—

	Ordinaire	Demifine	Fine	Surfine
Alcohol at 85°	25 litres	28	32	36
Sugar	12½ kilos	25	37½	50
Water	67 litres	57	46	34

It will be observed that in the superior grades the proportions of alcohol and sugar are increased with a corresponding diminution in the proportion of water.

The flavouring ingredients are extremely numerous and varied in character and their nature and proportions used are jealously guarded by the manufacturers as trade secrets.

The essential principles are extracted by *infusion* with hot spirit (if the aromatic principle is not too volatile), the ingredients being first moistened with boiling water; or by *maceration* with cold spirit which may require hours, days, or even many months, according to the solubility of the essential principles; by *digestion* or prolonged infusion or maceration in hermetically closed vessels when the aromatic principles are extracted only with difficulty by cold alcohol; or by *distillation* when only the natural essential oils or other volatile flavouring constituents are required. The following plants should always be distilled by steam: *absinth, anise, balms, caraway, citronella, fennel, juniper, hyssop, lavender, melilot, mint, orange, rose, sage,* and *thyme.*

Aromatic tinctures for use in flavouring liqueurs are sometimes prepared by a kind of fractional filtration. The ingredients in a finely divided state are made into a paste with spirit and placed in a large funnel plugged with cotton-wool. Alcohol is poured in and the extract allowed to filter through drop by drop. The first portions are the purest and strongest, those following decreasing in flavour until the latter becomes too weak or even foreign in character.

Careful *mixing* is essential to the successful manufacture of liqueurs. Two separate vessels should be employed, the one for the essences or flavouring ingredients dissolved in about three-quarters of the total amount of alcohol required by the formula, and the other containing the syrup together with the rest of the alcohol. In this way the danger of the aromatic principles being thrown out of solution on the addition of the syrup is obviated, and the process of clarification expedited. The admixture should always be made in the cold to avoid loss of the flavouring principles, and the vessels may be hermetically sealed and provided with a scale or gauge rod to indicate the quantity of the ingredients admixed. The liqueur should rest for some days after mixing, and any defects, detected by taste, remedied before colouring, clarifying, or filtering.

Filtration, when necessary, should be conducted as quickly as possible. The older methods with cotton, paper, or wool in copper or tin filters are slow and result in loss of spirit and flavour. A better method is to use paper-pulp brought to the consistency of thick soup with some of the liqueur to be cleared. This is added to the bulk of the liqueur and the whole passed through a hair sieve. Natural clearing is best if time permits.

Clarification or '*collage*' with 'fining' materials is best avoided if possible, but is often necessary. The principal materials and the proportions used are as follows: *albumen*, white of egg (one egg for every 10 litres); *gelatin* (30 grams per 100 litres); *isinglass* (10 grams per 100 litres); *milk* (1 litre boiled in 100 litres, with 15 grams of alum). Animal or vegetable carbon, alum, nitre, and various 'filtering powders,' as 'Poudre Lebœuf,' are also employed. For coloured liqueurs, which are apt to suffer by this treatment, filtration is preferable to 'collage.'

Liqueurs containing various flavouring ingredients improve by keeping, as time is required for the intimate blending of the various substances in solution. The effect of this 'maturing' is artificially brought about in ordinary liqueurs and those intended for immediate use by a process known as *tranchage*, which consists either in heating in a water-bath to about boiling-point, or by successive coolings with ice. The object is to suppress the penetrating flavour of the new spirit and to give a smooth uniform character to the product so that none of the different flavouring ingredients can be individually recognised. Tranchage should be carried out *before* the colouration, clarification, or filtration of the liqueur.

The place of *storage* of liqueurs should be kept at a uniform temperature of 15° to 20° and the liqueurs protected from strong light or direct sunshine, as this affects the colour, frequently causing it to change or to be precipitated.

Bitters are considered to be tonic and stomachic and to improve the appetite when taken in moderation. They are prepared by maceration without distillation. The substances most commonly used are cascarilla, gentian, orange peel, quassia and wormwood. The best known preparations are *Angostura, Khoosh, orange,* and *peach bitters.* A fundamental principle in most bitters is gentian. A bitter made according to the following formula, which represents the proportions necessary to make 20 gallons, may be taken as typical: 6 lbs. gentian; 5 lbs. cinnamon; 5 lbs. caraway seeds; 1 lb. juniper berries; ½ lb. cloves. Macerate in spirit of about 90° (or 60 p.c.) for 10 or 12 days; strain, filter, add a syrup consisting of 10 lbs. of sugar to 13 gallons of water, and colour with cochineal.

English bitters may be made by digesting 5 ounces of the outer rind of dried orange peel, 6 ounces of cinchona bark, 6 ounces of gentian, 8 ounces of *Carduus benedictus,* 8 ounces of centaury, 8 ounces of wormwood, and 4 ounces of orris root, with 12 gallons of spirit about proof strength, filtering and sweetening with 12 lbs. of sugar.

In the following brief description of the best known liqueurs and cordials, the formulæ given are not intended, in the case of proprietary articles, as *Angostura, Chartreuse,* &c., to represent the exact composition or mode of preparation of the liqueurs originally known under these names, and the manufacture of which is carefully preserved as trade secrets, but only to serve as a guide to the preparation of a more or less successful imitation or substitute in each instance.

Absinth (*v.* article ABSINTH in vol. I.).

Angostura. A well-known bitter originally in possession of the Capuchin Friars' Mission on the river Carony in South America, and called after the ancient name of a city in Venezuela, now Ciudad Bolivard.

The essential bitter principle is extracted from the bark of a plant belonging to the order *Rutacea,* genus *Galipea.* It has valuable febrifuge properties. The following formula is taken from the Scientific American Cyclopædia, 1903: 4 oz. gentian root; 10 oz. each of calisaya bark, Canada snake root, Virginia snake root, liquorice root, yellow bark, allspice, dandelion root, and Angostura bark; 6 oz. cardamon seeds; 4 oz. each of Tolu balsam, galanga, and Turkey rhubarb; 1 lb. each of orange peel and alkanet root; 1½ oz. each of caraway seed and cinnamon; ½ oz. cloves; 2 oz. each of catechu, coriander seed, nutmegs, and wormwood; 1 oz. mace; 1½ lb. red sanders wood and 8 oz. turmeric. The ingredients are pounded and macerated for 15 days in 50 gallons of proof spirit, 30 lbs. of honey added, and filtered.

Advocaat, a spirit made in Holland from spirit and yolk of eggs and sweetened with sugar. The average strength is about proof.

Alkermes, a liqueur originally made at Florence and highly esteemed in the South of Europe. The original formula for the Alkermes de S. M. Novella is as follows: Bay leaves and mace, 1 lb. each; nutmegs and cinnamon, 2 oz. each; cloves, 1 oz. all bruised; cognac brandy, 3½ gallons; macerate for 3 weeks with frequent agitation. Distil over 3 gallons; add 18 lbs. of clarified spirit of kermes and 1 pint of orange flower water, mix well and bottle.

Allasch, a superior kind of kümmel (*q.v.*) flavoured with caraway seeds, bitter almonds, angelica root, anise, iris root, and orange peel. It is usually supersaturated with sugar which crystallises out in the finished liqueur. Strength about 25 u.p. or 43 p.c. alcohol by volume.

Anisette. The principal varieties, differing somewhat in the flavourings used, are *Anisette d'Amsterdam* and *Anisette de Bordeaux.* This liqueur may be made as follows: 4 oz. aniseed; 1 oz. each of coriander and sweet fennel seeds bruised; ½ gallon of rectified spirits and 3 quarts of water. Macerate 5 or 6 days, distil over 7 pints and sweeten with 2½ lbs. of pure sugar. The alcoholic strength of anisette is usually about 52 p.c. of proof spirit or approximately 30 p.c. of absolute alcohol by volume.

Benedictine, so called from a monastery of this order in the north of France where the liqueur was first made. It is now produced on a large scale by a company at Fécamp, at a uniform strength of 75 p.c. proof spirit or 43 p.c. of alcohol.

This liqueur may be prepared by the following formula: cloves, 2 grams; nutmegs, 2 grams; cinnamon, 3 grams; balm, peppermint, freshly gathered angelica and genepi of the Alps, each 25 grams; calamus, 15 grams; cardamoms (small), 50 grams; arnica flowers, 8 grams. The materials are crushed and macerated for 2 days in 4 litres of alcohol at 85°; 3 litres of water added and the whole distilled, taking over 4 litres. A cold syrup made with 4 kilos. of sugar and 2 litres of water is added, the mixture brought up to 10 litres with water, coloured, and filtered.

Brandy (apricot, cherry, ginger, lemon, orange, peach, raspberry, &c.) by macerating the fresh fruits often for prolonged periods or mixing the juice with brandy, and sweetening with sugar syrup. Frequently essential oils are used, as ginger-brandy oil, essence of lemon, &c., and plain spirit instead of grape brandy. *Gin* and *whiskey* are similarly used for the preparation of fruit liqueurs, as sloe gin, cherry whiskey, &c., and, as in the case of brandy liqueurs, plain rectified spirit is commonly employed instead of gin or whiskey.

Chartreuse (*see* vol. i.).

Cocktail, a compounded drink much used in America. The spirit basis is brandy, gin, whiskey, or other spirits, and the different varieties, depending upon the kind of flavouring used, are very numerous and sold under fanciful names. A bottle of brandy cocktail may be made as follows: one-half brandy; one quarter water; and a wineglassful each of bitters, curaçoa, and gum syrup. Whiskey and gin cocktails may be made by the same recipe, substituting these spirits for brandy. The strength is usually from 50 to 75 p.c. of proof spirit.

Clove cordial may be prepared by the following formula. Bruised cloves, 1 oz. or essential oil, 1 dram to every 4 gallons of proof spirit. If distilled, this should be done over a quick fire. The necessary deep colouring is sometimes obtained by means of poppy flowers or cochineal, but more commonly with brandy colouring or red sanders wood. The cordial is improved by the addition of 1 dram of bruised pimento or 5 drops of the oil for every ounce of cloves. It is sweetened with about 3 lbs. of sugar to the gallon.

Crême de menthe is one of the most popular liqueurs in the United Kingdom and is typical of the class of 'crêmes,' which are highly sweetened and usually flavoured with only one characteristic ingredient, *e.g.* crême d'anis, cacao, café, menthe, noyau, orange, thé, vanille, &c.

The inferior grades are made by flavouring plain spirit with essential oils without distillation whilst the superior qualities are produced by macerating the flavouring ingredients (which sometimes include small quantities of others besides the principal one characteristic of the liqueur) with alcohol and subsequent distillation, sweetening, and colouring.

The following recipe for Crême de Menthe is given by De Brevans (The Manufacture of Liquors and Preserves, New York, 1893): peppermint, 600 grams; balm, 40 grams; cinnamon, 20 grams; sage, 10 grams; orris root, 10 grams; ginger, 15 grams. These are distilled with 5 litres of alcohol at 85°, the distillate sweetened with 3·75 kilos of white sugar, and made up to 10 litres.

Curaçoa, so called from the principal island of the Dutch West Indies where the peculiar oranges used for the manufacture of this liqueur, and known as 'Curaçoa apples,' are obtained. These are used before ripening and are exceedingly bitter.

The liqueur is now made chiefly in Amsterdam. The dried peel is rasped to a finely divided condition, macerated for several days in dilute spirit and distilled. A tincture made from various spices as cinnamon, mace, or cloves is often added to the distillate, which is then sweetened with syrup and coloured as desired with Brazil wood, saffron, or caramel. The flavour is said to be improved by the addition of about 1 p.c. of Jamaica rum. The alcoholic strength varies from 50 to 75 p.c. of proof spirit, the average being about 60 p.c. proof or approximately 35 p.c. of alcohol by volume.

The following formula is given by De Brevans: rasped skins of 18 or 20 oranges; cinnamon, 4 grams; mace, 2 grams; alcohol at 85°, 5 litres; white sugar, 1·75 kilos. Macerate for 14 days, distil without rectification, and colour with caramel.

Kirsch (see KIRSCHWASSER).

Kümmel, a liqueur made chiefly in Russia and to some extent in the other countries on the shores of the Baltic. The principal flavouring ingredient is caraway seeds. The inferior grades are, as usual, made from plain spirit and essential oils, and the superior qualities by maceration with spirit followed by distillation.

The following formulæ indicate the quantities necessary to make 20 gallons:—(*a*) inferior quality: 7 gallons of spirits of wine; ¼ lb. essential oil of caraway seed; 7½ drachms of fennel seed oil; 15 drops of bitter almond oil; syrup made with 40 lbs. of sugar in 12 gallons of water. When fined with alum or soda solution, it is ready for use. (*b*) Superior quality: 4 lbs. caraway seeds; ¼ lb. fennel; 2 oz. of Florentine iris root. These are macerated with 10 gallons of spirits of wine and 8 gallons of water, and distilled. The first part of the distillate is set aside because of its rough character, and about 8 gallons are then distilled over for making the fine kümmel, the last fraction of 3 or 4 gallons being used for the inferior grades. To the middle fraction a syrup made with 60 lbs. of sugar in 10 gallons of water is added, and the whole well mixed in an open heated vessel. The liquor is then cooled and made up with water to 20 gallons. It may be fined with isinglass and stored to mature and mellow.

The strength of kümmel varies considerably, viz. from about 60 to 100 p.c. of proof spirit, the average being 75 p.c. proof equivalent to 43 p.c. of alcohol by volume.

Maraschino. This liqueur was originally made at Zara in Dalmatia from the wild *marasca* cherry. The juice was fermented, distilled, flavoured with the bruised kernels and sweetened with honey. Other flavouring ingredients are now commonly used, as cherry leaves, kirschwasser, peach kernels, orris root, raspberries, vanilla, &c.

Imitation maraschino may be made from plain spirit flavoured with bitter almonds, raspberry juice and orange flower water, or with essential oils as neroli, noyau, jasmine, and vanilla.

The strength varies from 55 to 75 p.c. of proof spirit, average 69 p.c. proof or 39 p.c. of absolute alcohol by volume.

Noyau is distilled from brandy macerated with or distilled from bitter almonds, sometimes with the addition of other flavourings as cinnamon, coriander seed, ginger, mace, and nutmeg. The almonds are occasionally replaced by apricot or peach kernels or by oil of bitter almonds or its substitute nitrobenzene. The flavour is due chiefly to the presence of prussic acid and the liquor should therefore be used sparingly. It is frequently coloured pink.

Parfait amour may be made by flavouring spirit with the peel of 4 lemons, 1 drachm of essence of vanilla, and 3 lbs. of sugar to the gallon, colouring with cochineal. The essences of lemon, cloves, and mace are also employed in some varieties of this liqueur. The average strength is 60 p.c. of proof spirit or 34·5 p.c. of alcohol by volume.

Peppermint cordial (known also as 'Eau des Chasseurs' or 'Sportsman's cordial') is prepared from oil of peppermint, plain spirit, and sugar. The following is a recipe for making 100 gallons: English oil of peppermint, 5 oz., is added to 3 pints of rectified spirits of wine, well shaken, and placed in a cask capable of holding 100 gallons. 36 gallons of perfectly colourless and flavourless spirit at proof strength are poured in, and the whole well shaken for 10 minutes. A solution of pure sugar, 2¾ cwt. in about 35 gallons of pure soft water (preferably filtered rain water) is added, and the contents of the cask well rummaged for 15 minutes. Sufficient water to make the quantity up to 100 gallons and containing 5 oz. of alum in solution is next added, and the whole again well agitated for a quarter of an hour. The cask is then bunged down and allowed to rest for a fortnight.

On a small scale, peppermint cordial may be prepared by taking a pint each of peppermint water and gin or plain spirit of about 20 u.p. and adding ¾ lb. of sugar. Peppermint water is prepared by macerating peppermint flowers in about 4 times their weight of water containing about 5 p.c. of salt.

Ratafia. This term is applied to liqueurs or cordials the basis of which is the juice of fruits, obtained either by maceration or simple pressure. One of the most important is Ratafia de Cassis, made from black currants, but other pulpy fruits, especially apricots, cherries, gooseberries, oranges, peaches, raspberries, and strawberries are also commonly used. Various other flavourings as spices, ginger, orris root, &c., are occasionally added to give variety of flavour. The following formula for the preparation of cherry ratafia may be taken as typical: 20 litres of cherry juice; 20 litres of alcohol at 85°; 13·5 kilos. of sugar, and 4 to 8 litres of bitter almond water.

Trappistine. Originally prepared at one of the Trappist monasteries in Italy. Recipe: large absinthe, 20 grams; angelica, 40 grams; mint, 80 grams; cardamon, 40 grams; balm, 30 grams; myrrh, 20 grams; calamus, 20 grams; cinnamon, 4 grams; cloves, 4 grams; mace, 2 grams; alcohol at 85°, 4·5 litres; white sugar, 3·75 kilos. The method of preparation is similar to that described for Chartreuse (*v.* vol. I.). After macerating for 2 days, distil and rectify. Add syrup and colour green or yellow.

Vermouth. The principal varieties of vermouth are the French and Italian, the basis in each case being white wine flavoured with various herbs. Inferior kinds are made from brandy or other spirit sweetened and flavoured with essential oils. The French variety is less sweet and stronger in bitter principles, particularly wormwood, than the Italian.

The following recipe by Ollivero may be used for Italian vermouth: 100 litres of white wine of Picardy; coriander, 500 grams; rinds of bitter oranges, 250 grams; orris root, powdered, 250 grams; elder flowers, 200 grams; red cinchona, 150 grams; calamus, 150 grams; 125 grams each of large absinth, holy thistle, (*carduus benedictus*), elecampane (roots), little centaury, and germander; Chinese cinnamon, 100 grams; angelica root, 65 grams; 50 grams each of cloves, galanga, and nutmegs; and 30 grams of cassia. Digest for 5 or 6 days, draw off the liquor, size with fish glue and allow to stand for 15 days.

—	Specific gravity	Alcohol by volume	Alcohol by weight	Extract	Cane sugar	Other extractives	Ash
Absinthe .	0·9116	58·9	—	0·18	—	0·32	—
Angostura .	0·9540	49·7	—	5·85	4·16	1·69	—
Anisette de Bordeaux	1·0847	42·0	30·7	34·82	37·44	0·38	0·040
Bénédictine .	1·0709	52·0	38·5	36·00	32·57	3·43	0·043
Chartreuse .	1·0799	43·2	—	36·11	34·35	1·76	—
Crême de Menthe .	1·0447	48·0	36·5	28·28	27·63	0·65	0·068
Curaçoa .	1·0300	55·0	42·5	28·60	28·50	0·10	0·040
Ginger .	1·0481	47·5	36·0	27·79	25·92	1·87	0·141
Kümmel .	1·0830	33·9	24·8	32·02	31·18	0·84	0·058

The strength of vermouth is usually between 23 and 30 p.c. of proof spirit, the average being 27 p.c. or 15·5° of alcohol by volume.

The table in the preceding column, by König, shows the results of analysis of some of the best known liqueurs and cordials.

J. C.

LIQUEUR DE FERRAILLE. *Ferric acetate* *v.* Acetic acid.

LIQUID STORAX *v.* Balsams.

LIQUORICE. The root of *Glycyrrhiza glabra* (Linn.). Cultivated chiefly in Spain, Russia, Italy, and to a small extent in Germany and England. It requires deep, fertile soil. Wild plants supply a considerable quantity in Asia Minor, and in some portions of Russia. The Spanish product is generally preferred to the Russian, since the latter is somewhat bitter.

The following analyses are given by König—

	Water	Protein	Fat	Glucose	Saccharose	Other *N*-free extract	Fibre	Ash
Spanish liquorice	8·8	12·9	3·7	7·4	2·1	43·0	17·7	4·4
Russian ,,	8·7	9·3	3·1	6·0	10·4	38·4	18·8	5·4

Liquorice owes its characteristic sweet taste to the presence of *glycyrrhizin* (the calcium and potassium salts of glycyrrhizic acid) which is present to the extent of about 8 p.c. To extract this, the roots are treated with cold water, the liquid boiled to precipitate albuminoids, filtered, and dilute sulphuric acid added, when the glycyrrhizic acid is precipitated in pale yellow flocks, which soon become a dark brown, sticky mass. This is then washed until free from acid and dissolved in dilute ammonia. By evaporation to dryness of this liquid, the "glycyrrhinum ammoniacale" is obtained, which serves as a sweetening agent in the preparation of medicines, in porter-brewing, and also as a sweetmeat.

Liquorice also contains a yellow colouring matter, and from 2 to 4 p.c. of asparagin, malic acid, starch, a little tannin and other substances.

H.I.

LIQUORICE ROOT. *Radix Glycyrrhizæ.* (*Réglisse*, Fr.; *Süssholzwurzel*, Ger.) The root of the underground stems of the *Glycyrrhiza glabra* (Linn.), a plant inhabiting the south of Europe and Central Asia (*cf.* Bentl. a. Tim. 74). Liquorice, or its solid aqueous extract, the 'Spanish juice' of commerce, has long been a favourite demulcent in throat affections, and is used as a laxative. It finds also a considerable employment in porter-brewing.

The root was examined chemically by Pfaff (Syst. Mat. Med. 1, 187), Robiquet in 1809 (Ann. Chim. Phys. 72, 143), also by Trommsdorff (Taschenbuch, 1827, 1) and others (*cf.* Gm. 17, 56). It was found to contain *glycyrrhizin* or *liquorice sugar*, the most important constituent, together with an *acrid oil*, *asparagin*, *malic acid*, *starch*, traces of *tannin*, and other substances common to plants.

Glycyrrhizin has been further studied by Vogel (J. pr. Chem. [i] 28, 1); Lade (Annalen, 59, 224); Gorup-Besanez *ibid.* 118, 236); Roussin (J. Pharm. Chim. 12, 6); Habermann (Ber. 10, 870; Annalen, 197, 105); Sestini (Gazz. chim. ital. 8, 454); and more recently by Tschirch and Cederberg (Arch. Pharm. 245, 97) and Tschirch and Gauchmann (*ibid.* 247, 121). It consists of the potassium and calcium salts of a tribasic acid, *glycyrrhizic acid* $C_{44}H_{64}O_{19}$. Glycyrrhizic acid melts at 205°, it has a sweet taste and is optically inactive. A hexa-acetyl derivative has been obtained, m.p. 210°. Glycyrrhizic acid does not reduce ammoniacal silver solution or Fehling's solution. When fused with potash it yields acetic and oxalic acids; distilled with zinc dust, naphthalene; and when oxidised with potassium permanganate, phthalic acid. If glycyrrhizic acid is boiled for 5 hours with water containing 3 p.c. of sulphuric acid, air being excluded, *glycyrrhetic acid* $C_{32}H_{48}O_7$ (hitherto known as *glycyrrhetin*) is precipitated. It can be obtained crystalline from acetic acid, melts at 210°, is monobasic, and forms a diacetyl derivative melting at 219°. The solution from which this acid has separated contains glycuronic acid.

The drug contains about 2 p.c. of glycyrrhizic acid, also 0·2 p.c. of a fatty substance with a bitter taste, and dextrose. Mannitol is present in the liquid from which the crude glycyrrhizic acid has been precipitated with sulphuric acid but it is not present in the original drug.

By distilling Spanish liquorice root, Haensel (Pharm. Centh. 40, 533) obtained 0·03 p.c. of an ethereal oil; the Russian roots yield 0·035 p.c. These oils are not identical, for whilst the Russian oil is dextrorotatory, the Spanish is lævorotatory.

For the technical analysis of liquorice extracts, *see* Py (Pharm. Chim. [vi.] 5, 280); Trubeck (J. Amer. Chem. Soc. 22, 19); Hafner (Chem. Zentr. 1900, i. 68; ii. 501). A. S.

LITHARGE *v.* Lead.

LITHIA MICA *v.* Lithium.

LITHIUM. Sym. Li. At.w. 6·94 (Hagen, Mallet, Troost, Diehl, Stas, Dittmar, Richards and Willard). This metal occurs in combination with silica, alumina, and the alkali metals in *lepidolite* or *lithia mica*, *petalite* (containing phosphates of lithium, iron, and manganese), *spodumene*, *triphylene*, and *amblygonite*, usually to the extent of 3 to 6 p.c. (J. Soc. Chem. Ind. 18, 877). Also in psilomelane, in a hexagonal variety of zinc sulphide, schalenblende, and in many radioactive minerals particularly carnotite (Gleditsch, Compt. rend. 145, 1148; 146, 331); Ramsay, *ibid.* 146, 456; McCoy, Nature, 1907, 79).

Lithium is widely distributed. It occurs as chloride in most spring waters and in sea water. A mineral spring at Wheal Clifford, near Redruth, contains 26 grains per gallon (Miller, Brit. Assoc. Trans. 1864, 35); Phillips has found 34 grains per gallon in a salt spring in Huel Seton copper mines in Cornwall. It is found in most plants, especially in the leaves (Tschermak, Chem. Zentr. 1899, ii. 1127). The ash of tobacco has been found to contain 0·44 p.c. of lithium chloride (Fruehot, Compt. rend. 78, 1022). The presence of lithium in excess appears to be generally injurious to plants. It also occurs in all the organs of the human body, particularly the lungs (Herrmann, Pflügers Archiv. 109, 26).

Lithium was first isolated by Brandes, but first prepared in quantity by Bunsen (Pogg. Ann. 94, 107). The metal cannot be obtained by ignition of the carbonate with carbon, or of the hydroxide with iron, but is obtained by the electrolysis of a mixture of equal weights of lithium and potassium chlorides (Guntz, Compt. rend. 117, 732). Ruff and Johannsen (Zeitsch. Elektrochem. 12, 186) recommend a mixture of lithium bromide with 10–15 p.c. lithium chloride, using a carbon anode and two iron rods, 4 mm. diameter, as cathode, the current required being 100 ampères and 10 volts. According to Borschers (Chem. Zentr. 1895, ii. 13), lithium can be obtained from its ores by making the solution of the chlorides of the alkalis and alkaline earths slightly alkaline, evaporating in an iron vessel, fusing the residue thus obtained with ammonium chloride and electrolysing the mass with a current of 1000 amperes per square metre of cathode surface and 5 volts. The upper rim of the iron crucible is kept cool by a current of cold water, the surface thus being protected from the atmosphere by a thin layer of solidified metal. The metallic globules are then placed in a paraffin bath at 130°–200° when the pure metal rises to the surface. Lithium can also be formed by heating the hydroxide with magnesium in a tubulated iron retort when the metal distils over (Warren, Chem. News, 1896, 6); or by the electrolysis of lithium chloride in pyridine solution (Kahlenberg, J. physical. Chem. 1899, 3602).

The statement that traces of lithium are formed in the degradation of copper by radium emanation (Cameron and Ramsay, Chem. Soc. Trans. 1907, 1593) lacks confirmation (Perman, *ibid.* 1908, 1775; Curie and Gleditsch, Compt. rend. 147, 345).

Properties.—Lithium is a silver-white metal which tarnishes and oxidises less rapidly than potassium or sodium. It is softer than lead, but less tenacious. Its sp.gr. is 0·589 to 0·598 (Bunsen), lower than that of any known solid. It melts at 180° (Bunsen), 186° Kahlbaum, Zeitsch. anorg. Chem. 23, 220), and volatilises at a bright red heat in a current of hydrogen, forming *lithium hydride* LiH (Guntz, Compt. rend. 122, 244). At a temperature somewhat above its melting-point it burns with an intense white light. When heated, it burns in chlorine, bromine, iodine, and sulphur vapour, and in carbon dioxide. In water it oxidises, but does not fuse. It absorbs nitrogen even in the cold, being the only metal that does so (Deslandres, Compt. rend. 121, 886; Guntz, *ibid.* 245).

By nitric acid it is rapidly oxidised, often with fusion and ignition. In dilute sulphuric acid and in hydrochloric acid it dissolves quickly; solution is slow in strong sulphuric acid. At a temperature below 200° it attacks silica, glass, and porcelain. Like other alkaline metals it dissolves with formation of a blue solution in liquefied ammonia gas, a similar result being obtained when it dissolves in methylamine (Moissan, Compt. rend. 128, 26). When gently heated to 400° in a current of ammonia, *lithamide* $LiNH_2$ is formed (Titherley, Chem. Soc. Trans. 1894, 517; Moissan, Compt. rend. 127, 685; *ibid.*, 133, 715).

At the ordinary temperature, lithium with dry ammonia gas forms a liquid which, when rapidly evaporated at 70°, yields a brownish red solid, *lithium ammonia* $LiNH_3$ (Moissan, *l.c.*).

Lithium forms an amalgam with mercury

(Kerp and Böttger, Zeitsch. anorg. Chem. 25, 1) and alloys with antimony, tin, and lead of the type Li_3M (Lebeau, Compt. rend. 130, 502; *ibid.* 134, 231, 284). These alloys have higher melting-points than the constituents and are powerful reducing agents. It also forms compounds with arsenic (Lebeau, *ibid.* 129, 47) and with silicon (Moissan, *ibid.* 134, 1083; Wallace, Zeitsch. anorg. Chem. 63, 1).

Detection.—Lithium salts produce a fine, crimson colour in the blowpipe flame. They are usually colourless, and when in strong solution give a precipitate on addition of carbonates or sodium phosphate, in presence of ammonia. In presence of sodium, lithium can be detected by making the solution alkaline with ammonia, then adding $\frac{1}{10}$ of its volume of sodium hydrogen phosphate, after which enough alcohol is added to produce a heavy permanent precipitate. On boiling, the solution will become perfectly clear if lithium is absent, for lithium phosphate is insoluble in boiling alcohol (Benedict, Amer. Chem. J. 32, 480).

Estimation.—The estimation usually entails the separation from potassium and sodium. For this separation Mayer's process is most satisfactory (Annalen, 98, 193). The solution containing the alkalis as chlorides is treated with sodium phosphate (*absolutely* free from alkaline earth phosphates), and sufficient sodium hydroxide to keep the solution alkaline, and evaporated to dryness. Sufficient water is added to dissolve the soluble salts, the solution heated gently and filtered after 12 hours. The precipitate is washed with a mixture of 1 part of water and 1 part of ammonia (of which liquid 3920 parts dissolve only 1 part of lithium phosphate); the filtrate and first two washings are evaporated and taken up as before, any residue of lithium phosphate being added to the bulk of precipitate. The precipitate, dried at 100°, has the composition Li_3PO_4.

Kahlenberg and Krankopf (Amer. Chem. J. 30, 1104) recommended the following method. The solution of mixed chlorides is evaporated to dryness and the residue is boiled with pyridine. The solution is decanted through a small filter and the residue is again treated with pyridine several times. The pyridine filtrates are now distilled and the lithium chloride residue is converted into sulphate by evaporation with sulphuric acid and weighed as such. According to Schieffelin and Lamar (Amer. Chem. J. 24, 392) a good way of estimating lithia in lepidolite is to dissolve the alkali chlorides obtained in the usual way in about 10 c.c. of hot water, a drop of hydrochloric acid is added, then a little ammonia and ammonium oxalate; the solution is filtered and the filtrate evaporated until it commences to crystallise (about 1–2 c.c.). A drop of water and of hydrochloric acid is added, then 15 c.c. of amyl alcohol, it is then concentrated to half its volume, cooled and filtered into a platinum dish, the residue is washed with amyl alcohol, until the washings are free from lithium, the amyl alcohol extract is evaporated below the boiling-point and the residue converted to sulphate.

For methods of estimating lithium in mineral waters, compare Carnot (Compt. rend. 107, 336); Waller (J. Soc. Chem. Ind. 1890, 1066); Razoli (Gazz. chim. ital. 31, i. 40).

Extraction of salts.—Finely powdered lepidolite or petalite 10 parts, is mixed with barium carbonate 10, barium sulphate 5, potassium sulphate 3, and ignited at the highest temperature of a wind furnace. Two layers are thus produced, the lower of barium silicate and sulphate, the upper of white sulphate of potassium and lithium. It is lixiviated with water and treated with barium chloride to convert the alkalis into chlorides and to precipitate the sulphuric acid as barium sulphate. The solution is evaporated to dryness and digested with a mixture of equal parts of absolute alcohol and ether, in which the lithium chloride dissolves with only a trace of potassium and sodium chloride (Troost, Compt. rend. 43, 921).

According to Müller (Annalen, 85, 251), *triphylene* is dissolved in hydrochloric acid, the iron oxidised to ferric chloride by the addition of nitric acid, the phosphoric acid precipitated by a persalt of iron, the mixture evaporated to dryness, and extracted with water. Manganous and lithium chlorides are thus dissolved; the former is precipitated with barium sulphide, the excess of barium being removed by the addition of ammonium carbonate or sulphuric acid. The solution is evaporated with oxalic acid and the residual oxalate ignited to carbonate.

The finely ground and sifted lepidolite is made into a thin paste with concentrated sulphuric acid, in a warm brick trough, and digested and stirred until it commences to agglomerate. It is then calcined in a reverberatory furnace, and, while warm, well lixiviated with water and filtered. The lye is mixed with sufficient potassium sulphate to convert all the alumina into alum, and the solution decanted from the alum meal. The remaining alumina is precipitated by milk of lime, the alkalis are converted into chlorides by addition of barium chloride, and the solution evaporated to dryness. The chlorides of lithium and calcium are extracted with absolute alcohol, the alcohol evaporated, and the calcium precipitated by ammonium oxalate, and any heavy metals removed by a little ammonium sulphide. The solution is evaporated to dryness in a silver basin (*v.* A. W. Hofmann, Dingl. poly. J. 219, 183, and Felsinger, *ibid.* 222, 385).

Powdered amblygonite or other lithium ore is intimately mixed with powdered sodium bisulphite and the mixture heated in cast-iron retorts, the hydrofluoric acid and silicon fluoride disengaged being collected. The mass is then transferred to a refractory earthen vessel and heated to redness. The product is lixiviated, filtered, and aluminium, copper, and iron are precipitated by a very small proportion of sodium carbonate. After filtration it is again treated with sodium carbonate when lithium carbonate is precipitated. The insoluble residue of the lixiviated product is said to be rich in phosphorus and can be used as a manure (J. Soc. Chem. Ind. 1906, 884).

Finely powdered lepidolite is mixed with 10 p.c. more than its weight of sulphuric acid and heated with frequent stirring for 8 hours at 112°–340°; 97–99 p.c. of the ore is thus decomposed. The mass is leached with water and the silica separated. The solution is now treated with sufficient potassium sulphate to convert the aluminium sulphate to alum and allowed to stand for 6 days when precipitation is complete, the decanted liquor is treated with whiting, boiled, and the alum precipitated as alunite by adding aluminium hydroxide. The last traces of alumina are removed by again treating the filtrate with whiting. The solution is then boiled, made alkaline with slaked lime and concentrated. Copper sulphate and magnesium and iron oxides are removed in the usual way and the solution consisting of lithium sulphate is added to a solution of potassium carbonate, when lithium carbonate is precipitated, and is washed and dried (Schieffelin and Cappon, J. Soc. Chem. Ind. 1908, 549).

According to Wadman (*ibid.* 1907, 469; 1908, 122), pure lithium carbonate can be obtained by heating the ore with an alkaline sulphate such as K_2SO_4. The solution of sulphates thus obtained is now treated with sufficient ammonia to render the potassium sulphate insoluble and to precipitate iron, aluminium, and magnesium hydroxides. The precipitate is removed and the lithium precipitated as carbonate.

According to Zell (J. Soc. Chem. Ind. 1909, 1126), a pure lithium compound can be obtained by heating a lithium ore in the presence of carbon in an atmosphere of acetylene. Volatile lithium hydrogen carbide is thus formed and is decomposed by water into lithium hydroxide and acetylene.

Lithium oxide Li_2O may be prepared by ignition of the metal in air or oxygen (Holt and Sims, Chem. Soc. Trans. 1894, 443); in solution, by precipitation of the sulphate with barium hydroxide solution. A purer product is obtained by heating lithium hydroxide or its hydrate LiOH, or $Li(OH)\cdot H_2O$, in a platinum crucible in a current of dry hydrogen for about an hour at 780° (Forcrand, Compt. rend. 144, 1321). Lithium carbonate heated similarly at 780°–800° also yields pure lithium oxide (Forcrand, *l.c.* 1402). It is yellowish white and spongy, less soluble than the oxides of potassium and sodium. It melts below redness, and, as it corrodes platinum powerfully, should be fused in a silver vessel. The hydrated oxide may be obtained in small crystalline grains.

By mixing lithium hydroxide (Forcrand, Compt. rend. 146, 802) with hydrogen peroxide and then adding an equivalent volume of absolute alcohol, the compound

$$Li_2O_2\cdot H_2O_2,3H_2O$$

is formed which, when placed in a vacuum over phosphorus pentoxide, yields *lithium peroxide* Li_2O_2 (Forcrand, Compt. rend. 130, 1465).

Lithium chloride LiCl may be prepared by combination of lithium and chlorine, or by dissolving the carbonate or oxide in hydrochloric acid. When formed at low temperatures the crystals contain two molecules of water; at temperatures above 15° anhydrous octahedral crystals are produced, which are very hygroscopic; various hydrated chlorides are known (Bogorodsky, Chem. Zentr. 1894, ii. 514). It dissolves in absolute alcohol and in a mixture of alcohol and ether. At 0° 100 parts of water dissolve 63·7 parts, and at 100° 145 parts of the chloride.

Lithium chloride is more volatile than potassium chloride; less so than sodium chloride. Below a red heat it volatilises, losing a little hydrochloric acid and producing an equivalent amount of lithium oxide.

Lithium dissolves in the chloride, but the subchloride Li_2Cl could not be obtained (Guntz, Compt. rend. 1895, 121, 945; Ann. Chim. Phys. 1907, 10, 13). At −18° the chloride absorbs ammonia rapidly, forming a series of compounds with 1, 2, 3, and 4 molecules of ammonia (Bonnefoi, Compt. rend. 124, 771; *ibid.* 127, 367). With ethylamine and methylamine, it behaves similarly (Bonnefoi, *l.c.* and Compt. rend. 129, 1257). Lithium bromide (Bonnefoi, *ibid.* 130, 1394; Bogorodsky, *l.c.*), lithium iodide (Thirsoff, J. Russ. Phys. Chem. Soc. 25, 467; Bogorodsky, *l.c.*), and their double salts with other metallic halides (Kurnakoff and Sementschenko, Zeitsch. anal. Chem. 1899, 335; Dobroserdoff, J. Russ. Phys. Chem. Soc. 32, 774; Bogorodsky, *l.c.* 515; Duboin, Compt. rend. 141, 1015; Chassevant, *ibid.* 115, 113); also lithium fluoride (Poulenc, Bull. Soc. chim. [iii.] 11, 15; Wells and Foote, Amer. J. Sci. 1897, 466) have been prepared.

Lithium sulphate Li_2SO_4 is prepared by dissolving the carbonate or oxide in sulphuric acid. It forms monoclinic plates, soluble in alcohol and water. It produces a double sulphate with potassium sulphate, but does not form an acid sulphate or an alum.

Lithium carbonate Li_2CO_3 is prepared by the addition of a hot concentrated solution of lithium chloride to an ammoniacal solution of ammonium carbonate. It is a white powder, which decomposes at 600° (Lebeau, Compt. rend. 136, 1256), is reduced by heating with aluminium (Franck, Chem. Zeit. 1898, 22, 236), and is more fusible than the potassium and sodium salts. It is quite insoluble in absolute alcohol (Kobbe, Pharm. Zeit. 34, 312) and only slightly soluble in water but more readily so in aqueous solution of the alkalis, particularly ammonium salts (Geffcken, Zeitsch. anorg. Chem. 1905, 43, 197).

Its solubility in cold is greater than in hot water. The solubilities given by different observers are not concordant. According to Bevade (Bull. Soc. chim. [ii.] 43, 123), the solubility in 100 parts of water is as follows:—

Temperature	0°	10°	20°	50°	75°	100°
Parts . .	1·539	1·406	1·329	1·181	0·866	0·728

The solubility increases after continued boiling. *V.* further Draper (Chem. News, 55, 169) and Flückiger (Arch. Pharm. [iii.] 25, 509).

The commercial salt usually contains about 98·5 p.c. of lithium carbonate. Lithium forms a very soluble *urate*; for this reason the carbonate and citrate are administered to remove uric acid from the blood in gouty affections (Kebler, Amer. J. Pharm. 1898, 600).

Lithium carbide Li_2C_2, is obtained by heating lithium carbonate with sugar carbon in an electric furnace (Moissan, Compt. rend. 122, 362); or by heating lithium and carbon together in a vacuum (Guntz, *ibid.* 126, 1866); or in a stream of carbon di- or monoxide (Guntz, *ibid.* 123, 1273; Moissan, *ibid.* 127, 911). It is a powerful reducing agent; burns in fluorine, chlorine, bromine, iodine, oxygen, and combines with sulphur and selenium; it is not attacked by concentrated acids but readily by water, forming acetylene and lithium oxide.

Lithium nitride Li_3N is prepared by heating lithium in an iron dish very gently in a slow stream of nitrogen (Ouvrard, Compt. rend. 1892, 114, 120; Guntz, *ibid.* 123, 995). It is a brownish red or black spongy substance, difficult to obtain quite pure and is readily decomposed by water or when heated with hydrogen.

Lithium azoimide LiN_3,H_2O, formed by neutralising a solution of lithium hydroxide with azoimide, HN_3, crystallises in colourless, lustrous, hygroscopic needles which explode between 115–298 (Dennis and Benedict, Zeitsch. anorg. Chem. 1898, 17, 18; Curtius and Rissow, J. pr. Chem. 1898 [ii.] 58, 261).

Lithium citrate $Li_3C_6H_3O_7$ is prepared by the addition of 100 parts of lithium carbonate to a solution of 186·5 parts of citric acid (Umney, Year-book of Pharmacy, 1875, 559). It may be produced as a white, anhydrous, neutral, non-deliquescent powder, or in crystals containing 4 molecules of water. It is soluble in 25 parts of cold water. The commercial salt usually contains salts of potassium, sodium, and calcium, and frequently lithium carbonate or citric acid, and powdered lepidolite or petalite (C. Thompson, Pharm. J. [iii.] 13, 783; Dott, *ibid.* 1905, 440). The following salts of lithium are employed in medicine:—

Benzoate, caffeine sulphonate, dithiosalicylate, formate, guaiacate, hippurate, and iodate in uric acid diathesis; bitartrate, theobromine salicylate, potassium tartrate and acetate as diuretics; glycerophosphate in neurosthenia; borosulphite, sulphoichthyolate, and sozoiodolate as antiseptics (J. Soc. Chem. Ind. 1898, 736; Kebler, Amer. J. Pharm. 1899, 57).

According to Vulpian (J. Soc. Chem. Ind. 1889, 476) lithium salicylate is of greater effect than sodium salicylate in gout and in acute articular rheumatism.

Lithium quinate is used in the treatment of gout and analogous diseases (Johnson, J. Soc. Chem. Ind. 1899, 1051). According to Dumesnil (J. Pharm. Chim. 1906, 326), lithium theobromine, prepared by adding excess of theobromine to lithium hydroxide solution, is 4 or 5 times as active therapeutically as the same weight of theobromine.

Lithium salts react with casein giving readily digestible compounds suitable for medical purposes (Abel, J. Soc. Chem. Ind. 1899, 398).

Lithium oxalate (Foote and Andrew, Amer. Chem. J. 1905, 153), thymate (J. Soc. Chem. Ind. 1906, 714), and the double salts of lithium and the acid salts of piperazine with oxalic, tartaric, and citric acids (*ibid.* 1897, 758), are also very useful products.

Double urinates (Melikoff and Pissarjewsky, Ber. 30, 2902; Coninck and Chauvenet, Bull. Belg. Roy. Acad. 1905, 51, 182); lithium phosphates and arsenates (Schulten, Bull. Soc. chim. [iii.] 1, 479; Ouvrard, Compt. rend. 110, 1333; Rammelsberg, Chem. Zentr. 1891, ii. 790; Quartaroli, Gazz. chim. ital. 1907, i. 598); zirconates (Ouvrard, Compt. rend. 112, 1444; Venable and Clarke, Amer. Chem. J. 1896, 434); borates (Reischle, Zeitsch. anorg. Chem. 4, 169; Chatelier, Compt. rend. 124, 109); alumino silicates (Weyberg, Centr. Min. 1905, 646); platinocyanides (Reynolds, Proc. Roy. Soc. 1909, 82, 380), and tungstates (Feist, Ber. 21, 133) have been prepared. Lithium tungsten bronze, LiW_5O_{15} (Hallopeau, Compt. rend. 127, 512) is prepared by the electrolysis of lithium para-tungstate.

Z. K.

LITHOFRACTEUR *v.* EXPLOSIVES.

LITHOGRAPHIC STONE. A fine-grained limestone of uniform texture, breaking with an imperfect conchoidal fracture, and free from spots and veins. It must be compact enough to take a good polish and yet sufficiently porous to absorb the grease of the draughtsman's crayon; whilst being a limestone it can be etched with cold dilute acid. The only stones possessing these properties in a high degree are those from the large quarries at Solenhofen and Pappenheim in central Bavaria. Here the rock is a thin-bedded limestone of Upper Jurassic age. Two qualities are distinguished—a yellowish-drab and a bluish-grey, the latter being rather harder and more serviceable. They consist of 81–96 p.c. $CaCO_3$, 1–18 p.c. $MgCO_3$, with small amounts of alumina, ferric oxide, silica, &c. The quality of the stone depends, however, on physical characters rather than on chemical composition. Many attempts have been made to find lithographic stone at other localities, more particularly in the United States (*v.* G. P. Merrill, The Non-metallic Minerals, 2nd edit., New York, 1910).

L. J. S.

LITHOMARGE. (*Steinmark*, Ger.) An amorphous substance, resembling clay in composition (hydrated aluminium silicate with some iron) and in most of its physical properties, but firmer and more compact. It occurs on a large scale in the basaltic lavas of Antrim, where it is associated with bole, bauxite, and aluminous iron-ore. Some of the Irish lithomarge is of lavender colour, with white specks of bauxite, whilst other varieties are brown or blackish. The substance is known to the workmen as 'marge.' It may have resulted from the alteration of the basalt, and appears to resemble some of the steatitic laterites of India. Where peaty water comes in contact with the lithomarge, it occasionally deposits manganese oxide in considerable quantity (*v.* P. Argall, Journ. Geol. Soc. Ireland, 1886, 16, 102; G. H. Kinahan, *ibid.* 307). Lithomarge occurs in several Cornish mines; a fine yellowish variety, with purple veins, being found at Cook's Kitchen, near Redruth. Closely allied to lithomarge is the *teratolite* of Saxony, formerly reputed to possess such powerful medicinal qualities that it was described by old writers as *terra miraculosa Saxoniæ.*

L. J. S.

LITHOPONE. A pigment prepared by strongly heating a mixture of zinc sulphide and barium sulphate, obtained by mixing solutions of barium sulphide and zinc sulphate. Is a variable mixture of zinc oxide, zinc carbonate, zinc sulphide, and barium sulphate. The usual process of manufacture is to heat heavy spar with carbon, dissolve the mass in water and mix with a solution of zinc vitriol. The precipitate is washed, dried, and ignited, mixed with 2–3 p.c. of sal ammoniac and again ignited. While hot it is thrown into water, dried, and finely ground. Its value depends upon the amount of zinc sulphide present. For methods of analysis (*v.* J. Soc. Chem. Ind. 1902, 1145).

LITMUS. *Tournesol en pain.* This colouring matter is well known to the chemist, since white paper impregnated with its solution in a slightly acid or alkaline condition has long been employed, under the name of red and blue litmus-paper, to indicate the presence, in any solution, of alkalis or acids respectively. Alkalis change the colour of red litmus-paper to blue, acids turn blue litmus-paper red. In alkalimetry litmus tincture has, until recently, been the most generally adopted indicator. This use depends upon the fact that the free colouring matter of litmus is red, whereas its alkali salts are blue.

Commercial litmus has the form of small pale blue cubes, composed essentially of gypsum and chalk mixed with but comparatively little colouring matter, which is largely present in the form of a lake.

It is said to be prepared, chiefly in Holland, from various species of lichens, *e.g. Lecanora tartarea, Roccella tinctoria*, &c., the same, indeed, as are used in the manufacture of orchil (*q.v.*). Under the combined influence of ammonia and atmospheric oxygen the proximate principles contained in these lichens yield *orceïn*, the alkali salts of which are purple (orchil); but if potassium or sodium carbonate is present at the same time, the reaction proceeds further, and ultimately *azolitmin* (the colouring matter of litmus), the alkali salts of which are blue, is produced.

According to Gélis (J. Pharm. Chim. 24, 277; Revue Scient. 6, 50), litmus may be prepared as follows. Orchil-weed is ground and mixed with half its weight of potassium carbonate, and then repeatedly moistened with urine saturated with ammonium carbonate or with an aqueous solution of this salt; the mass soon acquires a brownish-red colour (3 days), which gradually becomes purple (20–25 days), and finally blue (30 days), yielding a litmus of the best quality in 40 days. The pulpy mass is mixed with chalk and gypsum, then moulded in the form of cubes, and dried in the shade.

By modifying the action of air and ammonia upon orcinol, through the addition of sodium carbonate, De Luynes also succeeded in obtaining the colouring matter of litmus (Compt. rend. 59, 49; Dingl. poly. J. 174, 61; Chem. Zentr. 1865, 127; J. 1864, 551). A mixture of 1 part orcinol, 25 parts cryst. sodium carbonate, 5 parts water, and 5 parts ammonia solution, was heated to 60°–80° for 4–5 days with frequent agitation. On diluting the blue solution thus obtained and acidifying slightly with hydrochloric acid, the colouring matter was precipitated. On washing and drying, it assumed a metallic lustre. It is sparingly soluble in water, but readily soluble in alcohol and in ether.

In making a litmus solution to be employed as indicator, the commercial litmus is extracted with boiling water, the filtered solution is slightly acidified with acetic acid, then carefully neutralised with ammonia, and boiled to expel any excess of the latter. Kept for any lengthened period in stoppered bottles, the solution becomes decolourised in consequence of a reductive fermentation; on exposure to air, however, the original colour is restored. This defect is prevented by saturating the solution with sodium chloride (Reichelt). (Compare also Bellamy, J. Pharm. Chim. [v.] 18, 433.) A dry litmus-extract may be prepared according to Vogel in the following manner (*ibid.* 45, 64, 70; Chem. News, 1864, 205). Twenty grams powdered commercial litmus are twice digested, each time with 150 c.c. cold distilled water. The second solution, which is alone employed, is divided into two equal portions, one of which is slightly acidified with nitric acid and then mixed with the other. The purplish solution thus obtained is evaporated to dryness on the water-bath, and the granular amorphous mass is kept in a stoppered bottle ready for dissolving in water when required.

For the employment and characteristics of litmus as an indicator *v.* R. T. Thomson (J. Soc. Chem. Ind. 6, 198); also art. ACIDIMETRY, vol. i.; Marsh (Chem. News, 61, 2); Berthelot (Ann. Chim. Phys. [vii.] 25, 39); Ronde (Pharm. Zeit. 41, 736); Lescouer (Compt. rend. 123, 811); Lüttke (Zeitsch. anal. Chem. 31, 692); Foerster (*ibid.* 28, 428); Glaser (*ibid.* 38, 273).

Litmus exhibits a characteristic absorption spectrum. Ether extracts it from an acid solution, and forms a yellow liquid, which absorbs the more refrangible end of the spectrum to a point midway between D and E. If the solution is coloured blue by adding a drop of ammonia, an absorption-band is formed, commencing at D, where it is extremely black, and gradually diminishing to E. A blue aqueous commercial solution shows a well-marked absorption-band at D. Addition of acid changes the colour to red, the band at D disappears, and the spectrum now resembles that of œnolin, the colouring matter of red wine (A. H. Allen, Com. Org. Analysis, 325). (Compare also Vogel, Praktische Spectralanalyse, 1877, 269.)

Our knowledge of the chemistry of the colouring matters contained in litmus is very meagre. Gélis (J. Pharm. Chim. 27, 477) extracted from it several colouring matters in the following manner. After extracting commercial litmus with water, the insoluble residue is boiled with dilute caustic alkali and the filtered solution is precipitated with basic lead acetate. The blue precipitate is washed by decantation until it begins to dissolve and colour the wash-water. It is then decomposed with hydrogen sulphide, exposed to air until free from excess of H_2S, collected on a filter and digested with dilute ammonia to extract the colouring matter. On adding acid to the filtered solution the main portion of the litmus colouring matters is thrown down as a red flocculent precipitate. The filtrate from this contains a very small quantity of colouring matter (α).

On extracting the dried red precipitate with ether and leaving the orange solution to spontaneous evaporation, it yields a bright-red residue (β) containing crystalline needles. This product is insoluble in water, but readily soluble in alcohol, also in alkalis with a violet colour. The portion insoluble in ether is dissolved in alcohol, and on allowing the blood-red solution to evaporate spontaneously it yields a large quantity of a reddish-purple product (γ) having a bronze lustre. This represents the colouring matter most abundant in litmus.

The residue, which is insoluble in water, in alcohol, and in ether, contains another product (δ) which is soluble in alkalis, from which it may be precipitated by acids. The three products β, γ, and δ, appear to contain nitrogen.

A more detailed examination of litmus was made in 1840 by Kane (Royal Soc. Trans. 1840, 298; Ann. Chim. Phys. [iii.] 2, 129; Annalen, 39, 57; J. Pharm. Chim. 1841, 569), who isolated from it the chief and characteristic colouring matters *azolitmin* and *erythrolitmin*, together with *erythroleïn* and *spaniolitmin.*

According to Kane, finely powdered commercial litmus is extracted with boiling water. Most of the colouring matter remains in the form of an insoluble lake in the residue, to which hydrochloric acid is added till effervescence ceases and the mixture is strongly acid. The insoluble matter mixed up with liberated colouring-matter is collected on a filter, washed free from acid, dried, and extracted with boiling alcohol. The alcoholic solution is filtered from an insoluble reddish-brown mass (impure azolitmin) and then evaporated to dryness, and the residue is digested with warm ether until it becomes no longer coloured. On distilling the filtered ethereal solution, *erythroleïn* is left as a purple semi-fluid oily substance. That portion of the alcoholic extract which is insoluble in ether consists of *erythrolitmin.*

The above-mentioned impure azolitmin is purified, either by dissolving it in a large quantity of boiling water and evaporating the solution to dryness, or by dissolving it in very dilute ammonia, evaporating the solution to dryness, neutralising any residual ammonia by dilute hydrochloric acid, and washing with alcohol until free from ammonium chloride and excess of hydrochloric acid. The residue represents purified *azolitmin.*

The colouring matter contained in the deeply coloured solution obtained in the first instance by boiling the commercial litmus with water and filtering, is isolated as follows. The solution is precipitated with neutral lead acetate, the purple precipitate thus obtained is well washed, suspended in water, and decomposed with hydrogen sulphide. The mixture of lead sulphide and liberated colouring matter thus obtained is well washed and digested with warm dilute ammonia ; the filtered deep-blue solution is evaporated to dryness, the residue is moistened with hydrochloric acid, washed free from ammonium chloride and any excess of hydrochloric acid, with warm alcohol. The residual deep brownish-red powder consists usually of nearly pure azolitmin, more rarely of *spaniolitmin*, a substance very similar to azolitmin, but which does not contain nitrogen.

Since spaniolitmin occurs so rarely in litmus, and erythroleïn is coloured reddish-purple and not blue by alkalis, Kane considers azolitmin and erythrolitmin to be the essential colouring matters of litmus, in which they are combined with ammonia, potash, and lime, and mixed with a considerable quantity of chalk, gypsum, &c.

Azolitmin is a deep brownish-red amorphous powder, insoluble in alcohol and sparingly soluble in water, but readily soluble in alkaline solutions with a pure blue colour. Its ammoniacal solution gives with metallic salt solutions blue or purple precipitates according as they are more or less basic in character. Kane's formula for it is $C_9H_{10}NO_5$, but Gerhardt considers it is best represented by $C_7H_7NO_4$. It differs from all the other colouring matters isolated from litmus by containing nitrogen. Gerhardt considered it to be derived from orcinol, possibly in accordance with the following equation :

$$C_7H_6O_2+NH_3+3O=C_7H_7NO_4+H_2O$$

or from orceïn thus $C_7H_7NO_3+O=C_7H_7NO_4$.

If the percentage composition assigned to this substance is correct, the explanation of the part played by the necessary alkaline carbonate in the manufacture of litmus may be that it facilitates and increases the oxidation of the orcinol, so that the orceïn at first formed is changed into azolitmin (Gerhardt, Ch. Org. 3, 816).

Scheitz (Zeitsch. anal. Chem. 1910, 49, 736) has isolated from litmus a blue colouring matter distinct from azolitmin in quantity equivalent to 1·5 p.c. of the weight of the purified material. It consists of a bright brown powder soluble in formic acid, pyridine, and ammonia, forming a bluish-violet solution with the last-named solvent. It absorbs ammonia gas with production of a dark blue ammonia compound, which dissolves in water to a reddish solution. This ammonia compound is a more delicate indicator than the corresponding derivative of azolitmin.

Erythrolitmin, which also constitutes one of the most important ingredients of litmus, is a bright-red powder, sparingly soluble in water and in ether. It is abundantly soluble in alcohol, from which it may be crystallised in the form of dark-red granular crystals. In strong caustic potash it dissolves with a blue colour. With ammonia it forms a blue compound which curiously enough is totally insoluble in water. With metallic salts it forms lakes of a fine purple colour. According to Kane its formula is $C_{13}H_{22}O_6$, and he considers it to be an oxidation product of his erythroleïc acid ($C_{13}H_{22}O_4$) obtained from orchil.

Erythroleïn forms a crimson semi-fluid mass, almost insoluble in water, soluble in ether and in alcohol with a red colour, and in ammonia with a purple colour. With metallic salts it gives purple lakes. Kane gives its formula as $C_{13}H_{22}O_2$. Its general properties are very similar to those of the above-mentioned erythroleïc acid.

Spaniolitmin occurs but rarely in litmus, hence its name. It is a bright-red substance, insoluble in alcohol and in ether, and very sparingly soluble in water. It dissolves in alkalis with a blue colour and gives lakes very similar to those of azolitmin. Kane's formula for it is $C_9H_7O_8$.

Under the influence of hydrogen sulphide, the colouring matters of litmus are decolourised, Kane's idea being, that a colourless hydrogen sulphide compound is thus formed. (*V.* also Malaguti, Ann. Chim. Phys. [iii.] 37, 206; Vogel, J. pr. Chem. [ii.] 16, 311.) Nascent hydrogen, and other reducing agents such as ferrous and stannous oxide, &c., decolourise them by reduction in the ordinary manner. Azolitmin thus yields colourless *leucazolitmin*, which, however, rapidly oxidises and becomes coloured on exposure to air. If stannous chloride is added to an ammoniacal solution of azolitmin, purple-coloured stannous-azolitmin is precipitated ; if this is boiled with slightly acidulated water there is formed the colourless compound of stannic oxide with leucazolitmin, which, if exposed to air, changes into the bright scarlet stannic-azolitmin.

Deoxidising agents such as sulphurous acid and sulphites do not decolourise the colouring-matters of litmus.

Azolitmin and erythrolitmin, suspended in water and submitted to the action of chlorine gas, are decolorised and give yellow chlorine derivatives, *chlorazolitmin* and *chlorerythrolitmin*, substances insoluble in water, but soluble in alcohol, ether, and in alkalis.

In his earliest memoir, Kane (Annalen, 36, 324) mentions that on heating the colouring matters of litmus mixed with chalk or gypsum, a red vapour is given off which condenses in the form of crystalline scales (atmérythrin) soluble in alcohol. When heated alone, this substance is not produced. Although Kane makes no subsequent mention of this body it is possible that it was indirubin or even indigotin, since at a later date, Wartha (Ber. 9, 217) states that he found some samples of litmus to contain indigotin, recognisable by the violet vapour given off on heating a few cubes of the commercial product in a test tube. Its presence may have been due to the use of urine containing indoxyl in the preparation of the litmus.

Wartha (*l.c.*) gives the following results of his examination of litmus. The commercial product is well shaken up with alcohol; the filtered purple solution thus obtained has a green fluorescence, and exhibits in the spectroscope a characteristic absorption band in the green with an almost total absorption of the violet end. The colouring matter (*a*) itself is obtained on evaporating the solution.

The litmus residue insoluble in alcohol is digested for 24 hours with distilled water, and the filtered deep-coloured solution is evaporated to dryness. The extract thus obtained is repeatedly treated with absolute alcohol containing a little glacial acetic acid and again evaporated, so that all traces of water may be removed, and there finally remains a brown powdery mass. On extracting this with absolute alcohol, a large quantity of a scarlet substance (*b*) is dissolved. It is similar to orceïn and dissolves in ammonia with a reddish-purple colour. That portion of the brown powder which is insoluble in the acidified alcohol is dissolved in water, the filtered solution is evaporated to dryness, and the residue is repeatedly washed with absolute alcohol and evaporated in order to expel all traces of acetic acid. The residual brown powder, which is very soluble in water, with a reddish-brown colour, but insoluble in alcohol and in ether, is the purified and extremely sensitive colouring matter of litmus (*c*). Its alkaline solution is blue, its aluminium and tin lakes are violet, and its calcium and barium lakes blue. It appears to be very similar to Kane's azolitmin, but it is said not to contain nitrogen. The yield of these various colouring matters is as follows: (*a*) 2·3 p.c., (*b*) 3·4 p.c., (*c*) 5·7 p.c. (Mitchell, Chem. News, 1876, 140).

An examination of the colouring matters of litmus was also made by Rochleder and Skraup (Wien. Anz. 1874, 118; Chem. Zentr. 1874, 424). Other references are Magner, J. Pharm. Chem. 12, 418; Desfosses, *ibid.* 14, 487; Peretti, *ibid.* 14, 539.

Of interest also in connection with this subject is the fact that when ethyl-amino-orsellinic acid is oxidised by air in alkaline solution it yields an orange coloured dye possessing basic properties (Heinrich and Dorschky, Ber. 1904, 37, 1416).

A peculiar blue colouring matter similar to litmus, and called *tournesol en drapeaux*, has long been manufactured at Grand-Gallargues, Département du Gard, France, from the *Croton tinctorium* belonging to the *Euphorbiaceæ*. Coarse linen cloth is steeped in the deep bluish-green sap expressed from the berries and the tops of the plant, then dried quickly in the open air, and exposed for 1–1½ hours between layers of straw to the ammoniacal vapours of lant or horse-dung (*aluminadon*), care being taken not to submit them to this influence too long. The cloth thus acquires a deep-blue colour. It is then steeped in the sap a second time and dried in air till it acquires a purple or dull green. These blue cloths are used by the Dutch farmers for making an infusion with which to impart a red colour to the outside of their cheese, the blue being changed to red by the lactic and butyric acids of the cheese.

According to Joly (Ann. Chim. Phys. [iii.] 6, 111) the colouring matter pervades the entire plant and is readily extracted therefrom by water heated to 50°–60°. On being evaporated, an azure-blue resinous mass remains. Acids change the blue colour of its aqueous solution red, and this blue is not restored by alkalis, the colour becoming thereby rather greenish. It is, therefore, probably quite distinct from the colouring matter of litmus. Possibly it is identical with the blue colouring matter which can be extracted from another plant belonging to the *Euphorbiaceæ*, viz. *Mercurialis perennis*. A. G. P.

LIVER OF SULPHUR. *Hepar sulphuri; potassa sulphurata.* This compound consists of a mixture of salts of potassium, chiefly the higher sulphide, and is prepared by fusing in a Hessian crucible a quantity of potassium carbonate with half its weight of flowers of sulphur. The fused mass is poured out on a greased flagstone and allowed to solidify, when it assumes a liver-brown colour; hence its name. It is alkaline, and acrid to the taste, and when quite dry is inodorous; but when moist it acquires the odour of sulphuretted hydrogen.

In medicine, it is given internally in cases of lepra and psoriasis; whilst externally it is used in the form of lotions, baths; as ointment in chronic skin-diseases, such as eczema, scabies, and pityriass. It is also largely used as a plant-spray.

LIXIVIATION. Lixiviation is the application of a liquid, generally water, to solid bodies for the purpose of extracting the soluble part. For instance, the preparation of pearl-ash by dissolving out the potassium carbonate from the wood ashes, and the preparation of sodium nitrate from the crude nitrate, of beet sugar by Schützenbach's process, are all applications of water to extract the soluble part. The extraction of gold from the tailings obtained from the stamp batteries, by means of dilute potassium cyanide solution in the presence of air, affords another example of the process of lixiviation.

In carrying out this process on a commercial scale, three things are sought to be attained: First, that the residue should be completely exhausted of soluble matter; second, that the solution obtained should be nearly saturated; and, thirdly, that the process should be continuous. A series of tanks is therefore provided, standing at the same level, and provided with false bottoms covered with a filtering bed, and with connecting tubes, pumps, and so on. Each of these tanks contains the substance to be lixiviated, and the water travels from tank to tank, increasing in saturation.

The process is so arranged that at any given moment a nearly saturated liquor is passing over a *fresh* supply of the substance, while clean water is running through the nearly exhausted residue. When the residue in any tank is completely exhausted it is removed, fresh stuff put in, and that tank made the last of the series. In some cases a pump is necessary between each tank to pump the liquid from beneath the false bottom into the next tank.

If the solution formed is of high sp.gr., so much pumping is not necessary. One detailed description will suffice. In the preparation of soda by the Leblanc process, the black ash (roughly speaking, soluble sodium carbonate and insoluble calcium sulphide) is lixiviated. For this purpose, four or more iron tanks are used, built side by side, each about 10 feet × 10 feet × 6 feet. Each tank has a false bottom of perforated iron plates, and a large cock in the bottom, by which all the liquor it contains can be run off. It has also an overflow pipe, rising from below the false bottom and communicating with the next tank, and a second overflow pipe which communicates with a trough outside. The first tank is connected with the last by a pipe. Any of these pipes can be closed by plugs or cocks. Suppose the process to be in full working order. Fresh black ash, broken in large lumps, has been placed in tank 4, on a bed of cinders laid over the false bottom. Tanks 3 and 2 contain partially exhausted black ash, and tank 1 completely exhausted black ash (tank waste). The overflow pipe between 3 and 4 is opened, and a pump connected with 1, which pumps the liquor over into 2. It flows from 2 to 3, from 3 to 4, until 4 is full. Tank 1 is now cut off, emptied, cleaned, and a fresh supply of black ash put in. While this is going on, fresh water is flowing into 2, and sufficiently saturated liquor flowing away from 4 by the outside overflow pipe. 4 is now connected with 1. The liquor is pumped out of 2 into 3, flows from 3 to 4, from 4 to 1. When 2 is empty of liquor it is in the same way cleaned out, and a fresh charge put in, and so the lixiviation is kept continuous, strong soda solution running off at one end, and exhausted tank waste being removed at the other.

LOADSTONE. A name applied to those specimens of the mineral magnetite (*q.v.*) which are magnetic with polarity, and are thus capable of orientating themselves when freely suspended. All specimens of magnetite are readily attracted by a magnet, but only few exhibit polarity in their natural state. Such specimens are found in exposed situations in mountainous districts, *e.g.* in the Ural and Harz Mountains, where they have no doubt been magnetised by the electric discharges of lightning. Such stones were at an early period mounted in iron frames and used as natural magnets. For historical details, *see* William Gilbert, De Magnete (1600; English edition with notes by S. P. Thompson, 1900). S. P. Thompson on Petrus Peregrinus's Epistola de Magnete (Proc. British Acad. 1907, vol. ii.).

L. J. S.

LOBELACRIN *v.* LOBELIA.

LOBELIA. *Indian tobacco.* (*Lobélie enflée* Fr.; *Lobeliakraut*, Ger.) The official lobelia, *Lobelia inflata*, was described by Linnæus in 1741 (Acta Soc. Reg. Scient. Upsal. 1746) from specimens cultivated by himself, but he does not ascribe to it any medicinal properties. It is an annual herbaceous, somewhat pubescent plant, attaining a height of from 9 to 18 inches, with inconspicuous bluish racemose inflorescence. It is indigenous to the eastern portions of North America, and is cultivated in European gardens Flück. a. Hanb. 399; Bentl. a. Trim. 162). According to J. U. and C. G. Lloyd (Pharm. J. [iii.] 17, 566), the first to employ lobelia in medicine was Thomson, an American herbalist of some notoriety about the end of the 18th century. The Indians, although they made use of the great lobelia, *L. syphilitica* (Linn.), were not acquainted with the *L. inflata*, as has been commonly supposed and as one of its names would imply. Gradually the drug has come into favour as an article of *materia medica*, and it now finds a place in the pharmacopœias. The herb should be gathered when, after flowering, some of the capsules have become inflated. In physiological action, lobelia resembles tobacco. It is an acrid, narcotic poison, but in small doses is expectorant or emetic, and is largely employed in diseases of the respiratory organs. The seed is more active than the herb, but the latter is almost exclusively employed in medicine. It is generally administered in the form of tincture, made with proof spirit or a mixture of alcohol and ether.

Much uncertainty still exists as to the active constituents of lobelia. Colhoun investigated the plant in 1834 (J. Pharm. Chim. [ii.] 20, 545), but the first definite results were obtained by Procter a few years later (Amer. J. Pharm. 9, 98; 13, 1). The seed was exhausted with spirit containing a little acetic acid, the solution evaporated, and the residue mixed with magnesia and extracted with ether. On evaporating the ether an acrid alkaloidal liquid, *lobeline*, remained, which, by conversion into acetate and treatment with animal charcoal, was obtained in a purer form. Lobelia was further studied by Pereira (Mat. Med. 2nd ed. 2, 584), Reinsch (Pharm. J. [i.] 3, 128), Bastick (*ibid.* [i.] 10, 217), F. F. Mayer (Amer. J. Pharm. 37, 209), Richardson (*ibid.* [iv.] 2, 293), and, more recently, by Lewis (Pharm. J. [iii.] 8, 561), Dragendorff and Rosen (Chem. Zentr. 1886, 873), J. U. and C. G. Lloyd (Pharm. J. [iii.] 17, 566, 686, 1037; 18, 135), and Dresser (Arch. exp. Path. u. Pharm. 26, 237). To obtain lobeline, Bastick only slightly modifies the process of Procter; Richardson precipitates an infusion of the drug with potassium mercuric iodide; Lewis mixes the drug with animal charcoal, extracts with water containing acetic acid, and substitutes, at the end of the process, amyl alcohol for the ether used by Procter. The lobeline of Lewis is of the consistence of honey. Dragendorff and Rosen obtain two active compounds, lobeline and a crystalline substance soluble in chloroform, but difficultly soluble in water. J. U. and C. G. Lloyd also find associated with lobeline—which, however, they describe as an amorphous solid—a second compound *inflatin*, which is crystalline. Taking care to avoid heat, and the contact of free alkaloid with alkalis, these observers follow a process similar to that of

Procter. Ether and ammonia are used to separate the alkaloid from its combination, instead of ether and magnesia. The crude product is purified by successive conversion into a salt in aqueous solution, and treatment with ether and ammonia. Finally, the ether is acidified and evaporated, leaving a residue partly amorphous and partly crystalline. From this residue carbon disulphide separates the crystalline portion, inflatin, leaving amorphous lobeline acetate undissolved. The latter, on standing, loses a little adhering volatile oil, and is purified by the method already described (*cf.* Monatsh. 11, 131).

Lobeline, according to J. U. and C. G. Lloyd, is an amorphous powder or glassy residue, without colour or odour, and extremely active, a very small quantity of its solution applied to the tongue causing immediate vomiting. It is soluble in alcohol, chloroform, ether, benzene, carbon disulphide, and slightly soluble in water. In a pure state it is very stable. Oxidised by permanganate it yields benzoic acid (Paschkis and Smita, Monatsh. 11, 131). Salts of lobeline are soluble in water or alcohol, but, excepting the acetate, not in carbon disulphide. The aqueous solution is precipitated by alkalis and alkaloidal reagents. According to the experiments of Dresser, the only active constituent in lobelia is lobeline. Inflatin, which may also be prepared direct from the herb or seeds, is odourless and tasteless. It possesses neither acid nor basic properties. It melts at 107°, is insoluble in water, but soluble in carbon disulphide, benzene, chloroform, ether, or alcohol.

Lobeline occurs in the plant, according to most observers, in combination with *lobelic acid*, a compound first obtained by Procter. It is precipitated from an aqueous decoction of lobelia by copper sulphate, and separated from its copper compound by treatment with sulphuretted hydrogen and extraction with ether. When purified, it consists, according to Lewis, of small acicular crystals, non-volatile, and soluble in water, alcohol, or ether. The substance described by Enders (Flück. a. Hanb. 400), which appeared to be a glucoside, 'lobelacrin,' Lewis regards as lobeline lobelate. J. U. and C. G. Lloyd, however, consider it a mixture of several of the plant's constituents. The 'lobeliin' of Reinsch is also an indefinite compound.

Lobelia contains traces of a *concrete volatile oil*, the 'lobelianin' of Pereira. It is crystalline, and melts at 71° (Procter, Reinsch, Lewis, Lloyd). Procter found in the seed 30 p.c. of a drying *fixed oil*, and this has to be removed, usually by means of a solvent, before it can be used for the preparation of the alkaloid.

For the physiological action of lobeline *v.* Edmunds (Amer. J. Physiol. 11, 79). A. S.

LOBELIANIN, LOBELIC ACID, LOBELIIN, LOBELINE *v.* Lobelia.

LOGANETIN, LOGANIN *v.* Nux vomica.

LOGWOOD. Logwood or Campeachy wood is one of the most important of all dyestuffs, and at the present time is very largely employed. Although for a long time it has successfully competed with the artificial colouring matters, its supremacy as a cotton dye has latterly been affected to a considerable extent by the introduction of the sulphide blacks.

Logwood appears to have been first imported into Europe by the Spaniards shortly after the discovery of America, and has been cultivated in Jamaica from the year 1715. In the time of Elizabeth, its employment as a dye was prohibited by Act of Parliament, and large quantities of the wood were burned, because it was said to produce fugitive colours.

It is derived from the *Hæmatoxylon campechianum* (Linn.), a tree which belongs to the family *Cæsalpiniacae*, and is a native of the warmer part of South America and some of the West Indian Islands. It also grows in the island of Mauritius, and trials indicate that this wood is of good quality (private communication).

Logwood usually comes into the market in large blocks weighing about 400 lbs.; these externally are of a deep brown colour, but internally have a much lighter tint. The best qualities come from Jamaica, Honduras, and St. Domingo, for the true Campeachy wood, at one time esteemed to be the best, is now practically exhausted.

The colouring principle of logwood, *hæmatoxylin*, was first isolated in a crystalline condition by Chevreul (Ann. Chim. Phys. [ii.] 82, 53, 126) who obtained it by extracting the wood with ether, evaporating the extract, and digesting the residue with alcohol. After distilling off the alcohol the residue was allowed to stand in contact with water, when the hæmatoxylin separated in crystals. It may also be prepared by similarly treating commercial logwood-extract which has been incorporated with a large quantity of sand (O. L. Erdmann, Annalen, 44, 292; J. pr. Chem. 26, 193; 36, 205; 75, 318). For this purpose ether containing water is preferable (Hesse, Annalen, 109, 332). It is, however, more easily obtained from the dark-coloured crusts which slowly separate when the concentrated logwood liquor stands for some time in a cool place. The crude mass is ground to a fine powder, extracted repeatedly with ether, the ethereal solution evaporated, and the residue left in contact with water, when dark-coloured crystals separate, which by recrystallisation from water containing a small quantity of sodium bisulphite, may be obtained colourless (W. H. Perkin and Yates, Chem. Soc. Trans. 1902, 81, 236).

Pure hæmatoxylin crystallises in prisms with $3H_2O$, and is sparingly soluble in cold, readily so in hot water. Its aqueous solution is coloured purple with alkalis, and this on exposure to air eventually assumes a brown tint. Hæmatoxylin is dextro-rotatory, a 1 p.c. aqueous solution having a rotation of 1·85 in a 200 mm. tube. It readily reduces salts of silver and gold, gives with alum a rose-red colouration, with iron alum a violet-black precipitate, and with neutral and basic lead acetates at first a colourless and then a blue deposit which darkens by air oxidation.

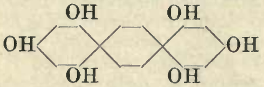
O. L. Erdmann (*l.c.*) was the first to submit hæmatoxylin to analysis, and proposed the formula $C_{40}H_{17}O_5$, which he subsequently altered to $C_{16}H_{14}O_6$. This latter formula was confirmed by Hesse (*l.c.*), and at the present day is accepted as correct.

By fusion with alkali, hæmatoxylin yields pyrogallol (Reim, Ber. 1871, 4, 331), and according to E. Erdmann and Schultz (Annalen, 216, 234) also formic acid. R. Meyer (Ber. 1879, 12, 1392) submitted hæmatoxylin to destructive distillation and considered that in this manner not only pyrogallol but also resorcinol is produced. According, however, to W. H. Perkin and Gilbody (Chem. Soc. Trans. 1902, 81, 245), no resorcinol is thus obtained.

Reim acetylated hæmatoxylin with acetyl chloride and prepared a substance which appeared to be the hexa-acetyl derivative

$$C_{16}H_8O_6(C_2H_3O)_6,$$

and as a result suggested the following constitution for this colouring principle:



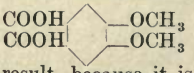
E. Erdmann and Schultz (Annalen, 1883, 216, 234) re-examined Reim's compound and showed that this was in reality a *pentaacetylhæmatoxylin* $C_{16}H_9O_6(C_2H_3O)_5$, m.p. 165°–166°, and that hæmatoxylin therefore contains five hydroxyl groups. This result was confirmed by the work of Herzig (Monatsh. 1894, 15, 143) who, by the action of sodium methoxide, and methyl iodide on hæmatoxylin, obtained the *tetramethyl derivative* $C_{16}H_{10}O_2(OMe)_4$, m.p. 139°–140°, a substance which still contains a hydroxyl group since on treatment with acetic anhydride it yields acetyltetramethylhæmatoxylin $C_{16}H_9O_2(OMe)_4(C_2H_3O)$, m.p. 178°–180°. It was thus shown that hæmatoxylin like brazilin, contains an alcoholic hydroxyl group which is not methylated by means of methyl iodide and sodium methoxide under the usual conditions, and indeed it has long been considered probable that these two colouring matters are closely allied in constitution (Liebermann, Ber. 1876, 9, 1883; compare also Hummel and A. G. Perkin, Chem. Soc. Trans. 1882, 41, 373).

The following derivatives of hæmatoxylin have also been prepared: *Pentamethylhæmatoxylin* $C_{16}H_9O(OCH_3)_5$ plates, m.p. 144°–147° (Herzig); *dibromhæmatoxylin* $C_{16}H_{12}Br_2O_6$ (Dralle, Ber. 1884, 17, 373); *penta-acetylbromhæmatoxylin* $C_{16}H_8BrO_6(C_2H_3O)_5$, needles, m.p. 110° (Buchka, *ibid.* 1884, 17, 685); *penta-acetyltetrabromhæmatoxylin* $C_{16}H_5Br_4O_6(C_2H_3O)_5$ (Dralle); and *hæmatoxylinphthalein* $C_{40}H_{30}O_{14}$ (Letts, Ber. 1879, 12, 1652).

Our main knowledge of the chemistry of hæmatoxylin and the fact that it is in reality hydroxybrazilin is due to the elaborate researches of W. H. Perkin and his pupils, and their results have arisen mainly from a study of the oxidation products of hæmatoxylin tetramethylether.

According to Perkin (Chem. Soc. Trans. 1902, 81, 1059), tetramethylhæmatoxylin is most readily prepared by treating the solution of hæmatoxylin in alcoholic potash with methyl sulphate, a method which had previously been found serviceable by Kostanecki and Lampe (Ber. 1902, 35, 1669) for the production of trimethylbrazilin from brazilin.

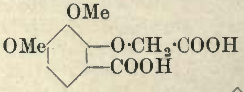
When tetramethylhæmatoxylin is oxidised with potassium permanganate (Perkin and Yates, *l.c.*), it yields *m-hemipinic acid*



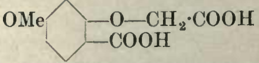
an important result, because it is thus certain that hæmatoxylin like brazilin (Gilbody, Perkin, and Yates, Chem. Soc. Trans. 1901, 79, 1400) contains a catechol nucleus. Consequently, whereas in the molecule of brazilin a resorcinol and a catechol nucleus occur, in hæmatoxylin pyrogallol and catechol groups are present.

In addition to *m*-hemipinic acid, large quantities of a second acid $C_{11}H_{12}O_7$, m.p. 215°, are produced. This is *2-carboxy-5:6-dimethoxyphenoxyacetic acid* (I.)

I.



II.



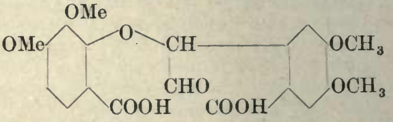
analogous to the *2-carboxy-5-methoxyphenoxyacetic acid* (II.), which was obtained in a similar manner from brazilin trimethyl ether (*see* Brazilin).

Finally, from the product of the oxidation a third compound *hæmatoxylinic acid* $C_{20}H_{20}O_{10}$, m.p. 180°, was isolated. This on reduction with sodium amalgam is converted quantitatively into an acid $C_{20}H_{20}O_9$, which is a monobasic lactonic acid, and it is therefore evident that the latter is produced in two stages, thus:

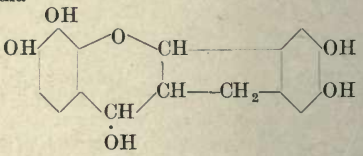
$$\underset{\text{Hæmatoxylinic acid.}}{C_{20}H_{20}O_{10}}+2H=\underset{\text{Dihydrohæmatoxylinic acid.}}{C_{20}H_{22}O_{10}}$$

$$C_{20}H_{22}O_{10}-H_2O=\underset{\text{Lactone of dihydro-hæmatoxylinic acid.}}{C_{20}H_{20}O_9}$$

The constitution at first assigned to hæmatoxylinic acid by these authors was as follows:

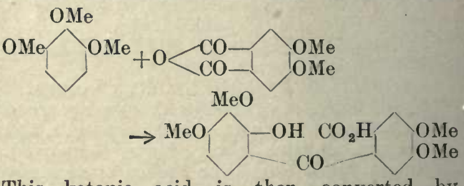


but this, and the corresponding hæmatoxylin formula



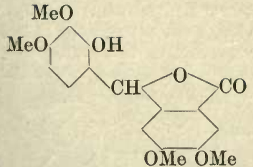
were subsequently modified, as the result of the synthesis of the lactone of the dihydro-hæmatoxylinic acid referred to above (Perkin and Robinson, Chem. Soc. Trans. 1908, 93, 492).

When aluminium chloride reacts with a mixture of pyrogallol trimethylether and *m*-hemipinic anhydride, *2′-hydroxy-3′:4′:4:5-tetramethoxybenzoylbenzoic acid* is produced:

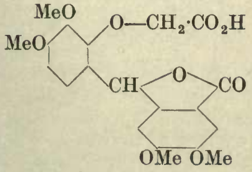


This ketonic acid is then converted by reduction with sodium amalgam into *2-m-meconyl-5:6-methoxyphenol* (1), which by treatment with chloracetic acid and sodium hydroxide gives the lactone of dihydrohæmatoxylinic acid (2).

1.

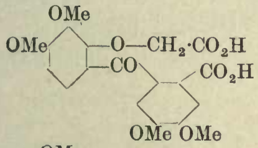


2.

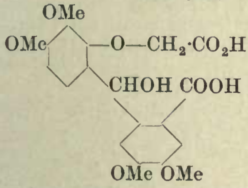


Consequently, the formulæ of *hæmatoxylinic acid* (3) and of *dihydrohæmatoxylinic acid* (4) are thus represented:

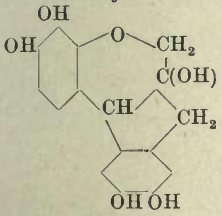
3.



4.

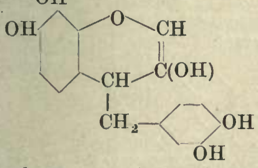


From these facts the constitution of hæmatoxylin itself naturally follows.

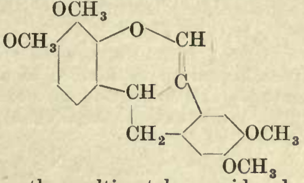


and this is identical with that which Pfeiffer (Chem. Zeit. 1904, 3, 380) from theoretical considerations suggested as possible.

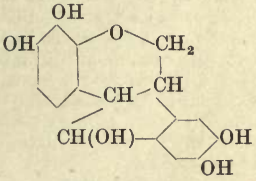
Other constitutional formulæ have been assigned to hæmatoxylin, of which that of Bollina, Kostanecki, and Tambor (Ber. 1902, 35, 1678), analogous to the brazilin formula of Feuerstein and Kostanecki (Ber. 1899, 32, 1024) is of interest:



It was, however, evident that such an expression does not account for the production of *m*-hemipinic acid or 2-carboxy-5:6-dimethoxyphenoxyacetic acid by the oxidation of hæmatoxylin tetramethyl ether. On the other hand, Kostanecki and Lampe (Ber. 1902, 35, 1667) at first suggested that previous to the degradation of the methyl ether by oxidation with permanganate an internal linkage is produced, with production of the following compound:



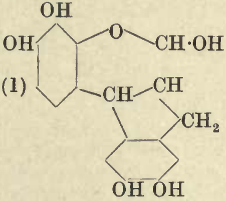
These authors ultimately considered, as W. H. Perkin contended, that a *m*-hemipinic residue is contained in hæmatoxylin tetramethyl ether, and as a result propose the following modification of their formula for this colouring matter:



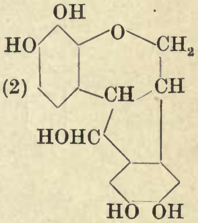
Hæmatoxylin.

Again, Herzig and Pollak (Monatsh. 1902, 23, 165), in a criticism of the earlier formula of Gilbody, Perkin, and Yates (*l.c.*), suggested two possible constitutions for brazilin, the second of which is identical with that of Kostanecki and Lampe (see above) and which applied to hæmatoxylin, are thus represented:

(1)



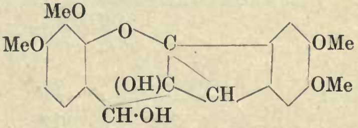
(2)



These formulæ of Kostanecki and Lampe and Herzig and Pollak cannot, however, be correct, as they do not account for the formation of hæmatoxylinic acid by the oxidation of tetramethylhæmatoxylin with permanganate (Gilbody, Perkin, and Yates, *l.c.*).

Herzig (Monatsh. 16, 906) submitted acetyl tetramethylhæmatoxylin to oxidation with chromic acid and obtained a new product, which on hydrolysis gave *tetramethyldehydrohæmatoxylin* $C_{16}H_5\cdot O(OMe)_4OH$. This latter, on acetylation, yielded *acetyltetramethyldehydrohæmatoxylin* $C_{16}H_5O(OMe)_4(OC_2H_3O)$ and by methylation *pentamethyldehydrohæmatoxylin.*

W. H. Perkin (Chem. Soc. Trans. 1902, 81, 1057) oxidised tetramethylhæmatoxylin with chromic acid, and obtained a substance *tetramethylhæmatoxylone* $C_{16}H_6O(OMe)_4(OH)_2$, corresponding in all its reactions with trimethylbrazilone. For this, at that time, the formula

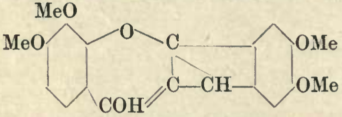


was proposed. In addition to this compound, 2-*carboxy*-5-6-*dimethoxyphenoxyacetic acid* and *m*-hemipinic acid were also produced during the oxidation. When digested with acetic anhydride, tetramethylhæmatoxylone gives *acetylanhydrotetramethylhæmatoxylone*

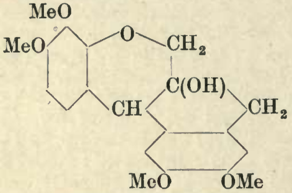
$C_{16}H_5O(OMe)_4OC_2H_3O$,

evidently identical with Herzig's acetyltetramethyldehydrohæmatoxylin referred to above.

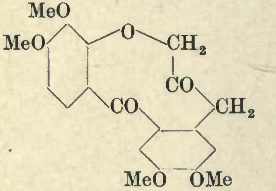
By hydrolysis, this compound gave anhydrotetramethylhæmatoxylone $C_{16}H_5O(OMe)_4OH$



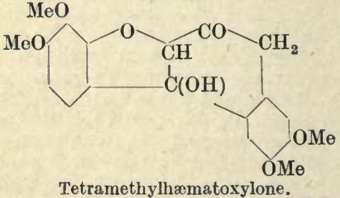
In a later paper, Perkin and Robinson (Chem. Soc. Trans. 1908, 498) discarded these expressions and assigned to tetramethylhæmatoxylone the constitution given below. These authors consider that during the oxidation of tetramethylhæmatoxylin with chromic acid, a destruction of the central linkage occurs, and the unstable diketone which is thus formed undergoes aldol condensation with the production of tetramethylhæmatoxylone.



Tetramethylhæmatoxylin.



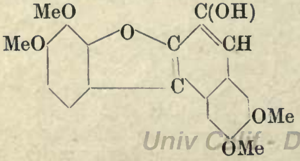
Diketone.



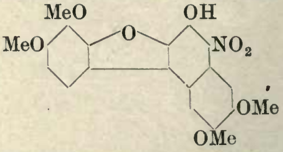
Tetramethylhæmatoxylone.

This formula indicates that tetramethylhæmatoxylone is a derivative both of coumaran and tetrahydronaphthalene.

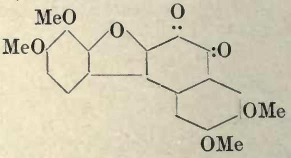
The formation of anhydrohæmatoxylone by means of acetic anhydride (*l.c.*) is due to the elimination of water from the aldol grouping in tetramethylhæmatoxylone, and the constitution thus given to this substance represents it as a derivative of β-naphthol, with which indeed it has many properties in common.



When acetylanhydrotetramethylhæmatoxylone is treated with nitric acid it readily reacts with the formation of the mononitro compound (Perkin and Robinson, *ibid.* 1909, 384).



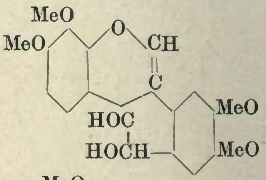
and from this substance by reduction with zinc dust and hydrochloric acid the corresponding amino derivative is produced. This, when oxidised by ferric chloride, yields *tetramethoxy-a-brazanquinone* (compare Kostanecki and Rost, *l.c.*):



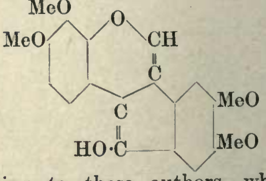
That this substance is an ortho-quinone is shown by its behaviour with *o*-tolylenediamine with which it condenses with formation of a characteristic quinoxaline. On reduction, the quinone is converted into the corresponding *dihydroxy* derivative.

Kostanecki and Rost (Ber. 1903, 36, 2202), on the other hand, proposed for the (1) tetramethylhæmatoxylone, and (2) anhydrotetramethylhæmatoxylone of Perkin the following expressions which harmonised with their suggested constitution for hæmatoxylin (*l.c.*):

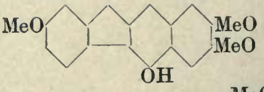
(1)



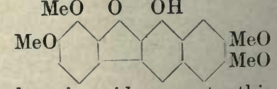
(2)



According to these authors, when tetramethylhæmatoxylone is treated with alcoholic sulphuric acid, a new compound (1′ or 4′) *hydroxy*-3 : 4 : 6′ : 7′-*tetramethoxybrazan* is formed, which is represented by one or other of the annexed formulæ:

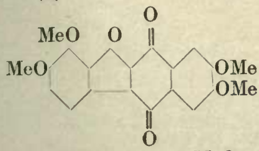


or

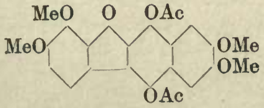


Oxidation with chromic acid converts this substance into 3 : 4 : 6′ : 7′-*tetramethoxybrazanquinone* (1), which by reduction and acetylation yields 3 : 4 : 6′ : 7′-*tetramethoxy* (1′ : 4′) *diacetoxybrazan* (2):

(1)

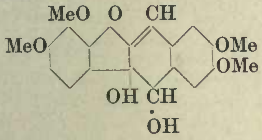


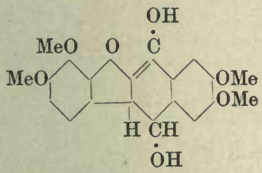
(2)



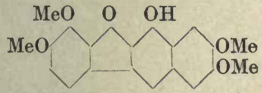
When distilled with zinc dust, both hydroxytetramethoxybrazan and tetramethoxybrazanquinone yield *naphthalene*.

Herzig and Pollak (Ber. 1904, 37, 631) also found that cold concentrated sulphuric acid converts tetramethylhæmatoxylone into an isomeric compound *ψ-tetramethylhæmatoxylone*, and suggested the following formulæ as applicable to this substance.

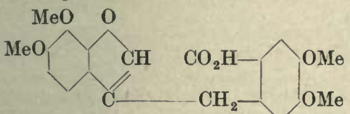




This, by loss of water, gives *β-anhydrotetramethylhæmatoxylone*, which is identical with Kostanecki and Rosts' hydroxytetramethoxybrazan:

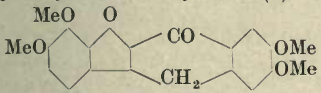


Perkin and Robinson (*l.c.*), as the result of a study of the work of Herzig and Pollak, have, however, shown that ψ-tetramethylhæmatoxyone is in reality a monobasic acid, and possesses the following constitution:

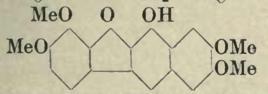


This, by elimination of water, passes into the compound (1) and by intramolecular change gives hydroxytetramethoxybrazan (2):

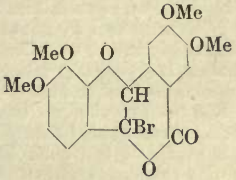
(1)



(2)



When ψ-tetramethylhæmatoxylone is treated with potassium hypobromite, a colourless precipitate soon separates. This crystallises in almost colourless prisms or needles, and possess the constitution of a *tetramethoxycumarono*-iso-*coumarinhydrobromide*:



For the theoretical considerations involved in the production of this interesting substance the original paper should be consulted.

Hæmatein. When oxidised under suitable conditions, hæmatoxylin readily passes into the colouring matter hæmatein, according to the equation $C_{16}H_{14}O_6 + O = C_{16}H_{12}O_6 + H_2O$.

Hæmatein was first produced by O. L. Erdmann (*l.c.*) by passing air through an ammoniacal solution of hæmatoxylin, and subsequently acidifying with acetic acid.

Erdmann and Schultz (*l.c.*), who adopted a somewhat similar procedure, succeeded in isolating hæmatein in leaflets which possessed a metallic lustre. Reim, on the other hand (Ber. 1871, 4, 331), treated an ethereal solution of hæmatoxylin with a little concentrated nitric acid.

By extracting 'aged' logwood with ether, Halberstadt and Reis (Ber. 1881, 14, 611) obtained 1 p.c. of a very pure crystalline hæmatein.

Hummel and Perkin (Chem. Soc. Trans. 1882, 41, 373) exposed an ammoniacal solution of logwood extract to the air for 2 or 3 days. The precipitated ammonia compound of hæmatein was collected, dissolved in water, dilute acetic acid added, and the mixture digested on the water-bath to dissolve as much as possible of the suspended amorphous hæmatein. The clear liquid after partial evaporation deposited crystals of the colouring matter, possessing a yellowish-green iridescence, and having the composition $C_{16}H_{12}O_6$.

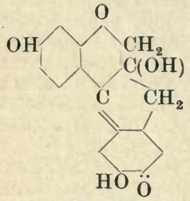
According to Mayer (Chem. Zentr. 1904, 1, 228), hæmatein may also be prepared by oxidising hæmatoxylin in aqueous solution with sodium iodate.

Engels, Perkin, and Robinson (Chem. Soc. Trans. 1908, 93, 1140) passed air for 6 hours through a solution of 15 grams of hæmatoxylin, dissolved in a solution of 15 c.c. of concentrated ammonia in 150 c.c. of water. The product of the oxidation was added in a thin stream to dilute acetic acid (250 c.c. of 10 p.c.) heated on the water-bath, when hæmatein separated in crystals.

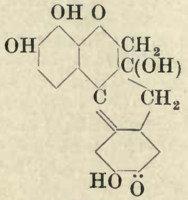
Hæmatein is very sparingly soluble in water and the usual solvents. Alkalis dissolve it readily; ammonia dissolves it with a rich brown-violet colour, whilst its strong alkaline solution has a rich purplish-blue colour. On exposure to air the colour of these alkaline solutions gradually becomes red and finally brown, the colouring matter being destroyed. By addition of potassium acetate to the boiling alcoholic solution of hæmatein, the monopotassium salt $C_{16}H_{11}O_6K$ is deposited (A. G. Perkin, Chem. Soc. Trans. 1899, 75, 443).

Sulphurous acid or sodium bisulphite solution converts hæmatein into a colourless addition product, readily soluble in water but no reduction hereby appears to occur, as on boiling the solution or by addition of acid, hæmatein is precipitated. With zinc and hydrochloric acid or with stannous chloride and caustic soda, a solution of hæmatein is decolourised, but on standing the liquid regains its former tint.

It has long been considered that hæmatein is hydroxybrazilein and this has now been clearly proved by a study of the behaviour of these compounds with reagents under similar circumstances. This relationship is at once evident from a comparison of the following formulæ (Engels, Perkin, and Robinson):



Brazilein.

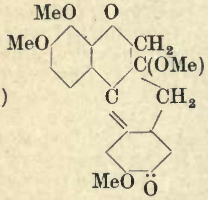


Hæmatein.

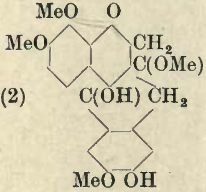
When hæmatein is methylated by means of alkali and methyl sulphate, the product consists essentially of tetramethylhæmatein and pentamethyldihydrohæmateinol.

Tetramethylhæmatein (1) crystallises in amber prisms, and when digested with dilute potassium hydroxide is converted by the addition of water into *tetramethyldihydrohæmateinol* (2) yellow prisms:

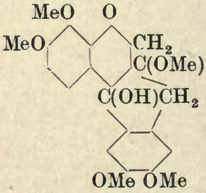
(1)



(2)



Pentamethyldihydrohæmateinol



the second product of the reaction crystallises in yellow plates, and is also produced when tetramethyldihydrohæmateinol is methylated with methyl sulphate and alkali.

In the year 1882, Hummel and A. G. Perkin (Chem. Soc. Trans. 41, 367) observed that hæmatein and also brazilein are converted by the action of mineral acids into orange or red salts, from which the original colouring matters could not be regenerated.

When hæmatein is dissolved in cold sulphuric acid, a reddish-brown solution is produced from which, by cautious addition of acetic acid, minute orange coloured prisms of *acid isohæmateinsulphate* $C_{16}H_{12}O_5SO_4$ are deposited. The reaction may be represented thus:

$$C_{16}H_{12}O_6+H_2SO_4=C_{16}H_{12}O_5SO_4+H_2O.$$

This substance, when left in contact with 80 p.c. alcohol, is gradually transformed, with loss of sulphuric acid, into a new compound crystallising in orange-red plates possessing a strong metallic lustre and to which the formula

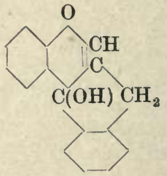
$$(C_{16}H_{12}O_6)_2C_{16}H_{12}O_5SO_4$$

was assigned. On the other hand, hydrochloric and hydrobromic acids in sealed tubes at 100° convert hæmatein respectively, into *isohæmatein chlorhydrin* $C_{16}H_{11}O_5{\cdot}Cl$ and *isohæmatein bromhydrin* $C_{16}H_{11}O_5Br$, which crystallise in orange red needles.

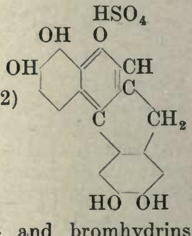
If to an aqueous solution of *iso*hæmatein chlorhydrin or bromhydrin silver hydroxide is added to remove the halogen, a solution of *isohæmatein* is obtained, which on evaporation leaves this substance as an amorphous mass possessing a green metallic lustre. *Iso*hæmatein and its salts dissolve in solutions of the alkaline hydroxides with a red-violet colour which is easily distinguished from the corresponding blue-violet solution of hæmatein; moreover the dyeing properties of these compounds and hæmatein differ considerably. Thus the *iso*hæmatein derivatives give, on cotton mordanted with alumina, a dull red inclining to chocolate, with strong iron a black, and with mixed alumina and iron a full chocolate. Again the tinctorial power of these compounds is much greater than that of the original hæmatein, and the colours are much faster.

As the result of the investigation of a large number of pyranol salts (Perkin, Robinson, and Turner, Chem. Soc. Trans. 1908, 93, 1085), it seems certain that these hæmatein salts are derivatives of 4 : 3-*indenobenzopyranol* (1), and that *iso*hæmatein sulphate possesses the constitution (2):

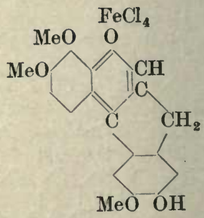
(1)



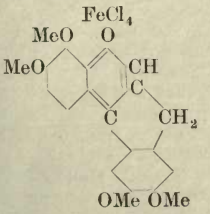
(2)



*Iso*hæmatein chlor- and bromhydrins are formulated similarly. Thus from tetramethylhæmatein, Engels, Perkin, and Robinson (*l.c.*) have prepared *5′-hydroxy*-7 : 8 : *4′-trimethoxy*-4 : 3-*indenobenzopyranol* (1 : 4) *anhydroferrichloride*:



which crystallises from acetic acid in well-defined elongated prisms. Pentamethyldihydrohæmateinol, on the other hand, gives 7 : 8 : 4′ : 5′-*tetramethoxy*-4 : 3-*indenobenzopyranol* (1 : 4) *anhydroferrichloride.*



Before being used by the dyer, logwood is reduced to chips or powder, and these products are known as ‘ chipped,’ ‘ rasped,’ or ‘ ground ’ wood. When first cut down the wood has a pale yellow colour and contains only hæmatoxylin, but during transport or storage this colour gradually deepens owing to a surface oxidation of the hæmatoxylin into hæmatein. Formerly, and even to some extent at the present time, it was the practice to submit the chipped or rasped logwood to what is known as the ‘ ageing ’ process, in order to facilitate the hæmatein formation. This consists in wetting the wood thoroughly with water, then forming it into heaps, 4 to 5 feet high, in large airy chambers. Very soon the mass begins to ferment, which is indicated by a rise of its internal temperature, the wood gradually darkens in colour, and during the operation the mixture is repeatedly turned over and remixed in order to avoid too vigorous a fermentation and to obtain an even result. Constant attention is necessary during this ‘ ageing ’ process, for if the reaction is allowed to proceed too far, a portion of the colouring matter is destroyed and ‘ burnt ’ or ‘ over-aged ’ wood is produced. In order to expedite this operation, the use of various oxidising agents has been suggested ; a sprinkling of the wood with ammonia has been said to exercise a beneficial result; but, on the other hand, such processes are best avoided, for it is difficult under these circumstances to control the reaction and prevent an over-oxidation.

Latterly this ageing operation has been less in vogue, not only on account of the increased employment of logwood extract, but because it is now recognised that where the mordant employed for dyeing purposes can exert an oxidising action, this preliminary treatment is unnecessary. Formerly, logwood blacks on wool were produced by means of an iron mordant, but this is now largely replaced by the use of potassium dichromate, which provides a mordant possessing the power of converting at least a portion of the hæmatoxylin into hæmatein.

Logwood extract is now prepared in enormous quantity not only in this country but also in Jamaica in the neighbourhood of the logwood plantations, and in the latter case an economy is naturally effected in the carriage of some varieties of the extract rather than that of the more bulky wood to this and other countries. Logwood extract is almost invariably prepared from the ‘ unaged ’ wood, because whereas hæmatoxylin is readily soluble in water, hæmatein is not. On this account, an aged wood is difficult to exhaust. For the manufacture on the large scale, two processes are in vogue known respectively as the ‘ American ’ and ‘ French ’ methods. These differ merely in the manner in which the wood is lixiviated, for this is carried out by the French process in open pans with warm or boiling water, whereas in the American process, closed vessels are used in which steam at from 15 to 30 lbs. pressure is employed. In both cases the liquid is afterwards concentrated, preferably in vacuum pans, and the product is sold at about 15°Tw. as *logwood liquor*, at 51°Tw. as *logwood extract*, or in the solid condition as *solid logwood extract.* As a rule, it is considered that the extract made at the lower temperature gives the brighter shade.

Certain processes are in use for the ‘ ageing ’ of ‘ logwood liquor,’ that is the conversion of the dissolved hæmatoxylin into hæmatein. For this purpose the following methods have been suggested : (*a*) treat the logwood liquor with bleaching powder solution ; (*b*) half neutralise with alkali or ammonia and blow air or oxygen through the liquid ; (*c*) employ air or oxygen for this purpose without the addition of alkali ; (*d*) boil with manganese dioxide (Weldon mud) and filter. Interesting also in this respect is the patented process of Haak (Chem. Zentr. 1905, ii. 867), who treats the extract with sodium nitrite.

A very important product somewhat recently introduced is the so-called crystalline hæmatein paste, which is a treacly extract containing in suspension minute crystals of hæmatein. The details of the preparation of this material, which appears to have been first introduced from Jamaica, although now also manufactured in this country, are kept secret. For experimental purposes, this paste may be employed as the source of a comparatively pure hæmatein, which can be isolated from it by dilution with glacial acetic acid and subsequent filtration (private communication).

Logwood and its extracts are enormously employed for the dyeing of blacks on silk, wool, and cotton, chiefly in conjunction with iron and chromium mordants. It also enters into the composition of numerous compound shades.

Bastard logwood. During the past few years, the growers of logwood in Jamaica have been greatly disturbed by the apparent increase on their properties of an unmerchantable variety of the tree known as ‘ bastard ’ logwood. Bastard logwood is practically devoid of hæmatoxylin, but contains instead a yellowish-green pigment which, when admixed with the commercial extract, reduces its characteristic tinctorial properties. Chips of the bastard logwood present a yellow, pale pink, white, or even chocolate coloured surface instead of the dark red or purple bronze tinted colour of the best Jamaican or Mexican logwoods of commerce.

So similar are the trees of the ‘ true ’ and the ‘ bastard ’ logwood, that it is frequently impossible to decide whether a tree is really a ‘ mulatto ’ or not. When first cut a bastard tree is frequently dark enough internally to indicate that it is a good red-wood tree, but instead of darkening with age, as all the best wood does, it remains the same colour or becomes lighter rather than darker.

Chemical tests readily distinguish between the red and bastard wood, for whereas alkaline solutions turn an extract of true logwood a purple colour, with a bastard extract the shade of yellow is merely deepened. Again mineral acids turn aqueous extracts of true logwood orange to bright red, whereas a bastard extract is not thereby affected.

Dyeing trials, employing stripe mordanted calico, are also serviceable because, in the case of the bastard variety, the aluminium mordant remains practically undyed. A. G. P.

LOKAO, a green dyestuff of Chinese origin, is, or rather was, since it has been supplanted by artificial colouring matters, met with in commerce in the form of thin laminæ of a dark bluish or bluish-green colour. Though formerly employed to some extent in Europe, it does not appear, owing to its extremely expensive nature, to have been extensively used. According to Crookes (Dyeing and Calico Printing, 429), lokao contains from 21·5 to 33 p.c. of ash, 9·3 p.c. of water, and 61·7 p.c. of colouring matter. It is insoluble in water, and the usual solvents, but dissolves in sulphuric acid with a red-brown colouration, and also in alkalis, but the solution thus obtained gradually acquires a brown tint.

According to Helot (Crookes, *l.c.*) and others, lokao requires for its preparation two distinct plants, the *Rhamnus dahurica* (Pall.) (hong. pi. lo. chou) and the *R. tinctoria* (Walldst. & Kit.) (pé. pi. lo. chou), the first of which is said to yield a deep and fast colour, whilst from the latter a weak but brilliant colour can be obtained. According to Rupe (Die Chemie der natürlichen Farbstoffe, 1900), the plant bark is extracted with hot water, the extract allowed to stand overnight, filtered, and then treated with potassium carbonate or milk of lime. Cotton yarn is immersed in this mixture, subsequently withdrawn and spread out in meadows overnight and a portion of the daytime, and the operation repeated ten or twenty times. The colouring matter is removed by rubbing the yarn with the hands in cold water, and the precipitate, which settles to the bottom of the receptacle, is washed by decantation, spread on paper and dried in the shade (*cp.* also Crookes, *l.c.*).

According to Cloez and Guignet (J. 1872, 1068) lokao or Chinese green is, in reality, a lake, and by treatment with ammonium carbonate is converted into the ammonium salt of the colouring matter *lokain* $NH_4{\cdot}C_{28}H_{33}O_{17}$. By the action of dilute sulphuric acid lokain is hydrolysed with formation of *lokaetin* $C_{18}H_{16}O_{10}$. glucose, and a soluble compound which is precipitated by basic lead acetate.

Kayser (Ber. 1885, 18, 3417) extracted finely powdered Chinese green with concentrated ammonium carbonate solution, added alcohol to the clear liquid, and thus obtained a precipitate of the crude ammonium salt of the colouring matter which he termed *lokaonic acid.* This was collected, extracted with ammonium carbonate, the solution precipitated by alcohol, and the operation repeated several times, the product being finally dissolved in water and the liquid evaporated to crystallisation with the addition of a little ammonia. Thus prepared the *diammonium* salt of lokaonic acid $C_{42}H_{46}O_{27}(NH_4)_2$ consists of small crystals possessing a bronzy lustre, which at 40°C. commences to lose ammonia, and at 100° gives the mono-ammonium salt $C_{42}H_{47}O_{27}(NH_4)$. The *potassium* salt

$$C_{42}H_{46}O_{27}K_2$$

separates in the form of a blue amorphous powder, when a concentrated aqueous solution of the diammonium salt is treated with alcoholic potash; whereas the *barium* salt $C_{42}H_{46}O_{27}Ba$, obtained by means of barium chloride, has a similar appearance, the lead salt $C_{42}H_{46}O_{27}Pb$ is a dark brown powder.

Lokaonic acid $C_{42}H_{48}O_{27}$, prepared by the decomposition of the diammonium salt with oxalic acid, consists of a bluish-black powder, which, when rubbed, develops a metallic lustre. It is insoluble in the usual solvents, but dissolves in solution of the alkaline hydroxides and ammonia with a pure blue tint. Treatment with sulphuretted hydrogen changes this to a blood-red colour, which passes to green on exposing the liquid to air. Digested with dilute sulphuric acid on the water-bath lokaonic acid is hydrolysed with formation of *lokanic acid* and a sugar *lokaose.*

Lokanic acid $C_{36}H_{36}O_{21}$ is a violet-black crystalline powder insoluble in water, alcohol, ether, and chloroform, but soluble in alkaline solutions with a violet-blue colouration.

The *ammonium* salt $C_{36}H_{35}O_{21}NH_4$, the *barium* salt $C_{36}H_{34}O_{21}Ba$, and the *lead* salt $C_{36}H_{34}O_{21}Pb$, are described by Kayser.

Hot 50 p.c. potassium hydroxide solution converts lokanic acid into *phloroglucinol* and *delokanic acid* $C_{15}H_9O_6$, which consists of a brown powder dissolved by dilute alkalis, whereas nitric acid gives with lokanic acid *nitrophloroglucinol.*

Lokaose $C_6H_{12}O_6$, obtained by the hydrolysis of lokaonic acid, crystallises in colourless needles, and is optically inactive.

According to Persoz, cotton can be dyed in a weak alkaline solution of lokao, and it behaves also as a vat dyestuff, for which purpose it may be reduced by faintly acid or alkaline stannous chloride. The colour thus obtained is blue, and can be converted into green by the subsequent employment of a yellow dyestuff.

In order to dye cotton a green with lokao, Persoz recommends a bath prepared by adding the pigment to a solution of soap, whereas for silk Michel obtained excellent results by employing lokao and alum solution in the presence of lime salts. For Chinese and other methods of employing this dyestuff, *see* Crookes (*l.c.*), and Rupe (*l.c.*). A. G. P.

LÖLLINGITE. A native ferric arsenide.

LONCHOCARPUS (*Lonchocarpus cyanescens*). The *Lonchocarpus cyanescens* (Benth.), a leguminous plant of the sub-order *Paplionaceæ*, is a woody climber from 10 to 14 feet long. The young leaves contain an indigo-yielding principle, and on this account the plant is employed by the tribes of Sierra Leone and the interior and those of Western Soudan as the source of a blue dye. In the former countries the young leaves are collected along with some more matured ones, roughly pounded and dried in the sun. In this state it is sent into the market as 'Gara,' and sold to the dyers. The natives of Western Soudan employ the young and tender buds, which are collected, pounded when quite raw, made into balls, and dried in the sun. For dyeing purposes the 'Gara' is covered with water, treated with potash and the bark of the *Morinda citrifolia* (Linn.), and left to ferment for some days. The cloth to be dyed is thrown into the vat, left there for some time, and dried in the sun. An examination of 'Gara' by Perkin indicated the presence of approximately 0·62 p.c. of indigotin (J. Soc. Chem. Ind. 1907, 389). Apparently also this plant is utilised in Northern Nigeria as a dyestuff in the form of a similar preparation to that described above, and for the manufacture of a crude indigo. A sample of this leaf product contained approximately 0·65 p.c. of indigotin, whereas in the indigo the presence of 21·47 p.c. of indigotin and 1·33 p.c. of indirubin was detected (Perkin, J. Soc. Chem. Ind. 1909, 353). The botanical examination of the former, and also of plant débris contained in the latter, by V. H. Blackman, indicated that they were derived from the *L. cyanescens*, or some closely related form. Rawson and Knecht (J. Soc. Dyers. 1888, 66) have described similar leaf and crude indigo products, which had been sent to this country by Sir. T. Goldie, Governor of the Royal Niger Co., and these respectively contained 0·51 p.c. of indigotin, and 39·12 p.c. of indigotin, together with 4·75 p.c. of indirubin. A more recent examination of the leaf fragments in Rawson and Knecht's samples has shown that these possessed the same structure as those of the *L. cyanescens* (Perkin, *l.c.*), and it thus appears evident that in Western Africa this plant is extensively employed for dyeing and the preparation of indigo. There is reason to presume that the indigo-yielding principle present in the young leaves of the *L. cyanescens* gradually disappears when these reach maturity, as samples of the latter examined in this country were devoid of indigo-producing property. The *L. cyanescens* is probably identical with the 'Taroom akkar' described by Bancroft (Philosophy of Permanent Colours 1813, i. 189 and 191). A. G. P.

LONDON WHITE. *Flakewhite* (*v.* PIGMENTS).

LORETIN. Trade name for *m*-iodohydroxyquinoline sulphonic acid $(C_9NH_4I(OH)HSO_3)$ used as a germicide in surgical dressings (*v.* SYNTHETIC DRUGS).

LOSOPHAN *v.* SYNTHETIC DRUGS.

LOTUS ARABICUS. The *Lotus arabicus* (Linn.) is a leguminous plant, indigenous to Egypt and Northern Africa, and in the young condition is extremely poisonous. The subject has been investigated by Dunstan and Henry (Phil. Trans. 1901, 194, 515).

Lotusin, the active principle, can be isolated by extracting the dried plant with methyl alcohol. The extract is evaporated, the residue treated with water to remove chlorophyll and resin, and from the aqueous solution tannin and other impurities are precipitated by means of lead acetate. The filtrate, on evaporation, leaves a syrupy residue, from which crystals of lotusin slowly separate. In the pure condition lotusin $C_{28}H_{31}O_{16}N$ forms yellow needles, and when hydrolysed by digestion with hydrochloric acid, or by means of an enzyme *lotase*, also found in the plant, yields dextrose, lotoflavin, and hydrocyanic acid, according to the following equation:

$$C_{28}H_{31}O_{16}N+2H_2O$$
$$=2C_6H_{12}O_6+C_{15}H_{10}O_6+HCN.$$

When warmed with alcoholic potash (20 per cent.) lotusin is gradually decomposed with production of ammonia and *lotusinic acid*:

$$C_{28}H_{31}O_{16}N+2H_2O=\underset{\text{Lotusinic acid.}}{C_{28}H_{32}O_{18}}+NH_3.$$

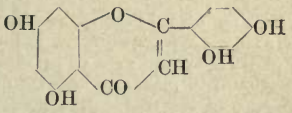
This compound is monobasic, gives yellow crystalline salts, and is hydrolysed by dilute hydrochloric acid with formation of *lotoflavin*, *dextrose* and *heptogluconic acid*:

$$C_{28}H_{32}O_{18}+2H_2O$$
$$=C_{15}H_{10}O_6+C_6H_{12}O_6+C_7H_{14}O_8.$$

Lotoflavin $C_{15}H_{10}O_6$ crystallises in yellow needles, soluble in alkaline solutions with a yellow colour. By fusion with alkali, *phloroglucinol* and *β-resorcylic acid* are produced.

With acetic anhydride lotoflavin gives a *tetraacetyl* compound $C_{15}H_6O_6(C_2H_3O)_4$, colourless needles, m.p. 176°–178°, and when methylated by means of methyl iodide the *trimethyl ether* $C_{15}H_7O_3(OCH_3)_3$ is obtained. This latter compound exists in two forms, viz. the α-form yellow rosettes, m.p. 125°, and the β-form glistening needles, m.p. 175°, which are mutually convertible. Both varieties give by means of acetic anhydride the same *monoacetyl lotoflavin trimethyl ether* $C_{15}H_6O_3(C_2H_3O)(OCH_3)_3$, yellow needles, m.p. 147°.

According to Dunstan and Henry, lotoflavin is probably a *tetrahydroxyflavone*, and possesses the formula:

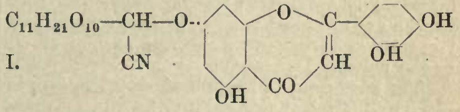


The hydrolysis of the cyanogenetic glucoside lotusin, with formation of maltose, lotoflavin and hydrocyanic acid, may also be expressed as follows:

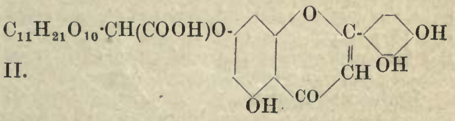
$$C_{28}H_{31}NO_{16}+H_2O$$
$$=C_{12}H_{22}O_{11}+C_{15}H_{10}O_6+HCN.$$

The following constitutions are respectively assigned to lotusin (1) and lotusinic acid (2):

I.



II.



A. G. P.

LOTUSIN *v.* GLUCOSIDES; LOTUS ARABICUS.

LUBAN MATI or **MEYETI** *v.* OLEO-RESINS.

LUBRICANTS. The purpose of lubricants is to reduce friction between surfaces which move one upon another.

As the value of a lubricant depends almost entirely upon the conditions of speed and pressure under which it is used, it is necessary to outline the theory of lubrication before describing the preparation and properties of lubricating oils and greases.

Static friction. If two clean surfaces of the same metal, say lead, are pressed together they will adhere firmly. In cases where metals work together without lubrication this '*seizing*' is only prevented by the existence of a '*contamination film*' on the surface of the metal. Thus the so-called 'solid friction' observed in such cases is really the friction of surfaces lubricated by an extremely thin film (*e.g.* of air).

Thurston, experimenting with sperm and lard oils, found that the friction rapidly increased with pressure up to about 70 lbs., and then increased less rapidly or remained constant.

With plastic substances, *e.g.* axle grease, under ordinary loads the frictional coefficient is least when at rest and gradually increases with increasing speed owing to the resistance of the grease to shear.

With liquids the reduction of static friction depends on the thickness of the film which remains on the bearing surfaces under the loads commonly used. Different liquids vary much in this respect, and the effect seems to depend less on the viscosity of the oil than on its 'oiliness' (*v. infra*).

Low-speed friction. In this case the film of oil is so thin that the irregularities of the surfaces engage one another, causing abrasion. This does not matter if the surfaces are of proper materials, but in some cases it may lead to seizing of considerable areas and so much distortion of the surface that at higher speeds the formation of the 'pressure film' may be prevented and serious over-heating of the bearing may result.

The friction of lubricated bearings at low speeds is really solid friction, *i.e.* it is (1) independent of velocity and area of bearing surface, (2) proportional to pressure, and (3) dependent on the nature of the surfaces, which should be made of dissimilar metals.

Where a complete oil film cannot form, the oiliness of the lubricant is very important, but as the speed increases the oil film thickens and the friction depends more on the viscosity of the oil and less on its oiliness.

Friction, especially at moderate speeds, depends very much on the manner in which the lubricant is applied to the bearing. The best results are obtained with bath lubrication, and the friction increases as the free supply of oil to the journal decreases.

The coefficient of friction at very low speeds —0·0005–0·01 feet per minute—is often greater than the static coefficient, but the change from one to the other is continuous. From about 6·0 feet per minute the coefficient of friction steadily decreases with increase of speed.

High-speed lubrication. At a speed depending on the nature of the lubricant and on the load the surfaces begin to separate, and a comparatively thick 'pressure film' forms between them, being carried into the bearing on the surface of the moving part.

The maintenance of a pressure film between two plane and parallel surfaces depends upon the *inertia* and the *viscosity* of the oil, but in the case of plane surfaces inclined to one another—and this is the case met with in practice—the liquid wedges itself between them and forces them apart.

To this action is due the great carrying power of cylindrical bearings, which in use always wear so that the radius of curvature of the brass is greater than that of the journal. The two surfaces are thus inclined to each other, and the journal, as it rotates, carries the lubricant into the space between the journal and the brass, where it is wedged under a pressure which increases to a maximum at the point where the two approach most nearly.

In the design of bearings great care has to be taken that oil-ways are not cut in this neighbourhood of maximum pressure, or the pressure of oil which should carry the load is released and serious friction results.

The theory of the pressure film has been worked out in great detail, mathematically, by Osborne Reynolds, but only his general results can be given here. At speeds sufficiently high to ensure the formation of the pressure film the following laws appear to be very nearly true:—

(1) The friction is independent of the load;

(2) The friction varies directly as the area of the contact surfaces; directly as the speed; and as the viscosity of the lubricant.

These are the laws of 'fluid friction.'

Above speeds of 100 feet per minute low speed effects are not observed and the friction is nearly proportional to the square root of the speed. This is probably due to lessened viscosity of the lubricant brought about by rise of temperature. From 490 to 790 feet per minute the friction is proportional to the fifth root of the speed, and above 1970 feet per minute it is practically independent of the speed.

With alternating pressures, especially when the alternations are rapid, *e.g.* in the big ends of connecting rods, a given bearing will sustain much greater loads without seizing than it would if the pressure were continually in the same direction, because the oil is trapped between the surfaces at each reversal of the stress.

Friction in ball and roller bearings is practically independent of the presence of any lubricant, the chief function of the oil used being to prevent rusting of the polished surfaces.

A mineral oil of moderate specific gravity is therefore a suitable lubricant for such bearings.

COMMON LUBRICANTS.

Lubricants are divisible into four classes:

(*a*) Fats and liquid waxes;

(*b*) Mineral oils;

(*c*) Blended oils;

(*d*) Greases and solid lubricants.

(*a*) **Fats and liquid waxes.** These are comprised under the name of fixed oils (*v.* OILS, FIXED, AND FATS). The fixed oils principally used as lubricants are: tallow oil, lard oil, neat's foot oil, olive oil, rape oil, and castor oil. For delicate machinery, such as clocks and watches, hazel-nut oil, ben oil, porpoise oil, and dolphin oil (blackfish oil) are used.

Sperm oil and Arctic sperm oil are liquid waxes, and are excellent lubricants because of their oiliness, and because their viscosity is less affected by temperature than is that of other oils.

Vegetable oils and all semi-drying oils, including fish oils and blubber oils (except porpoise and dolphin oils), are unsuitable for lubrication, and their addition to lubricating oils constitutes adulteration.

The fixed oils are seldom used alone as lubricants except for textile machinery, in which there is a risk of the oil being splashed on the fabric. Mineral oils are very liable to make stains which cannot be washed out subsequently without injury to the material.

(*b*) **Mineral oils** are derived from crude petroleum, shale and lignite, and consist of saturated, unsaturated, and closed-chain hydrocarbons of b.p. over 300°. Those of sp.gr. up to 0·900 are usually distillation products, while those of sp.gr. higher than 0·910 are either 'reduced oils' or oils that have been distilled with steam *in vacuô*. Heavy oils that have been distilled under atmospheric pressure are unsuitable for use as lubricants because of the presence in them of products of 'cracking' (*v.* PETROLEUM AND SHALE OIL).

(*c*) **Blended oils.** Mineral oils are miscible with all fatty oils except castor oil, and mixtures containing 20–30 p.c. of good fixed oil, *e.g.* sperm oil, are the best lubricants available for ordinary loads and speeds. Blown oils (partially oxidised oils) are soluble in mineral oils, and are sometimes used to give body to the lighter grades, but such blended oils have a great tendency to gum, and, though cheap, are not to be recommended.

(*d*) **Greases** and **solid lubricants.** The chief solid lubricants are graphite, soapstone (talc, steatite, French chalk), mica, and asbestos. These are seldom used alone, but are usually incorporated in a grease, the advantage being that under ordinary conditions the frictional resistance is merely that due to the resistance to shear of the grease, while under excessive pressure, though the grease may melt and run off the bearing, the solid lubricant remains and prevents damage. Filling materials, such as barytes and chalk, are sometimes added to greases, but they are not lubricants, and their addition is detrimental.

Anti-friction metals (*v.* ANTIMONY) may be regarded as solid lubricants, but their chief purpose is to afford a material into which the shaft can bed itself quickly.

Greases may be natural fats, *e.g.* tallow, but are more commonly prepared by adding to mineral or fixed oils alkali metal soaps or, more often, aluminium, lime or lead soaps of fatty acids or resin acids. Such greases frequently contain a considerable quantity of water, but if this is thoroughly incorporated in the grease it has no bad effect upon its properties as a lubricant.

Boiled greases are prepared by dissolving lime soap in mineral oil; they are very good for medium and heavy machinery.

'**Set**' or **axle greases** are made by adding to a mixture of mineral oil (100 gallons) and good slaked lime (500 lbs.), called the *lime part*, a certain proportion of resin oil (2–25 p.c.), called the *set*. The mixture is run at once into the packages in which it is to be sold, and in a short time sets to a solid or semi-solid mass, according to the proportion of resin oil added (*v.* also Archbutt, J. Soc. Chem. Ind. 1901, 1193).

Cup greases are prepared by saponifying fat, usually horse-fat, with freshly slaked lime in a large kettle heated by a steam jacket and provided with a mechanical stirrer. The usual proportions are 2000 lbs. fat, 200 lbs. lime, and 140 gallons of water. When saponification is complete and the excess of water has evaporated, a light-coloured mineral oil, sp.gr. 0·885–0·910 (about 100 gallons), is sprayed on the contents of the kettle until the right consistency is attained. The oil must previously be heated to 190°F.

Engine greases are made by incorporating cold mineral oil with hot soluble soda or potash soap. It is important that the soap should be neutral (Redwood).

Thickened mineral oils are often made by incorporating aluminium oleate with a light oil. The soap is made as follows: 112 lbs. oleic acid is mixed with 20 gallons hot water and a solution of 16¼ lbs. 77 p.c. caustic soda in 10 gallons water, and boiled until the formation of sodium oleate is complete. 70 lbs. alum, dissolved in 20 gallons water, are then added to the solution when aluminium oleate separates in greasy masses. It is freed from moisture by pressure (Hurst).

Railway waggon grease is usually composed of tallow, palm oil, soap, and water; and is prepared by heating the tallow and palm oil to 180°F., and running in a solution of sodium carbonate at 200°F. The whole is stirred well and run into tubs to set. It is usual to vary the composition of the grease according to the season of the year; the following are typical formulæ:

	Summer	Medium	Winter
Tallow . .	22	20	18
Palm oil . .	12	12	12
Sperm oil . .	1	1·5	2
Soda crystals .	5	5	5
Water . .	60	61·5	63
	100	100	100

The grease in use on the Midland Railway is prepared by dissolving 6 cwt. of palm oil in 12 cwt. of water and adding to the solution 6 cwt. of tallow and 2 cwt. of dark mineral oil.

Another English railway grease:—

	Summer	Winter
Tallow . .	504 parts	420 parts
Palm oil . .	280 „	280 „
Sperm oil .	22 „	35 „
Caustic soda .	120 „	126 „
Water . .	1370 „	1524 „

Other preparations are made of tallow with colza oil, soda, and water in various proportions; and, for fine machines, of tallow with castor oil, &c., &c.

Palm-oil lubricants. Although palm oil may be used alone, its melting-point is too low for most purposes; to correct this, tallow and other fats are added to the amount of one-third or one-half of the total weight of the lubricant. A small quantity of soda should form a part of these lubricants, as by its use the free fatty acids which are contained in palm-oil are saponified and their action on the metals with which they come in contact is destroyed. Soda also is the medium by which water is introduced into the mixture.

Lead-soap lubricants. Lead salts yield on saponification with fats solid combinations called lead-soaps; they are hard at low temperatures, viscous at ordinary temperatures, but sufficiently fluid on heating by friction. The melting-point of lubricants prepared from these substances is high, and they are therefore less suited for high speeds. So-called 'anti-friction lubricants' are composed of lead-soaps. A basic lead acetate (sugar of lead) is combined with the requisite quantity of fat in the following manner. The lead solution is thus prepared: Sugar of lead 10 parts, litharge 10 parts, and soft water 110 parts, are boiled with frequent stirring for an hour and a half or two hours. The mass is then allowed to rest, and the clear fluid drawn off and restored to 100 parts by the addition of water. It is then heated to from 145°F. to 165°F. and immediately mixed with ordinary fat (colza oil, lard, and sometimes neats-foot oil), as, *e.g.*, solution of sugar of lead 100 parts, colza oil 80 parts, lard 80 parts. The preparation should show a uniform grey colour, and, after melting, congeal at from 100°F. to 122°F. (Brannt).

Soap lubricants. Ordinary soft soap, or fat combined with potash, is serviceable for some purposes, but is liable to have a part of the potash lye not fixed, by which damage is done to metals.

The following are from Brannt (Practical Treatise on Animal and Vegetable Fats and Oils):—

Caoutchouc lubricants for belts. Caoutchouc 20 parts, linseed oil 1000 parts. Melt the caoutchouc together with the same quantity of linseed oil, and as soon as the mixture commences to evolve vapours, stir in 20 parts of linseed oil and afterwards add the remainder of the oil by instalments of 100 parts.

Asphaltum waggon grease. Asphaltum 32 parts, black pitch 8 parts, petroleum 8 parts, litharge 8 parts, water 80 parts.

Naphthalene grease. Naphthalene 100 parts, colza oil 50–100 parts. Crude naphthalene is used.

Resin lubricant. Common resin 100 parts, resin oil 50 parts, lard 300 parts.

Graphite waggon grease. Tallow 36 parts, lard 9 parts, palm oil 9 parts, graphite 2 parts.

Graphite lubricants for quick-moving axles, Tallow 100 parts, graphite 100 parts; especially adapted for shafts revolving with great velocity without great load, as circular saws, ventilators, &c.

Lubricant for cutting tools. This is usually a solution of soft soap and soda in water.

PHYSICAL PROPERTIES AND TESTING OF LUBRICANTS.

A. **Viscosity.** For methods of determining viscosity, *see* PETROLEUM. The methods there given are equally applicable to all lubricating oils.

The determination of the consistency of fats and greases is of importance, but the methods available are entirely empirical.

In *Kissling's apparatus* a pointed rod of glass or metal, weighted at the top, slides vertically through a hole in a fixed plate. The point of the rod presses on the surface of the grease contained in a small beaker, and the time taken for it to penetrate a definite distance into the fat is a measure of the stiffness of the latter.

Kunkler's apparatus consists of a metal cylinder having an orifice at the lower end through which the grease is squeezed by a weighted piston. The whole apparatus is surrounded by a water-jacket so that the temperature of the test can be regulated.

In any determination of the consistency of fats, great attention must be paid to the preliminary treatment they receive, as they are extremely sensitive to mechanical disturbance and to change of temperature. After the grease has been placed in position it is necessary to leave it for 24 hours before proceeding with the test.

B. **Specific gravity.** This property is used as an indication of the nature and purity of oils, and it forms the basis of the classification of the mineral oils. There is, however, no necessary connection between sp.gr. and lubricating power; *e.g.* it is well known that mineral oils commonly have less lubricating power than fatty oils of the same sp.gr. (*see* also PETROLEUM AND SHALE OIL).

The sp.gr. of oils may be determined by the sp.gr. bottle, by the Sprengel tube, or by the Westphal balance, but with viscous oils these methods are liable to be tedious, and hydrometers are commonly used for the purpose.

It is frequently necessary to know the density of an oil at a temperature at which it cannot conveniently be determined experimentally; it can then be calculated with sufficient accuracy (1 in 4000) from the following formula, if the density of the oil at 60°F. is known: $D = d - kt$, where d = the density of the oil at 60°F.,

$$k = \begin{cases} 0{\cdot}000368 \text{ for a fixed oil,} \\ 0{\cdot}000367 \text{ for a Scotch mineral oil,} \\ 0{\cdot}000345 \text{ for a Russian mineral oil,} \\ 0{\cdot}000350 \text{ for an American mineral oil,} \end{cases}$$

t = the number of degrees above 60°F., and D = the required density.

C. **Flash-point.** This is the temperature at which the oil gives off sufficient vapour to form an explosive mixture with air in the standard apparatus employed (for details *see* PETROLEUM). It is usually stated that only oils of flash-point over 350°–400°F. should be used as lubricants, but the loss on evaporation is at least as good a test.

D. **Volatility.** It is obviously desirable that lubricating oils should not evaporate to any considerable extent at the temperatures at which they are used. The fatty oils are satisfactory in this respect, but mineral oils frequently contain as much as 15 p.c. of hydrocarbons volatile at 100° C.

Archbutt's apparatus for the determination of this loss consists of a copper tube placed horizontally across an air-bath by which it can be kept at any desired temperature. The oil to be tested, usually 0·5 gram, is placed in a platinum tray within this tube and subjected to a current of air, previously heated to the temperature of the bath, passing at the rate of 2 litres per minute for exactly 1 hour.

In some cases the oil is tested in a current of steam, but the procedure is quite similar to that when air is used.

As an example of its use, an oil intended for cylinders working at 160 lbs. pressure is tested at 370°F. when it should not lose more than 0·5–1·0 p.c. of its weight. With machine oils and spindle oils, even at much lower temperatures, the permissible loss is much greater.

E. **Setting-point** (the *cold test*). With most oils this is taken as the temperature at which they cease to flow, but in the case of Scotch shale oils the setting-point is the temperature at which solid paraffin is first deposited.

The oil, contained in a corked tube, is cooled in water, or in ice and salt, until it ceases to flow on reversing the tube. It is necessary to maintain the temperature constant for about 20 minutes before observing the condition of the oil (*v.* Salkowsky, J. Soc. Chem. Ind. 1888, 37; and Holde, *ibid.* 1890, 112; 1896, 138, 160), and in Hofmeister's method this is attained by using solutions of various salts, of such concentrations that they are saturated at their freezing-points. The result is that freezing takes place with formation of a eutectic mixture, and the temperature remains constant till the whole is solidified.

Schultze's method, used in Germany, depends on finding the temperature at which the oil flows through a tube of 6 mm. diameter at a rate of 10 mm. per minute under a pressure equal to 50 mm. of water.

F. **Melting-point of fats** and **greases.** This is frequently of importance, as a grease loses its power of reducing friction under great pressure should it become liquefied. As in the case of determination of consistency, attention must be paid to the preliminary treatment of the grease, and it should, in most cases, be left undisturbed for 24 hours before the test is made.

Many methods are used, most of which depend on observing the temperature at which the grease begins to flow under its own weight (*v.* Bensemann, J. Soc. Chem. Ind. 1885, 535; Cook, Chem. Soc. Proc. 1897, 74).

G. **The colour of oils** is of some importance, and Redwood uses Lovibond's tintometer (*v.* art. COLORIMETERS) for making a numerical record of this characteristic. Most mineral oils exhibit a fluorescence, usually of a blue or green colour, but this is not of much importance as a test (*v.* PETROLEUM).

H. **Oiliness.** The most important property of oils and greases which are to be used under conditions of low speed and high pressure (under 100 feet per minute and over 70 lbs. per square inch), is that called '*oiliness*' (*unctuosity, lubricity*). It depends on (1) interfacial action, which causes oils to spread themselves over metallic surfaces, and (2) on the power of the film to resist disruption.

Oiliness may be defined as the power of a lubricant to maintain an unbroken film under a heavy load; it cannot be measured in any exact way, and information as to the extent to which any given oil possess this property may best be obtained by properly conducted tests on mechanisms resembling those on which it will be used. This property is not necessarily connected with viscosity, being possessed in much greater degree by fixed oils than by mineral oils of the same viscosity. This is the reason that mineral oils must be blended with fatty oils to get the best lubricants for ordinary machinery.

Oil-testing machines are made of many different designs, and may be used to investigate:

(1) Comparative oiliness or greasiness of lubricants;

(2) Frictional effects due to viscosity;

(3) Effects of temperature on friction;

(4) Effects of different loads;

(5) Effects due to varying speeds;

(6) Effects produced by different metals working in contact;

(7) Effects resulting from different methods of applying the lubricant.

Most of these effects, except (1), are amenable to calculation, or can be more easily determined in some other way; Nos. (6) and (7) are rather concerned with the design of bearings than with lubricants.

In most machines an experimental journal runs in brasses loaded in a manner which can be regulated by the operator, *e.g.* by a spring. The detailed description of such machines hardly falls within the scope of this article, and it is sufficient to say that Thurston's oil-testing machine is largely used (for a detailed description *see* Archbutt and Deeley, Lubricants and Lubrication, 332; Hurst, Lubricating Oils, Fats, and Greases, 254 *et seq*). Machines of similar type are those of R. H. Smith, A. Martins, Ingham and Stapfer, Stroudley, Goodman, and Lahmeyer (A. and D. chap. ix.).

These testing machines all suffer from the disadvantage that, at the speeds at which they are usually run, the frictional effects observed are due solely to the viscosity of the oil used, and therefore only give information as to that property; information which could better be obtained with a viscosimeter.

Machines of what is known as the *disc and collar* type are of much more use in investigating the 'oiliness' of lubricants. In them the oil is fed between a rotating disc and a stationary plate, a load is applied to force the two together, and low speeds are used. The best known machines of this class are MacNaught's, Woodbury's, Deprez and Napoli's, and Tower's.

Bailey's pendulum oil-tester is specially designed for use with oils intended for watches, clocks, and other small machines.

CHEMICAL PROPERTIES OF LUBRICANTS.

The chemical methods used for the examination of lubricants are those used for oils in general (*v.* PETROLEUM and OILS, FIXED, AND FATS).

The chemical properties of oils which are of special importance with reference to their use as lubricants are: (1) corrosive action on metals, which is closely connected with the acidity of the oil; (2) their tendency to gum or resinify; and (3) their liability to decomposition under the conditions of use.

(1) Most fatty oils, even when freshly prepared, contain some fatty acid, the amount of which increases with time of storage of the unrefined oil. This cannot be avoided, and is one of the chief reasons that such oils have been largely superseded by mineral or blended oils. The addition of resin or resin oil to a lubricant will often increase the acidity owing to the resin acids present.

Crude petroleum normally contains small amounts of organic acids, but refined mineral oils ought to be practically free from acidity. In many cases where they do not conform to this standard they are found to contain free sulphuric acid, which has been left in the oil owing to imperfect washing after refining with acid.

The extent of the corrosive action of an oil on metals is proportional to its acidity, but is conditioned by the access of air or water to the metal. In absence of air and water even a grease containing 70 p.c. of fatty acids has little or no action on metals (Burstyn, Dingl. poly. J. 217, 314; Redwood, J. Soc. Chem. Ind. 1886, 362; Fox, Analyst, 1883, 8, 116; Donath, J.

Soc. Chem. Ind. 1895, 283). The acidity is usually determined by titration, and is expressed in terms of alkali required to neutralise it, or as oleic acid.

(2) The *tendency to gum* in the case of fatty oils is closely associated with their drying properties. Such oils as linseed oil are impossible as lubricants. The semi-drying oils are not used as lubricants with the single exception of rape oil, the least oxidisable, which is largely used owing to its low cost.

A rough idea of the drying properties of oils can be obtained by coating them on pieces of clean glass and observing the length of time they take to set, or to arrive at the same consistency. Another way is to place drops of the oils at the upper end of an inclined steel plate, and observe the distances they travel before coming to rest. Care must be taken to distinguish those cases in which the thickening of an oil is due to its acidity, the corrosive action resulting in the formation of metallic soaps which dissolve in the oil.

Mineral lubricating oils can absorb small quantities of oxygen at a high temperature (Bach, J. Soc. Chem. Ind. 1889, 990; Ostrejko, J. Soc. Chem. Ind. 1896, 26, 345, and 645), but under ordinary conditions such oxidation is practically *nil*. Any tendency to gum in this case is due to evaporation of the lighter constituents with deposition of asphaltic and tarry matters (Holde, J. Soc. Chem. Ind. 1894, 668; 1895, 894). The amount of bituminous matter present can be determined by extraction with light petroleum (Bender, J. Soc. Chem. Ind. 1891, 354). Closely associated with the gumming tendencies of oils is their liability to cause spontaneous combustion of cotton waste, &c., with which they come in contact. For this reason mineral oils have entirely superseded fixed oils in many cotton mills.

(3) The danger of *decomposition* is present in those bearings which run at a high temperature, *e.g.* hot-neck rolls, but the commonest case where this has to be considered is that of cylinders of steam, gas, and oil engines. For these pure fixed oils should never be used, as in presence of steam they are hydrolysed to glycerol and fatty acids which rapidly corrode the cylinder and piston, forming large lumps of metallic soap. Steam cylinders are best lubricated with 'reduced' mineral oils of high viscosity, density, and flash-point, but very satisfactory results are obtained in practice by using lighter grades of mineral oils containing up to 30 p.c. of fixed oils or 'blown oils.'

For the lubrication of the cylinders of gas and oil engines a pure mineral oil should be used, preferably one which will evaporate without leaving any residue. The high temperature of the walls of such cylinders and the presence of flame cause such carbonisation of the oil and, unless care is used in its selection, this may cause serious trouble.

See OILS, FIXED, AND FATS; PETROLEUM; also Encyclop. Britt. 1910, arts. Lubricants and Lubrication; Archbutt and Deeley, Lubrication and Lubricants; Lewkowitsch, Chemical Technology of Oils, Fats, and Waxes; Redwood, Lubricants, Oils, and Greases; G. H. Hurst, Lubricating Oils, Fats, and Greases; Carpenter and Leask, Soap, Candles, Lubricants, and Glycerin, 258 *et seq.*

LUMINOUS PAINT *v.* BARIUM SULPHIDE.

LUNAR CAUSTIC. Silver nitrate fused and cast into rods or sticks.

LUPEOL. A substance of the formula $C_{30}H_{50}O$ found associated with cinnamic acid in *Palaquium* [*Dichopsis*] *Treubii* (Burck.). Crystallises in fine needles, dextrorotatory $\alpha_{D} = +27{\cdot}2^{\circ}$ in chloroform, m.p. 190°–192° (Jungfleisch and Leroux, Compt. rend. 1907, 144, 1435; *cf.* Van. Romburgh, *ibid.* 1907, 926).

LUPINES. *Lupinus luteus* (Linn.); *L. angustifolius* (Linn.); *L. albus* (Linn.). The above three varieties, whose flowers are yellow, blue, and white respectively, are the chief species grown. They are often grown for green manure on account of their nitrogen-collecting powers, and are employed to enrich poor sandy soils in nitrogenous organic matter. They are only occasionally used as food either for men or animals, because of their bitter taste, but in times of famine they are sometimes used as an addition to rye-bread.

The following gives the mean composition of several varieties of the seed (König):—

	Water	Protein	Fat	N-free extract	Crude fibre	Ash
White lupines	15·9	28·8	6·8	33·6	11·9	3·0
Black ,, .	14·3	38·8	4·6	23·9	14·5	3·9
Blue ,, .	14·3	29·7	5·3	35·6	12·2	2·9
Yellow ,, .	14·7	37·8	4·3	25·5	14·2	3·5

The "protein" of lupines contains a considerable proportion (10–20 p.c.) of non-albuminoids. A portion of the non-albuminoid nitrogen exists in the form of alkaloid-like substances. Blue and white lupines contain a substance *lupanin* $C_{15}H_{24}N_2O$, which can exist in two forms: a liquid which forms a hydrochloride $C_{15}H_{24}N_2O{\cdot}HCl,2H_2O$, crystallising in prisms melting at 132°–133°; and a solid, crystallising in monoclinic crystals, which melt at 99°, and which forms a hydrochloride of the same composition as the other, but melting at 105°–106°. *Lupinin* $C_{21}H_{38}N_2(OH)_2$ occurs in yellow lupines; it forms crystals melting at 67°–68°. *Lupinidin*, another liquid alkaloid-like substance, consists of a solution of a crystalline hydrate $C_8H_{15}N + H_2O$ in the oily base $C_8H_{15}N$. The latter is a thick, oily liquid easily soluble in alcohol and ether, smells like hemlock and has an intensely bitter taste. It oxidises rapidly by exposure to air and acts as a weak poison.

These alkaloid-like substances are present both in the seeds and in the leaves and stems, and thus render the plant unpalatable to animals. The poisonous properties of lupines, often fatal to sheep, were formerly ascribed to these alkaloids, but according to Kuhn and Liebscher, they are due to 'Ichtrogen,' a substance produced by the growth of a fungus which attacks lupines, and which can be extracted from diseased plants by treatment with water.

Lupines are sometimes deprived of their bitter taste before being given to animals. This can be done by an hour's steaming and washing with water; according to Kellner this treatment removes practically the whole of the alkaloids (95 p.c.), while it also removes about 3–4 p.c. of the nitrogenous substances, and 15–20 p.c. of the total dry matter. In spite of this loss the treated lupines are of greater feeding value than those untreated.

Of the proteids in lupines, conglutin is the largest constituent. The 'nitrogen-free extract' of lupines consists largely of gums and pectin bodies, together with starch and cane sugar. The blue lupine contains about 11 p.c. of *lupeose* (β-galactan); by heating with dilute sulphuric acid it splits up into *d*-fructose and galactose.

The following are analyses of the ash of lupines (König) :—

	K_2O	Na_2O	CaO	MgO	Fe_2O_3	P_2O_5	SO_3	SiO_2	Cl
Yellow lupines	30·5	0·7	7·1	12·8	0·7	38·6	8·7	0·2	0·8
Blue ,,	30·9	1·0	10·6	9·7	0·6	37·1	7·8	1·0	0·4
White ,,	33·7	17·9	7·8	6·2	—	25·7	6·8	0·9	2·1

H. I.

LUPININE *v.* VEGETO-ALKALOIDS.

LUPULIN *v.* OLEO-RESINS.

LUTECIENNE. A mixture of Fast Red A with Orange II. (β-naphthol orange), the sodium salt of *p*-sulphobenzene-azo-β-naphthol, comes into commerce under this name. Known also as French Red. The name is also given to the alkaline salts of dibromodinitro-fluoresceïn, prepared by simultaneous nitration and bromination of fluoresceïn in alcoholic solution or by nitration of dibromofluoresceïn in acetic acid or aqueous solution.

LUTECIUM. Sym. Lu. At.wt. 174. The identification of this rare earth metal has resulted from the systematic examination of Marignac's ytterbia (Compt. rend. 1878, 87, 578), which is isolated from the least basic portions of the yttria earths derived from xenotime or ytterbite (gadolinite) (*v.* CERITE METALS). Prolonged fractionation in nitric acid of the crude ytterbium nitrate removed yttrium, erbium, and finally thulium, a trace of thorium being separated with hydrogen peroxide. The atomic weight of the elements present in the final fractions rose from 169·9 to 173·8. The most soluble fractions, which give the highest atomic weights, showed 34 characteristic lines in the spark spectrum and the band γ (λ517·5–λ513) in the absorption spectrum which are characteristic of lutecium (Urbain, Compt. rend. 1907, 145, 759; *cf.* Auer von Welsbach, Sitzungsber. Wien. Akad. 1907, 468). The commercially separated yttrium earths from ytterbite have been further fractionated as chromates to remove yttrium, and crystallised as nitrates, and as double nitrates with bismuth and magnesium to precipitate cerium and lanthanum. After removing the excess of bismuth and magnesium, the lutecium fraction was precipitated as oxalate, converted into nitrate, and fractionated to eliminate successively erbium, yttrium and neoytterbium. The most soluble lutecium fraction, converted into chloride with sulphur chloride (*v.* CERIUM), was heated till scandium and thorium chlorides were volatilised. *Lutecium chloride* is more volatile than neoytterbium chloride (Urbain, Bourion, and Maillard, Compt. rend. 1909, 149, 127). The xenotime earths were freed from cerium, gadolinium, terbium and dysprosium by fractionating the ethyl sulphates; the most soluble ytterbium fraction (containing yttrium, erbium, and thulium) was converted into nitrate, and decomposed fractionally in nitric acid when neoytterbium and lutecium were obtained in the most easily decomposable portions.

Lutecia (*lutecium oxide*) Lu_2O_3 is less basic than neoytterbia, and can be separated from it by fractional precipitation with caustic alkali; it is less paramagnetic than the latter oxide, the magnetic susceptibilities being in the ratio $Yb_2O_3 : Lu_2O_3 = 53 : 13$ (Urbain, Compt. rend. 1908, 146, 406).

The final uncrystallisable mother liquors obtained in the separation of lutecium from ytterbite (but not from xenotime) probably contain a new element *Celtium* indicated by a characteristic arc spectrum. The magnetic susceptibility of celtium oxide is three or four times less than that of lutecia, and in basic strength the former oxide is intermediate between the latter and scandia (Urbain, Compt. rend. 1911, 152, 141).

G. T. M.

LUTEOLIN. The sodium salt of *m*-xylidinsulphonic-azo-diphenylamine. An orange-yellow dye discovered by Witt in 1883. No longer used. Also the colouring matter of weld (*q.v.*).

LUTES are used for packing joints, repairing fractures, and coating vessels externally to render them impervious to vapours, &c. For a lute to be effective it is important that the surfaces to which it is applied should be *clean*, and in the case of lutes that are applied in a molten or semi-fluid state it is preferable previously to heat the parts that are to be joined.

Of lutes for joints which are not to be subjected to high temperature may be mentioned: (1) Soaked bladder stretched and tied over a joint or employed to secure another lute on the joint. (2) India-rubber bands, or caoutchouc melted or dissolved in coal tar, naphtha, or other solvent. (3) A solution of 1 part caoutchouc in 2 parts hot linseed oil mixed with 3 parts pipeclay; this mixture remains soft and is very impervious. (4) Linseed or almond meal made into a paste with water, milk, glue, or lime-water. (5) A mixture of white lead and oil spread upon strips of linen or bundles of tow. (6) Quicklime reduced to a dry powder by addition of a small quantity of water, and mixed with white of egg diluted with its own volume of water, is spread on linen strips and rapidly applied to the joint. This lute dries quickly and adheres strongly to glass. (7) *Lute d'âne*, a very strong cement prepared by mixing strong glue with recently slaked lime, with subsequent addition of white of egg. (8) Chalk and linseed oil (glazier's putty). (9) Plaster of Paris made into a paste with water, gum water, or glue, and coated when dry, if the joint is to be gas-tight, with melted paraffin or oil. (10) *Fat lute*, consisting of a mixture of clay and boiled linseed oil, is applied and retained by bladder or other substance, to hot joints or to prevent escape of corrosive vapours. (11) A mixture of clay with a solution of gelatin in pyroligneous acid.

For joints which are to resist considerable internal pressure, especially the joints of steam pipes, a mixture is applied consisting of equal parts of red lead and white lead made into a paste with linseed oil and mixed with tow. Other lutes for this purpose are: (1) 12 of Paris white, 5 of red ochre, 2½ of Venetian red, and ½ of plumbago, ground and mixed to a stiff paste with boiled linseed oil (Thompson, Eng. Pat. 27975, 1895). (2) Metallic zinc powder mixed with tow or whiting and made into a paste with linseed oil or wood oil (Boneville & Co. Fr. Pat. 332788). (3) 6 parts graphite, 3 parts slaked lime, 8 parts powdered barytes, and 7 parts of boiled linseed oil.

For making permanent joints and closing joints between metal and glass, &c., various compositions containing beeswax are used. Beeswax when melted with one-eighth its weight of turpentine becomes less brittle and, when the materials are melted in equal proportions, the product becomes pliant when held in the hand, melts easily, and is known as *soft cement*. *Cap cement* or *hard cement*, for closing the covers, &c., of scientific apparatus, is prepared by mixing and melting 1 part beeswax, 5 parts resin, and 1 part dried red ochre or other colouring matter. The mixture is heated to 100°C. until all frothing has ceased, and is cooled with frequent stirring to prevent settlement of the pigment.

Bottle lutes are used to cover the stoppers or corks of bottles. That most commonly employed is sealing wax; paraffin wax is also good. Wholesale dealers usually lute the stoppers of acid bottles with a paste of linseed meal and water.

Plumber's lute is made by adding 2 parts of fine brickdust to 1 part of melted black resin and stirring in thoroughly.

A waterproof cement, introduced by Edmund Davy, is prepared by melting together 2 parts by weight of common *pitch* and 1 part of *gutta percha*, with constant stirring. The resultant homogeneous fluid adheres with great tenacity to metal, stone, wood, &c., if applied to warm surfaces of those substances, and, although hard, is not brittle. It softens when heated and passes through various stages of viscosity until above 100°F. it forms a thin fluid. It appears to be absolutely unaffected by contact with water.

Two good *acid-proof* lutes are: (1) Pipeclay made into a stiff paste with hot coal-tar; (2) equal parts of pitch and resin melted together and incorporated with 1 part of plaster of Paris.

A useful laboratory cement is obtained by mixing litharge to a stiff paste with glycerol. This quickly sets to a hard mass, impervious to water or gases.

Acetone collodion, a solution of collodion in acetone, is very useful as a lute in the laboratory. Painted on with a brush, it quickly dries to a hard film which is proof against water and dilute acids, and is perfectly impervious to gases. It may be used to lute cork or rubber stoppers, to cover rubber tubing, to waterproof labels, &c., but it should not be subjected to a temperature above 150°C.

A lute acquiring a hardness equal to that of marble, and known as *oxychloride of zinc cement* (Sorel's cement), is prepared by dissolving 3 p.c. of borax in a solution of zinc chloride of 1·49–1·65 sp.gr. with addition of sufficient recently ignited zinc oxide to produce the proper consistency.

Magnesia cement is prepared by makng a paste of powdered magnesite and 10–20 p.c. conc. hydrochloric acid, forming it into blocks, igniting, and finally grinding to powder. With water this yields a strong cement which quickly sets hard, but is not absolutely fireproof.

Bruyère's hydraulic cement is prepared by heating to bright redness for 3 hours a mixture of 3 parts clay and 1 part slaked lime, and powdering the product.

A cement employed for closing leaks in boilers, &c., is prepared by mixing 6 parts clay and 1 part iron filings to a paste with boiled linseed oil.

Iron cement, for permanently closing joints in iron, consists of a mixture of 100 parts iron filings, 3–20 parts flowers of sulphur, and 3–5 parts ammonium chloride, mixed with water to a paste and applied quickly. The larger proportion of sulphur is required when the iron filings are fine. The mixture soon becomes hot, with evolution of ammonia and sulphuretted hydrogen, and in a short time becomes almost as hard as iron. It is stated that the best iron lute consists of a mixture of 100 parts iron filings with only 1 or 2 parts of sal ammoniac and no sulphur. This lute, however, though stronger, requires a considerable time to set.

For coating earthenware, a paste is applied consisting of a mixture of equal parts of zinc white and fine sand, made into a paste with a concentrated solution of zinc chloride. *Willis' lute* for the same purpose consists of a paste made with slaked lime and a solution of 2 oz. borax in 1 pint water. It is applied with a brush, and when dry is covered with a plastic mixture of slaked lime and linseed oil and is ready for use after a few days.

Among lutes for resisting high temperatures may be mentioned Stourbridge clay made into a paste with water, which withstands a higher temperature than any other lute in general use, and *Windsor loam*, a natural mixture of clay and sand. Both are used for coating vessels and for packing hot joints of metal vessels. With the addition of about one-tenth part of borax these clays are useful for glazing earthenware vessels. Leaks and fractures in furnace linings, &c., may be stopped with *ganister*, a highly silicious fireclay.

Gas retorts and similar vessels closed temporarily to withstand high temperatures are usually merely luted with mortar.

For luting crucibles, a paste of fireclay and powdered firebrick is useful, preferably with addition of a small proportion of borax to render the lute coherent.

A most valuable mixture for repairing broken furnaces, &c., consists of a paste of firebrick and liquid sodium silicate. Even considerable openings, if roughly filled with broken firebricks, may be sealed with this lute (*v.* CEMENTS).

A fireproof cement for repairing retorts, &c., is made by taking 200 cwt. china clay, 100 cwt. barytes, 40 gall. sodium silicate (100°Tw.), 24 gall. water, and 28 lbs. borax, mixing well and adding magnesite to the extent of 25 p.c. of the mixture (Williams, Eng. Pat. 18064, 1903).

A lining for furnaces and crucibles may be made from 4 parts granular corundum, ground to a fine powder, mixed with 1 part powdered graphite and made into a paste with 10 p.c. of sodium silicate (Crowley and Payne, Eng. Pat. 8627, 1906; *v.* also Kilburn Scott, J. Soc. Chem. Ind. 1905, 501).

LUTIDINES, LUTIDINIC ACID, *v.* BONE-OIL.

LYCETOL. Trade name for dimethyl piperazine tartrate.

LYDIAN STONE or **LYDITE.** A black, jaspideous or cherty variety of quartz, which from its hardness and the closeness of its grain has been used as a touchstone for testing the quality of gold, whence its name *basanite*. The metal to be tested is rubbed on the polished surface of the stone, and the streak thus produced is compared with the streaks made by a series of alloys of known composition; the observer judging of the purity of the metal by the colour of the mark and by its behaviour when treated with a drop of acid. Lydite is also used as a hone-stone. Most Lydian stone has a schistose structure, and may be described as a hornstone-slate, or *Kieselschiefer*. The Lydian stone of Devon and east Cornwall is a fine-grained, indurated, carbonaceous shale, belonging to the Culm-measures. L. J. S.

LYDDITE *v.* EXPLOSIVES.

LYDIN. A synonym for mauve or aniline purple.

LYSINE $NH_2[CH_2]_4CH(NH_2)CO_2H$, *αε-diaminohexoic acid*, was discovered by Dreschel (J. pr. Chem. 1889, [ii.] 39, 425) among the products of hydrolysis of casein by hydrochloric acid and stannous chloride; it is produced by the hydrolysis of other proteins, conglutin, egg albumen, fibrin (Siegfried, Ber. 1891, 24, 418), and gelatin (Ernst Fischer, Arch. Anat. u. Physiol. 1891, 265); it occurs in antipeptone prepared from fibrin (Kutscher, Zeitsch. physiol. Chem. 1898, 25, 195); together with arginine it forms the chief product of hydrolysis of the protamines sturine, β-cyprinine, and crenilabrine (Kossel, Zeitsch. physiol. Chem. 1899, 26, 588; 1904, 40, 565; 1910, 69, 138); and it also occurs among the hydrolytic products of the proteins of the seeds of various conifers, and the seedlings of *Lupinus luteus* (Linn.) (Schulze and Winterstein, Zeitsch. physiol. Chem. 1899, 28, 459, 465; 1901, 33, 547).

Dreschel (Chem. Zentr. 1891, ii. 712) showed that lysine is a diaminocaproic acid, and Ellinger (Ber. 1899, 32, 3542) proved that the two amino groups are in the αε- positions, because on decomposition by putrefaction in an atmosphere of hydrogen, lysine is partially converted into cadaverine (pentamethylenediamine)

$$NH_2[CH_2]_4CH(NH_2)CO_2H = CO_2 + NH_2[CH_2]_5NH_2.$$

The synthesis of *i*-lysine has been effected by Fischer and Weigert (Sitzungsber. K. Akad. Wiss. Berlin, 1902, 270) from ethyl γ-cyanopropylmalonate; when this compound is treated with ethyl nitrite it gives ethyl α-oximino-δ-cyanovalerate $CN[CH_2]_3C(NOH)CO_2Et$, which on reduction with sodium in alcoholic solution, yields αε-diaminohexoic acid or *i*-lysine

$$NH_2[CH_2]_3CH(NH_2)CO_2H,$$

this is isolated by successive transformation into the phosphotungstate and picrate; the *picrate* forms thick needles that darken at 230°; the *hydrochloride* is crystalline and melts at 183°–186° (corr.); the *phenylcarbimide* forms colourless needles, m.p. 182°–185° (corr.); these derivatives differ from the corresponding derivatives of the naturally occurring *d*-lysine in being optically inactive and having slightly different melting-points. A further synthesis of *i*-lysine from ethyl cyanopropylphthaliminomalonate is described by Sörensen (Chem. Zentr. 1903, ii. 33); when this compound is reduced with sodium in alcoholic solution it yields the corresponding amino compound

$$C_6H_4:(CO)_2:N{\cdot}C(CO_2Et)_2[CH_2]_4NH_2,$$

which is transformed by the action of concentrated hydrochloric acid into *i*-αε-diaminohexoic acid (*i*-lysine).

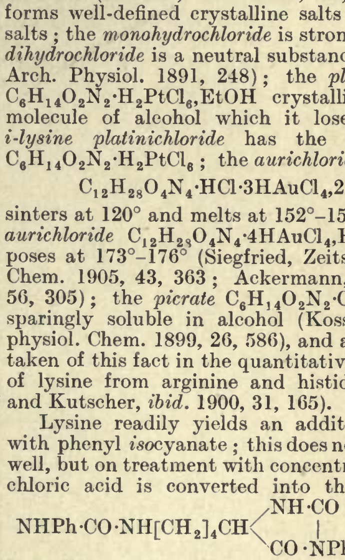
i-Lysine can also be obtained by a synthetic process from piperidine (Julius von Braun, Ber. 1909, 42, 839). The opening of the piperidine ring by phosphorus pentachloride affords among other products, benzoyl-ε-leucinenitrile $COPh{\cdot}NH[CH_2]_5CN$, which contains the skeleton of lysine, and yields on hydrolysis ε-benzoylaminohexoic acid $COPh{\cdot}NH[CH_2]_5CO_2H$; this on bromination forms the α-bromo derivative $COPh{\cdot}NH[CH_2]_4CHBr{\cdot}CO_2H$, which reacts with ammonia to give α-amino-ε-benzoylaminohexoic acid $COPh{\cdot}NH[CH_2]_4CH(NH_2)CO_2H$, from which *i*-lysine is obtained by hydrolysis.

Derivatives. *Salts.*—*d*-Lysine is a syrup (Winterstein, Zeitsch. physiol. Chem. 1905, 45, 77), it has $[\alpha]_D + 17{\cdot}5°$ in hydrochloric acid solution (Lawroff, *ibid.* 1899, 28, 388), and forms well-defined crystalline salts and double salts; the *monohydrochloride* is strongly acid, the *dihydrochloride* is a neutral substance (Dreschel, Arch. Physiol. 1891, 248); the *platinichloride* $C_6H_{14}O_2N_2{\cdot}H_2PtCl_6,EtOH$ crystallises with 1 molecule of alcohol which it loses at 120°; *i-lysine platinichloride* has the composition $C_6H_{14}O_2N_2{\cdot}H_2PtCl_6$; the *aurichloride*

$$C_{12}H_{28}O_4N_4{\cdot}HCl{\cdot}3HAuCl_4,2H_2O$$

sinters at 120° and melts at 152°–155°; *i-lysine aurichloride* $C_{12}H_{28}O_4N_4{\cdot}4HAuCl_4,H_2O$ decomposes at 173°–176° (Siegfried, Zeitsch. physiol. Chem. 1905, 43, 363; Ackermann, *ibid.* 1908, 56, 305); the *picrate* $C_6H_{14}O_2N_2{\cdot}C_6H_3N_3O_7$ is sparingly soluble in alcohol (Kossel, Zeitsch. physiol. Chem. 1899, 26, 586), and advantage is taken of this fact in the quantitative separation of lysine from arginine and histidine (Kossel and Kutscher, *ibid.* 1900, 31, 165).

Lysine readily yields an additive product with phenyl *iso*cyanate; this does not crystallise well, but on treatment with concentrated hydrochloric acid is converted into the *hydantoin*



$$NHPh{\cdot}CO{\cdot}NH[CH_2]_4CH\left\langle\begin{array}{l}NH{\cdot}CO\\ \quad\ \ |\\ CO{\cdot}NPh\end{array}\right.$$

, which is crystalline and melts at 183°–184° (Herzog, Zeitsch. physiol. Chem. 1902, 34, 525); the corresponding derivative of *i*-lysine has m.p. 156° (von Braun, Ber. 1909, 42, 839). *Lysuric acid*, the dibenzoyl derivative of lysine, has m.p. 144°–145°; the *acid barium salt*

$$2(C_6H_{12}Bz_2N_2O_2),(C_6H_{11}Bz_2N_2O_2)_2Ba,2H_2O$$

crystallises in beautiful needles, m.p. 144°–148°, at which temperature it becomes anhydrous; the *normal barium salt* $(C_{20}H_{21}N_2O_4)_2Ba,1\frac{1}{2}H_2O$ is a white crystalline powder, m.p. 168°; the *acid sodium salt* is white and crystalline, m.p. 108°–109°, and contains H_2O; the *acid strontium salt* contains $2H_2O$, crystallises in plates, and has m.p. 137°–138°; the *normal strontium salt* contains H_2O and is crystalline; the silver salt $C_{20}H_{21}N_2O_4Ag,1\frac{1}{2}H_2O$ is white and amorphous (Dreschel, Ber. 1895, 28, 3189; Willdenow, Zeitsch. physiol. Chem. 1898, 25, 523). *Methyl lysine hydrochloride* prepared by the action of methyl alcohol and hydrogen chloride on *i*-lysine hydrochloride, has m.p. 218° (decomp.); *lysine anhydride*, obtained by heating the methyl ester at 100°, forms the *picrate* $C_{12}H_{24}O_2N_4{\cdot}2C_6H_3O_7N_3$ yellow prisms or plates decomposing at 230°

(corr.), and the *hydrochloride*, microscopic colourless needles decomposing at 270° (corr.) (Fischer and Suzuki, Sitzungsber. K. Akad. Wiss. Berlin, 1904, 1333). *d-Lysyl-lysine dipicrate* $C_{12}H_{26}O_3N_4,(C_6H_3O_7N_3)_2$, m.p. 238°–242° was isolated from the products of hydrolysis of pepsin extract (Hugounenq and Morel, Compt. rend. 1909, 148, 236); *i-lysyl-lysine* $C_{12}H_{26}O_3N_4$ forms a yellow crystalline *picrate*, m.p. 185° (corr.), and a *hydrochloride* crystallising in short twin prisms, m.p. 205° (corr.) (Fischer and Suzuki, Ber. 1905, 38, 4173).

Lysine yields carbamide when decomposed by barium hydroxide (Dreschel, Ber. 1890, 23, 3096); it is oxidised by barium permanganate, yielding glutaric acid as the chief product (Zickgraf, Ber. 1902, 35, 3401); and when the sulphate or hydrochloride is treated with barium or silver nitrite, αε-dihydroxyhexoic acid, an aminohydroxyhexoic acid, m.p. 200°–201°, and a small amount of an alkaline yellow amorphous substance $C_6H_{13}O_3N$, m.p. 176°–178°, are produced (Szydlowski, Monatsh. 1906, 27, 821).

M. A. W.

M

MACE. *Description.*—Mace is the dried arillus or seed coat of the nutmeg, the latter being the fruit of *Myristica fragrans* (Houtt.) (or *Myristica argentea* (Warb.), *see* below).

The tree is a native of the Malay Archipelago, and is cultivated in both the East and West Indies.

The fruit (nutmeg) is surrounded by four coats: a thick pericarp on the outside, then the crimson arillus, then a thick tegument, and finally a thin membrane closely adherent to the kernel.

Many other species of *Myristica* are known in addition to *M. fragrans* (Banda or true mace), but only one yields aromatic seeds, viz. *M. argentea*, which furnishes the Papuan or Macassar mace.

The chief varieties of mace which appear on the British market are Penang, Singapore, Java, and West Indian, the first being the most highly esteemed. All these are derived from *Myristica fragrans*, but a small quantity of Macassar mace is also imported, and this variety has hitherto been sold as "mace" without any question being raised as to its genuineness. As it appears in commerce mace has a yellow-brown colour, the lighter the better. The arillus, when unbroken, is about 1½ inch long and ¾ inch wide at the base. It is usually flattened, the tapering segments or blades being from ⅛ to ¼ inch wide. Macassar mace is of a dull brown colour and has much wider blades. Both varieties have a similar aromatic flavour, but that of Macassar mace is distinctly acrid (*v.* Holmes, Pharm. J. 1908, 652). The sole use of mace is as a flavouring agent and condiment.

Composition.—The chief constituents of mace are a volatile oil to which the flavour is mainly due, a fixed oil and a carbohydrate, amylodextrin, the granules of which are easily visible under the microscope and turn red on treatment with iodine. The following table shows the composition of Banda and Macassar mace, and also of false or Bombay mace (*see* below).

(From Winton, Ogden and Mitchell, U.S. Dept. of Agric., Bul. 13 and 65, and other sources.)

			Ether extract				
	Water	Ash	Volatile oil	Fixed oil	Amylo-dex-trin	Crude fibre	Nitro-gen
Mace (*Myristica fragrans*)	5·67 to 12·04	1·62 to 4·10	4·04 to 10·80	21·20 to 29·08	22 60 to 31·60	2·90 to 8·90	0·73 to 1·12
Macassar mace .	4·18	2·01	5·89	53·50	10·40	4·57	1·11
Bombay mace .	0·32 to 7·04	1·36 to 1·98	0·00 to 0·67	56·70 to 59·80	16·20	3·21 to 8·17	0·81 to 0·79

Adulteration.—The only sophistication to which whole mace is liable is the addition of Bombay mace which is derived from *Myristica malabarica* (Lam.). The arillus of this species is about 2½ inches long by ¾ inch wide, and the numerous blades are narrow and their vermiform ends are coiled in a tangled mass at the apex. It is of a deep red-brown colour, and almost devoid of aroma. As it is quite useless as a flavouring agent, and its price is about one-fourth that of genuine mace, its presence in the latter can only serve the purposes of fraud.

Bombay mace is also the chief adulterant of ground mace, but potato, arrowroot, the cereal starches, and ground olive stones may possibly be found.

Detection of adulteration.—The presence of any of the above adulterants is best detected by means of the microscope. Banda and Macassar mace are practically indistinguishable from one another, but the presence of Bombay mace is at once revealed by the appearance of the dark orange-coloured oil cells, the contents of which when treated with alkali assume a blood-red tint. The oil cells in Banda and Papua mace are fewer in number, of a light yellow colour, and alter only slightly in appearance when treated with alkali. A further characteristic, which however can only be seen in transverse sections, is that the epidermal cells in Bombay mace are radially elongated whilst in the case of the other two varieties the elongation is tangential.

Chemical tests for the presence of Bombay mace are also available (Schneider, J. Pharmacol. 4, 57; Hefelmann, Pharm. Zeit. 1891, 122; Busse, Zeitsch. Nahr. u. Genussm. 1904, 590).

For the estimation of Bombay mace in the presence of Banda mace, provided that Macassar mace be absent, the determination of the fixed ether extract will afford a fair basis for calculation. Soltsien (Zeitsch. öffentl. Chem. 3, 253) recommends a preliminary extraction with light petroleum, the extract thus obtained being ten times greater from Bombay than from Banda mace.

The information thus obtained should be supplemented by comparison, under the microscope, of the sample with a mixture of Banda and Bombay maces in the proportions indicated. If there is a great discrepancy in the number of the characteristic orange-coloured oil cells the presence of Macassar mace may be suspected. The following test for this variety may also be applied (Griebel, Zeitsch. Nahr. Genussm. 1909, 202):—

Shake up 0·1 gram of the sample with 10 c.c. of light petroleum for 1 minute, filter and mix 2 c.c. of the filtrate with 2 c.c. of glacial acetic acid, and add concentrated sulphuric acid so as to form a layer under the acetic acid solution. In the presence of not less than about 20 p.c. of Macassar mace a red ring forms at the junction of the two layers, within two minutes. Banda mace similarly treated yields only a yellow ring within the same period, whilst Bombay mace produces no colour at all. Comparison experiments with samples of known authenticity should always be made.

Further confirmation of the presence of Bombay mace may be obtained by estimating the essential oil, preferably by Cripps's process (Analyst, 1909, 519), and the characters of the fixed oil may also be of use. These are shown in the following table (Spaeth, *ibid.* 1895, 200):—

RESULTS OF EXAMINATION OF THE FIXED OIL OF MACE.

	Melting point	Saponification number	Iodine number	Refraction index	Meissl number
True mace	25·0° to 26·0°	169·9–173·0	75·6–80·8	1·48–1·487	4·1–4·2
Macassar mace					—
Bombay mace	31·0° to 31·5°	189·4–191·4	50·4–53·5	1·463	1·0–1·1

Standards.—The standard fixed by the United States Department of Agriculture is as follows: Mace should contain not less than 20 nor more than 30 p.c. of fixed ether extract; not more than 3 p.c. of total ash; not more than 0·5 p.c. of ash insoluble in hydrochloric acid; and not more than 10 p.c. of fibre.

Soltsien (Zeitsch. öffentl. Chem. 3, 253) suggests that the ether extract after removal of the fat by light petroleum should never exceed 5·5 p.c. C. H. C.

MACE OIL *v.* OILS, ESSENTIAL.

MACLURIN *v.* OLD FUSTIC.

MADDER. Madder is the ground root of the *Rubia tinctorum* (Linn.), and has been cultivated for dyeing purposes from a remote antiquity, so remote indeed that one is unable to say with certainty from which countries it originated. It is known to have been employed by the ancient Egyptians, Persians, and Indians, probably by the latter in the first instance, and more recently by the ancient Greeks and Romans. About the time of the Crusades the cultivation of madder was introduced into Italy and probably also into France. The Moors cultivated it in Spain, and during the 16th century it was brought to Holland. Colbert introduced it into Avignon in 1666, Frantzen into Alsace in 1729, but only towards 1760–1790 did it become important. During the wars of the Republic, its cultivation was largely abandoned, and only after 1815 did this again become regular.

Owing to the beauty and fastness of the tints it yields, and the variation in colour that can be produced from it by a variation in the mordant, it was considered until recently as perhaps the most important dyestuff known. Although the commercial value of this product has been reduced to a minimum, through the introduction of artificial alizarin, it has still considerable scientific interest.

The plant is an herbaceous perennial belonging to the natural family of the *Rubiaceæ*, and its valuable portion is entirely the root, which is usually of considerable length but does not exceed an ordinary slate pencil in thickness. Old roots are richer in colour than young ones, and the plant is consequently left in the soil for at least 18 and sometimes for 28 months. It is subsequently removed from the soil, usually washed with water, allowed to dry in the sun or artificially by means of kilns, then finely ground and packed in casks. In certain districts, before grinding, it was stored in pits for several months, by which its tinctorial power was said to be greatly enhanced; but these and other refinements of its preparation are now of so little importance as to be hardly worthy of mention. The whole root bears in many countries the name 'alizari' or 'lizari,' whence we have the name 'alizarin.' Madder was principally cultivated in Holland, France, and Turkey, and to a less extent in Belgium, Italy, and Germany, and North and South America, but the small quantity which enters this country is principally obtained from Holland. Perhaps no substance was submitted to so much examination by the older chemists as madder, and in many of the earlier works on dyeing much space is occupied by a description of these researches.

The isolation of the most important colouring matters of madder, alizarin, and purpurin, occurred as far back as 1826 and 1828, and was due to the chemists, Robiquet and Colin; but it is a matter of doubt, whether they were successful in obtaining these substances in a state of chemical purity. By many of the earlier workers it was considered that these colouring matters did not exist as such in madder, but were present in combination with sugar or some other substance. About 1823, Kuhlmann extracted a bitter-sweet yellow amorphous compound from the root and named it xanthin, and a similar yellow substance was also isolated by Runge and Watt. In 1848, Higgin observed that if a cold aqueous solution of madder which has a deep yellow colour and an intensely bitter taste was allowed to stand for some time or was heated to 50°, it lost these characteristics, and a gelatinous flocculent precipitate was formed in which all the tinctorial power of the original infusion resided. Higgin considered, therefore, that the xanthin of madder must during this process have been converted into alizarin, and that the change was probably brought about by the action of some ferment contained in the madder, and extracted along with the xanthin by cold water. Somewhat later (1851), Schunck isolated from madder a substance which he called rubian, as a dark, brownish-yellow, transparent, amorphous hard mass, which by hydrolysis with acids or by the action of the special madder ferment, which he termed 'erythrozym' was converted into glucose, alizarin, and other substances.

The next important step was due to Rochleder, who prepared the alizarin glucoside in a crystalline condition and named it ruberythric acid. It appeared to possess the formula

$C_{20}H_{22}O_{11}$, and its hydrolysis could be represented according to the following equation:

$$C_{20}H_{22}O_{11} = H_2O + \underset{\text{Alizarin.}}{C_{14}H_8O_4} + \underset{\text{Sugar.}}{C_6H_{12}O_6}.$$

Subsequently, Schunck prepared a crystalline compound, rubianic acid, which he regarded as an oxidation product of rubian, and which proved to be identical with the ruberythric acid of Rochleder.

Finally, this portion of the subject was exhaustively examined by Liebermann and Bergami, who assigned the formula $C_{26}H_{28}O_{14}$ to ruberythric acid, and proved that its hydrolysis with acid proceeds as follows:

$$C_{26}H_{28}O_{14} + 2H_2O = C_{14}H_8O_4 + 2C_6H_{12}O_6.$$

For the preparation of the glucoside, madder (1 kilo.) is extracted with boiling absolute alcohol (8–9 litres) for 2 to 4 hours, and the mixture filtered hot. The alcoholic extract is evaporated to about one-quarter its bulk, and on cooling a yellowish-brown crystalline precipitate of the impure glucoside separates. After filtering and evaporating the filtrate still further, crystals of cane sugar separate, and by adding water to the remaining alcoholic solution impure alizarin is precipitated. In this way, according to Liebermann and Bergami, 1 kilo. of madder gave

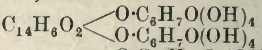
Impure glucoside . .	50–60 grams	(5–6 p.c.)
„ sugar . .	15–30 „	(1·5–3 „)
„ colouring matter	30–40 „	(3–4 „)

The impure glucoside, which becomes resinous on drying, is dissolved in water, the solution is precipitated with lead acetate, filtered and the filtrate treated with basic lead acetate. The pink coloured precipitate is well washed, suspended in water, decomposed with sulphuretted hydrogen, and the lead sulphide which contains also the liberated ruberythric acid is collected and washed with cold water. The ruberythric acid is removed from the lead sulphide by means of boiling alcohol, the yellow extract is partially evaporated, water and some quantity of barium hydroxide solution are added, and after filtering off a white precipitate, an excess of barium hydroxide is added to the filtrate. The dark cherry-red precipitate of barium ruberythrate is dissolved in acetic acid, the solution is filtered, barely neutralised with ammonia, and then treated with tribasic lead acetate. The resulting red precipitate is washed with alcohol, suspended in alcohol and decomposed by hydrogen sulphide, and the liquid and precipitate together are heated to boiling and filtered hot. On cooling, the amber-coloured solution yields pale yellow needles of ruberythric acid which are recrystallised from hot water. The latter portion of this process, employed by Liebermann and Bergami, is due to Rochleder.

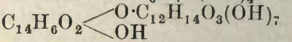
Ruberythric acid crystallises in silky needles of a pure yellow colour, melts at 258°–260°, and when strongly heated yields a sublimate of alizarin. It dissolves in caustic alkaline solutions with a cherry-red colour, which on boiling changes to violet, and on acidification a precipitate of alizarin separates. With potassium carbonate solutions, dark-red needles of potassium ruberythrate are produced. Ruberythric acid is not precipitated with lead acetate, but basic lead acetate gives a red flocculent precipitate. It possesses no dyeing power.

By the action of sodium acetate and acetic anhydride, Liebermann and Bergami obtained an octoacetyl derivative $C_{26}H_{20}O_6(C_2H_3O_2)_8$, which crystallises in yellow needles, melting at 230°.

Schunck and Marchlewski, by means of the method of Schotten and Baumann, obtained a hexabenzoyl, and a heptabenzoyl compound. The fact that ruberythric acid gives an octoacetyl derivative renders two constitutions possible for this substance, viz.:

I. 

$$C_{14}H_6O_2 \begin{cases} O{\cdot}C_6H_7O(OH)_4 \\ O{\cdot}C_6H_7O(OH)_4 \end{cases}$$

II. 

$$C_{14}H_6O_2 \begin{cases} O{\cdot}C_{12}H_{14}O_3(OH)_7 \\ OH \end{cases}$$

and of these the second is most probably correct, as an explanation is thus afforded of the well-characterised red-coloured salts which can be obtained from it.

Erythrozym, the madder enzyme, was prepared by Schunck by extracting madder with water at a low temperature (38°) and precipitating the solution with alcohol. When dried, it consisted of a brown amorphous mass. Under its influence, ruberythric acid is hydrolysed with formation of alizarin and glucose. This reaction no doubt takes place in the incompletely dried root on storing, and it is evidently due to this fact that madder was said to dye more readily after this treatment. In dyeing with madder, moreover, the presence of this enzyme will no doubt exercise a beneficial effect, because as it is frequently the practice to employ at first a cold dyebath and then to gradually raise the temperature, hydrolysis of the glucoside, which is itself devoid of tinctorial property, will thereby occur with formation of the colouring matter.

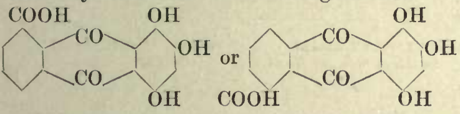
Though purpurin is considered to exist in madder in the form of glucoside, such a compound has not yet been isolated, and some uncertainty exists on this point. During some experiments carried out by the writer, it was found that an alcoholic extract of madder, on standing in cold weather, deposited a considerable quantity of cane sugar contaminated with a red precipitate. This latter was soluble in water, and on treating the solution with cold dilute acid, gave a precipitate of impure purpurin and appeared to consist of an acid calcium salt of this substance. On the other hand, it was not ascertained whether all varieties of madder behave similarly in this respect, and the matter requires further investigation. Presuming, however, that a purpurin glucoside is present in madder, it is evident that this compound is far less stable than ruberythric acid, and is hydrolysed by dilute acids at a temperature at which the latter is unaffected.

Kopp's process for the extraction of madder.—Based on this assumption, the commercial process of Kopp was devised, and this is specially interesting as it affords a fairly complete method for the isolation of the phenolic constituents of this dyestuff.

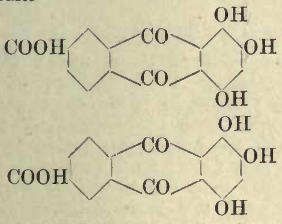
Ground madder is extracted with a cold aqueous solution of sulphurous acid, and the solution, after addition of 2 to 3 p.c. of hydrochloric acid (33 p.c.), is heated to 60°. A red flocculent precipitate of purpurin is thus thrown down which was collected, washed, dried, and sold under the name of 'commercial purpurine' or 'Kopp's purpurine.' This product is still prepared to a very small extent in France for the manufacture of a rose red lake, and for this purpose gives results differing in some respects from those produced by the artificial dyestuff.

Kopp's purpurine, in fact, is not pure purpurin, but consists mainly of a mixture of this colouring matter with three other substances: *pseudoPurpurin*, *Purpuroxanthin*, and *Purpuroxanthin carboxylic acid* or *Mungistin*.

pseudoPurpurin was first isolated from Kopp's commercial product by Schutzenberger and Schiffert, but the fact that it consists of a purpurin carboxylic acid is due to the investigation of Rosenstiehl. It consists of small red prismatic needles, and differs from purpurin in that it is more readily soluble in benzene. It melts at 218° to 220°, with evolution of carbon dioxide and formation of purpurin, and this decomposition is said to occur gradually at from 180° to 195°. Purpurin is also produced by boiling *pseudo*purpurin with dilute caustic alkali, and by long boiling with water or alcohol. The constitution of *pseudo*purpurin is represented by one of the two following formulæ:

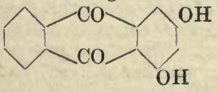


It has not been prepared synthetically, but it is interesting to observe that an isomeric compound which is obtained by the oxidation of alizarin carboxylic acid, and for which also the two formulæ



are possible, differs markedly from *pseudo*purpurin, and is an exceedingly stable compound (Perkin and Cope).

Purpuroxanthin or Xanthopurpurin, which forms glistening yellow needles, melting at 262°–263°, is a dihydroxyanthraquinone isomeric with alizarin, and was isolated from Kopp's purpurine by Schutzenberger and Schiffert. These authors also found that purpuroxanthin can be produced by digesting purpurin with phosphorus iodide and water, or by the action of a boiling alkaline stannous chloride solution on this colouring matter. The reverse action occurs, according to Rosenstiehl, when an alkaline solution of purpuroxanthin is boiled with excess of air, purpurin being thus produced. Purpuroxanthin was synthesised by Noah by heating 3:5-dihydroxybenzoic acid with benzoic acid in the presence of sulphuric acid, and possesses the following constitution:



According to Plath, the dimethyl ether melts at 178°–180°, and the diacetyl derivative (Liebermann) at 183°–184°.

Purpuroxanthin dyes aluminium mordanted fabrics a yellow colour (Schutzenberger and Schiffert).

Purpuroxanthin carboxylic acid (*Mungistin*) was discovered by Schunck and Römer in the crude purpurin. It crystallises from acetic acid in golden yellow leaflets, melts at 231°, and dissolves in alkaline solutions and ammonia with a red colouration. By heating above its melting-point or by boiling with alkalis, it is converted into purpuroxanthin. It has not been prepared synthetically, but probably contains its carboxyl group, in a similar position to that present in *pseudo*purpurin. It is said to dye aluminium mordanted fabrics an orange-red colour, which is, however, not fast to the action either of soap or light.

Green alizarin.—The sulphurous acid liquid from which the purpurin precipitate has been removed, is boiled for 2 hours, when the ruberythric acid and certain other glucosides present are hydrolysed and a deep green precipitate separates. This at one time was a commercial article, and was known under the name of 'green alizarin.'

Chlororubin.—The green tinge of this product arises from the presence in madder of a considerable quantity of a peculiar substance, possibly a glucoside, termed *chlorogenin* or *rubichloric acid*, but little or nothing is known of its chemical nature. It is also present in chay root, *Morinda* root, in certain species of *Galium* and in the *Gardenia grandiflora*. This compound, which has been obtained in the form of a colourless syrup and to which the formula $C_{14}H_8O_9$ has been assigned, on digestion with boiling dilute mineral acid, is converted into chlororubin and formic acid. Chlororubin consists of a dark green amorphous powder which is insoluble in all the usual solvents, but dissolves in alkaline solutions with a blood-red colour.

Yellow alizarin.—In order to obtain this product, the dried and finely powdered 'green alizarin' was extracted at 150° with petroleum oil (toluene or coal-tar solvent naphtha is more suitable for laboratory purposes), by which means the alizarin and other phenolic constituents pass into solution, whereas the chlororubin remains undissolved. The petroleum extract after cooling is agitated with 10 p.c. caustic soda solution, and the dark violet-coloured alkaline liquid thus produced is removed and neutralised with acid. The bright yellow precipitate was collected, washed, and dried and sold under the name of 'yellow alizarin.'

The alizarin prepared in this manner is not completely pure as it contains a small quantity of a mixture of non-tinctorial substances, which are derivatives of anthraquinone. To remove these, an alkaline solution of the 'yellow alizarin' is treated with milk of lime, which precipitates the alizarin in the form of its calcium compound. This, when collected, well washed, and decomposed with acid, gives a very pure alizarin which is best crystallised from solvent naphtha.

If the reddish-brown filtrate from the calcium alizarate is neutralised with acid, a small quantity of a dull yellow precipitate separates which is approximately equal to 0·02 p.c. of the madder employed. A preliminary examination of this product, carried out by the writer several years ago, indicated that it consisted of at least four yellow crystalline substances, with no special properties that would permit of their ready separation.

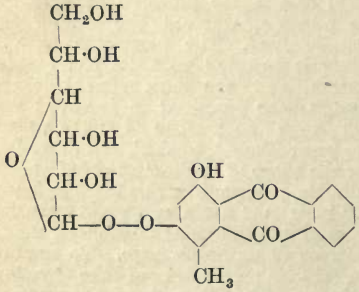
Schunck during his examination of madder obtained various yellow crystalline and amorphous products, by the action of acids and alkalis on his rubian. The individuality of most of these substances, to which the names rubiretin, verantin, rubiadin, rubianin, rubiafin, rubiagin, rubiadipin, rubidehydran, rubihydran, and rubiacic acid were assigned, has been doubted by later writers, and but one of these—namely, rubiadin—has been characterised. On the other hand, it is quite possible that certain of these may exist in the mixture of yellow non-tinctorial substances previously referred to. For a description of his compounds, the original papers of Schunck should be referred to.

Rubiadin glucoside (Schunck and Marchlewski). Madder is extracted with boiling water, the solution precipitated with lead acetate, and the filtrate treated with ammonia, by which means a second lead precipitate is formed. The latter is decomposed with sulphuric acid, the lead sulphate removed, and the clear liquid boiled with addition of hydrochloric acid. A dark green precipitate separates, only a portion of which dissolves in boiling alcohol. On treating the alcoholic extract with lead acetate, the alizarin present can be removed, and addition of baryta water now precipitates the barium salt of the rubiadin glucoside, which is decomposed by dilute hydrochloric acid. It crystallises from alcohol in citron yellow needles, melts at 270° with decomposition, and when hydrolysed by acid gives rubiadin and glucose

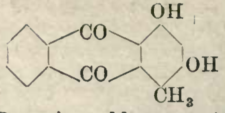
$$C_{21}H_{20}O_9+H_2O=C_{15}H_{10}O_4+C_6H_{12}O_6$$

Penta-acetylrubiadin glucoside, yellow needles, melts at 237°.

According to Marchlewski, the constitution of this glucoside is best expressed as follows:



Rubiadin, prepared by the hydrolysis of the glucoside, forms yellow needles, melting about 290°, soluble in alkalis with a red colouration. By oxidation with chromic acid it gives phthalic acid. Rubiadin, according to Schunck and Marchlewski, is a methyl purpuroxanthin and possesses the following constitution:



Rubiacin (Runge's madder orange) is a yellow crystalline substance obtained directly from the madder root, and is formed according to Schunck by the decomposition of a glucoside. It separates in small quantity from an infusion of madder made with only a little cold water, after it has become sour by 12 hours' standing. It crystallises in the form of plates and needles having a strong reddish-green lustre. Alkalis dissolve it with a purple colour.

The following table illustrates the analysis of madder by the sulphurous acid extraction method.

Madder is extracted with dilute sulphurous acid solution and the extract heated to 60°.

- Precipitate consists of Purpurin, Pseudo-purpurin, Purpuroxanthin carboxylic acid, Purpuroxanthin.
- Filtrate is digested with boiling dilute H_2SO_4, and the resulting precipitate of green alizarin extracted with boiling toluene or petroleum.
  - Chlororubin remains undissolved.
  - The toluene extract is agitated with caustic soda solution, and the alkaline liquid is treated with Baryta water.
    - Precipitate consists of calcium alizarate, which when decomposed with acid gives alizarin.
    - Filtrate on acidification gives a precipitate of yellow non-tinctorial derivatives of anthraquinone.

COMMERCIAL PREPARATIONS OF MADDER.

The principal of these were: Garancine, Garanceux, Flowers of Madder, Commercial Alizarin or Pincoffin, and Madder extract.

Garancine.—The preparation of this product results from the observation in 1827 of Robiquet and Colin, that by treating ground madder with an equal weight of concentrated sulphuric acid, the various principles of the madder were destroyed with the exception of the colouring matter alizarin. We now know further that the glucoside of the root is decomposed by the action of the acid. This first product was termed *charbon sulphurique*, but soon the method of its preparation was slightly altered, and it then received the name *garancine*.

Garancine was made by mixing, in a wooden tank with false bottom, 100 kilos. ground madder, 1000 litres water, and 2 kilos. sulphuric acid, 168°Tw. (sp.gr. 1·84), stirring up and allowing the whole to macerate for about 12 hours. The liquid is then drawn off, the residue is mixed with a little water and 30 kilos. strong sulphuric acid, and the whole is boiled for 2–3 hours. After running off the acid liquor, the garancine remaining is washed with water till free from acid, drained, pressed, dried and ground.

The colouring power of garancine is 3–4 times that of good madder, it dyes more readily, giving yellower toned reds and pinks, and greyer lilacs. They are not quite so fast to soap as the madder colours, but since, in the case of printed calicoes, the unmordanted white parts are not so much soiled in the dye-bath, the operation of soaping can be omitted.

Garanceux or *Spent Garancine* was introduced in 1843 by L. Schwarz of Mulhouse. It was simply a low quality of garancine prepared in the above manner from the spent madder of the dye-baths, and made by each calico-printer for himself, by way of economy. Its colouring power is about one-fourth that of good garancine.

Flowers of madder was first made in 1851 by Julian and Rogner of Sorgues. It can be prepared by macerating ground madder for several hours with cold water very slightly acidulated with sulphuric acid (1–2 p.c. on the weight of madder), then washing, draining, pressing, drying, and grinding. In this manner all soluble, mucilaginous, and sugary matter, &c., is removed, decomposition of the glucoside by fermentation occurs, and the residue has nearly double the colouring power of the original madder. The waste liquors were neutralised, allowed to ferment with the addition of yeast, and then distilled to gain the alcohol. 100 kilos. madder yielded 45–60 kilos. flowers of madder and 10 litres alcohol, suitable for making varnish, &c.

Commercial Alizarin or *Pincoffin* was introduced in 1852 by Schunck and Pincoff, who prepared it by submitting ordinary garancine to the action of high pressure and superheated (150°C.) steam. By this treatment the verantin and rubiretin present in the garancine were said to be destroyed, while the alizarin remained intact, and the product yielded in consequence more brilliant purples, and less soaping was required to clear the whites or unmordanted portions of printed calicoes.

Madder extracts.—Already in 1826, attempts were made by Gaudin to apply mordants along with the colouring matter of madder directly to calico, in the form of an extract, *i.e.* as a steam-colour, instead of by dyeing, and in 1837 Gastard succeeded in doing this successfully on a large scale by means of a product named *colorine.* The expense, however, of this and other early madder extracts retarded their application, but, their utility having been clearly demonstrated, the endeavours of numerous chemists were directed to their production in a reasonably cheap manner. Madder extracts consisted of variable mixtures of the two colouring matters of madder, alizarin and purpurin, or of each separately, in a more or less pure condition. Since the introduction of artificial alizarin, just when their manufacture had been perfected, they lost all their importance. The following were the chief methods of production employed.

Leitenberger's process consisted in first extracting all the purpurin from ground madder by water heated to 55°C., and afterwards dissolving out the less soluble alizarin from the dried residual madder by means of wood-spirit. The aqueous solution was precipitated by lime, the washed calcium-purpurin lake was then decomposed with hydrochloric acid, the liberated purpurin collected and washed, when it was ready for use. The alcoholic solution of alizarin was merely precipitated by water, collected and washed. Alizarin and purpurin extracts were thus obtained.

Paraf's method (1868) consisted in extracting madder with superheated water, with or without the addition of a small quantity of alum or sulphuric acid, then collecting and washing the flocculent alizarin precipitate which separated out on cooling.

The preparation of Kopp's 'purpurine,' 'green alizarine,' and 'yellow alizarine' are given earlier in this article.

Pernod's madder-extract, once largely used, was prepared by extracting garancine with boiling water very slightly acidified with sulphuric acid, collecting and washing the precipitate thrown down on cooling, and extracting the dried precipitate with boiling alcohol. After recovering the major portion of the alcohol by distillation, the remaining solution was mixed with water, and the precipitated alizarin was collected and washed.

USE OF MADDER IN DYEING.

Previous to 1870, madder and its derivative garancine were the dyestuffs *par excellence* of the calico-printer and Turkey-red dyer.

By the former, it was used because of its characteristic property of yielding a variety of colours with the aluminium, tin, and iron mordants, viz. red and pink, orange, lilac and black; also brown or chocolate, by employing a mixture of aluminium and iron mordants. Further, all these colours are fast to soap and light. To the calico-printer both the alizarin and the purpurin of the madder were of use, though undoubtedly the alizarin would, in most styles of work, be the essential colouring matter. The Turkey-red dyer employed madder, and afterwards garancine, because they yielded, by his peculiar process, the most brilliant and most permanent red on cotton which was known. In this case the alizarin was the all-important colouring matter, since the purpurin, although fixed on the fibre at first, was modified and more or less removed during the operations of clearing, no doubt chiefly by the action of the stannous salts employed. Alizarin, in conjunction with aluminium and iron mordants, gives a bluish-red and a comparatively bright lilac; purpurin, a yellowish-red and a greyish-lilac, respectively.

The method of applying madder in Turkey-red dyeing was similar to that now employed in the case of alizarin.

Another interesting feature in connection with the application of this dyestuff is that, if the madder was deficient in lime, it was necessary to add a certain proportion of chalk to the dye-bath; it now appears that calcium is a normal constituent of the madder colours, especially those obtained with aluminium and iron mordants.

Madder has also been used in the past, and is even now employed to a small extent, by the indigo dyer and the woollen dyer.

Literature.—Robiquet and Colin, Ann. Chim. Phys. [ii.] 34, 225; Robiquet, *ibid.* 63, 311; Annalen, 20, 196; Kuhlmann, J. Pharm. Chim. 14, 354; Zenneck, Pogg. Ann. 13, 261; Decaisne, J. Pharm. Chim. 24, 424; Gaulthier de Claubry and Persoz, Annalen, 2, 31; Runge, J. pr. Chem. [i.] 5, 362, 374; Higgin, Phil. Mag. [iii.] 33, 282; J. pr. Chem. [i.] 46, 1; Schutzenberger, Bull. Soc. Chim. [ii.] 4, 12; Schunck, Phil. Trans. 141, 433; 142, 67; 145, 389; Annalen, 66, 174; 81, 151, 344; 87, 345, 351; Schunck and Römer, Ber. 10, 172, 551, 790; Debus, Annalen, 66, 351; Wolff and Strecker, *ibid.* 75, 3; K. Moy, *ibid.* 54, 346; H. Koechlin, *ibid.* 59, 344; Schiel, *ibid.* 60, 79; De Lalande, J. 1874, 486; E. Kopp, Bull. Soc. Ind. Mulh. 1861, 31, 9; 1867, 37, 437; Rochleder, Annalen, 80, 323; 82, 207; Schwarz, *ibid.* 80, 333; Willigk, *ibid.* 82, 339; Stenhouse, *ibid.* 130, 341, 343; Bolley and Rosa, Dingl. poly. J. 171, 446; Strecker, J. 1868, 479; Rosentiehl, Ber. 7, 1546, 10, 1178; Liebermann and Bergami, Ber. 25, 2241; Liebermann and Plath, Ber. 10, 1618; Liebermann and Friedländer, Ber. 29, 2851; Schunck and Marchlewski, Chem. Soc. Trans., 63, 969, 1137; 65, 182; Gmelin, Handb. 16, 32; 14, 129; Perkin and Cope, Chem. Soc. Trans. 65, 848. A. G. P.

MADDER CAMPHOR *v.* CAMPHORS.

MADDER LAKE *v.* LAKES.

MAFOUREIRA NUT. A nut imported from Portuguese East Africa containing about 60 p.c. of fat, solid at ordinary temperatures and consisting mainly of palmitin and olein, together with some free fatty acids, chiefly oleic acid. Used in the manufacture of lubricants, soap, and candles. The supply is practically unlimited, the tree bearing the nut growing wild all over the country.

MAGDALA RED *v.* AZINES.

MAGENTA *v.* TRIPHENYLMETHANE COLOURING MATTERS

MAGISTERY. The term magistery was employed by the older chemists to denote the white precipitates which form on the addition of water to strongly acidified solutions of certain metals.

MAGISTRAL. An old medical term signifying a sovereign remedy, employed by the Spanish smelters of Mexico and South America to the roasted and powdered copper pyrites, which is added to the stamped silver ores in the *torta* or magma, obtained in the *patio* process of decomposing horn silver (*v.* SILVER).

MAGMA. A pasty or semifluid mixture. Applied in medicine to the residuum obtained after expressing certain substances to extract the fluid parts of them, or after treating a substance with some menstruum; a thick ointment or confection (Dunglison).

MAGNALIUM. An alloy of magnesium and aluminium (*v.* ALUMINIUM).

MAGNESIA ALBA. A hydrated basic magnesium carbonate (*v.* MAGNESIUM).

MAGNESIA NIGRA. An old name for native manganese dioxide (*v.* MANGANESE).

MAGNESITE, a mineral consisting of magnesium carbonate $MgCO_3$, and belonging to the calcite group of the rhombohedral carbonates. To French mineralogists it is known as giobertite or baudissérite, the name magnésite being applied by them to meerschaum. Crystals are of rare occurrence: they usually have the form of the primary rhombohedron, parallel to the faces of which are perfect cleavages. The angle between the faces of this rhombohedron is 72° 36′ (the corresponding angle in calcite being 74° 55′). Sp.gr. of crystals, 3·1; hardness. 4. More often the mineral occurs as dull white, compact or earthy masses, with the appearance of unglazed porcelain or chalk. Sometimes it is crystalline and granular, then resembling saccharoidal marble. Analyses of massive material show 85 to 96 p.c. $MgCO_3$, with calcium and iron carbonates and often a little silica. A ferriferous variety is known as breunnerite or brownspar.

The mineral occurs as an alteration product of olivine-rocks and serpentine; but in some instances (*e.g.* in the Alps) it has been produced by the action of solutions of magnesium hydrogen carbonate on limestone. Deposits have been worked commercially in Eubœa in the Grecian Archipelago, Veitsch in Styria, and several other places in the eastern Alps, the 'Chalk Hills' near Salem in Madras, in several counties of California, at Grenville in Quebec, and recently in the Transvaal.

Magnesite is used for the preparation of Epsom-salts and other salts of magnesium, and for the production of carbon dioxide. Calcined magnesite is made into refractory bricks for lining basic steel furnaces and electric furnaces. The strong cement made by mixing calcined magnesite with magnesium chloride is employed for the construction of fireproof partitions, flooring, artificial stone, tiles, emery-wheels, grindstones, &c. Other applications of magnesite are in the manufacture of paper and paint, and as a non-conducting covering on boilers and steam-pipes. L. J. S.

MAGNESIUM. Sym. Mg. At.wt. 24·32. The compounds of magnesium most widely occurring in nature are *magnesite* $MgCO_3$, *kieserite* $MgSO_4,H_2O$, *kainite* $MgSO_4{\cdot}KCl,6H_2O$, *carnallite* $MgCl_2{\cdot}KCl,6H_2O$, and the many silicates, as *enstatite, talc, meerschaum, augite, olivine,* and *serpentine.* Together with calcium it frequently occurs in huge mountain masses as *dolomite* $(MgCa)CO_3$. The sulphate $MgSO_4,7H_2O$ is one of the principal saline constituents of many springs, and the chloride occurs in sea water.

Preparation of the metal.—Magnesium, in an impure state, was first obtained by Davy in 1808 by electrolysis, and also by reducing the oxide in a current of the vapour of potassium. In 1830, Bussy obtained it in larger quantity and in a purer form by heating anhydrous magnesium chloride to redness with potassium. On dissolving out the residual chlorides the metal was obtained as a powder which could be readily fused into globules. Bunsen subsequently prepared it by electrolysis of the fused chloride, using a battery of ten zinc-carbon cells. The operation was conducted in a porcelain crucible, of which the upper part was divided by a vertical partition, ground to the right size out of an ordinary crucible lid. The crucible was fitted with a tile cover, through which the poles of gas carbon were inserted, one on each side of the partition. The negative carbon pole was cut like a saw, in such a manner as to form overhanging ledges, under which the light magnesium collected, and was thus prevented from floating to the surface and burning at the high temperature employed.

As the anhydrous chloride is difficult to prepare, Matthiessen improved the process by substituting a mixture of three equivalents of potassium chloride with four of magnesium chloride. A little ammonium chloride is added, the mixture fused and electrolysed in Bunsen's apparatus; it is, however, unnecessary to cut the negative pole, as the magnesium is heavier than the fused mixture. In small quantities, the metal may be readily obtained by electrolysing this mixture in a clay tobacco pipe heated over a lamp, the negative pole being formed by an iron wire inserted down the stem, and the positive by a piece of gas-carbon just touching the surface of the fused mass.

Manufacture.—The first steps towards the preparation of magnesium on an industrial scale were taken by Deville and Caron, whose process essentially consisted in heating a mixture of anhydrous magnesium chloride, fluorspar, and sodium. In the earlier experiments 600 grams of the fused chloride, 480 grams of finely-powdered fluorspar, and 230 grams of sodium in small pieces were employed. The fused magnesium chloride is obtained by evaporating to dryness a mixed solution of magnesium and ammonium chlorides, and fusion of the residue. Magnesium chloride alone cannot be fused without decomposition, hence the use of the ammonium chloride, which prevents this.

The dry mixture, in the proportions mentioned, is then introduced into a red-hot earthen crucible and the cover pressed down by a weight while the violent reaction occurs. When all action ceases, the contents are stirred with an iron rod, which causes the minute globules of metal to coalesce. After being left to cool, all the magnesium may be collected as a ball upon the rod before the melt becomes solid. The metal is then hammered to free it from slag, and should amount to about three-fourths of the theoretical equivalent of the sodium used.

Wöhler subsequently showed that the troublesome preparation of the anhydrous chloride may be avoided by using instead a mixture of magnesium chloride with one-sixth of its weight of sodium chloride, or of a mixture of sodium and potassium chlorides.

Deville and Caron also showed that the metal may be distilled at nearly the same temperature as zinc, in carbon-lined vessels, in an atmosphere of hydrogen, and were thus enabled to obtain it in a very pure form, free from carbon, silicon, and nitrogen.

Sonstadt, in 1863, introduced a few improvements in the process of Deville and Caron. An iron crucible was substituted for the earthen one, and the mixture used consisted of magnesium and sodium chlorides with one-fifth its weight of sodium. The heating is continued for about half an hour after the whole crucible has been raised to full redness.

In a later patent, Sonstadt extends the whole process to a manufacturing scale, and adopts an enlargement of Deville and Caron's method of purification by distillation. The 'magnesium still' consists of two wrought-iron vessels placed vertically over each other; the upper one serves as the crucible, and is connected with the lower one, which acts as receiver, by means of an iron condensing tube, which projects upwards into the crucible to within an inch of the lid. The whole apparatus can be rendered air-tight. The crucible filled with crude magnesium to the level of the top of the tube is fixed in a furnace and surrounded by fuel; the receiver is fitted into a recess of the fire grating, and projects below. Before commencing the distillation, the wrought-iron lid is screwed down, and the air displaced by a current of hydrogen or coal-gas. The receiver is cooled by external application of water. The crucible is maintained at an almost white heat until the operation is complete. The whole apparatus is then removed from the furnace and cooled; on taking to pieces, the magnesium is found as a solid mass in the receiver. This may then be remelted and cast into ingots.

Magnesium was formerly prepared on a large scale in this country by the Magnesium Metal Company, at Patricroft, near Manchester.

Von Püttner (Eng. Pat. 1031, Jan. 24, 1885) prepared the metal by a process very like the reduction of zinc, which metal magnesium very closely resembles. The magnesium mineral is first treated so that the metal is present entirely as oxide. This is then intimately mixed with carbonaceous matter, to which may advantageously be added oxide of iron, and heated to whiteness in retorts. The vapourised metal is condensed and collected in receivers similar to those used in the zinc manufacture.

Gerhard and Smith (Eng. Pat. 16651, Dec. 19, 1884) describe a process for the electrolytic deposition of magnesium as follows. Magnesium ammonium sulphate is prepared by crystallising together 228 parts of magnesium sulphate and 132 parts of ammonium sulphate. This is dissolved in 35,000 parts of water, and the electrodeposition is effected in this solution at a temperature from 150° to 212°F. If a white metal is desired, a nickel anode is employed; for magnesium bronze, a copper anode. In the latter case the most suitable bath is formed by dissolving 360 parts of magnesium ammonium sulphate, 550 parts of potassium cyanide, and 550 parts of ammonium carbonate in 35,000 parts of water.

According to J. W. Swan (J. Soc. Chem. Ind. 20, 666), the electrolytic method has superseded the chemical method. The electrolyte used is carnallite. The principal factory is at Hemelingen, Germany. Most of the recent patents deal with the form of the electrolytic cell. Briefly the details of the process, according to Borchers, are as follows. An anhydrous electrolyte consisting of chlorides having the composition corresponding to the formula $MgCl_2{\cdot}KCl{\cdot}NaCl$ is prepared by heating the crystallised salts in an iron pan. Magnesium chloride cannot be used alone, as it decomposes on heating with the liberation of hydrochloric acid and the formation of oxychloride. This reaction takes place to a certain extent in spite of the presence of the alkaline chlorides; and if the oxide is not removed as also any magnesium sulphate present, the globules of magnesium formed during electrolysis fail to unite to form a clean metal. The sulphate is therefore decomposed after fusion of the chlorides by stirring in some carbon or sawdust, when oxide is produced. The oxide is then converted to chloride by the addition of ammonium chloride, when a clear bath should result. The fused mass is then emptied into the electrolytic cells which are usually of iron and form the cathode. The anode is a carbon rod surrounded by a porcelain cylinder and cap from which a tube passes for leading off the chlorine. The apparatus is kept in a furnace and the temperature is maintained somewhat above the melting-point of magnesium. The current density is about 1000 amperes per square metre with a pressure of 7 to 8 volts. The resulting metal and salts are poured into a mould, and after cooling the buttons of magnesium are separated and remelted with pure carnallite in an iron crucible, the temperature being raised until the magnesium floats on the flux, and is so liquated from impurities. The magnesium is ladled off, remelted, and poured into ingots.

Properties.—Magnesium is a brilliant white metal resembling silver. When heated *in vacuô* to the temperature of the softening of porcelain it sublimes, and deposits itself upon the cooler parts of the vessel in beautiful silver-white crystals (Dumas, Compt. rend. 90, 1027). During the heating it gives off about one and a half times its volume of gas; 20 grams of the metal yielded 12·3 c.c. of hydrogen and 4·1 c.c. of carbon monoxide. The faces of the crystals are often curved and the edges rounded; the usual form is a regular hexagonal prism, the basal planes being less brilliant than the prism faces. The angle of the corresponding rhombohedron is 80° 3′, and is intermediate between those of zinc and arsenic (Des Cloizeaux, Compt. rend. 90, 1101). Its sp.gr. is 1·74–1·75. It melts just below 800° (V. Meyer, Ber. 20, 497), and the boiling-point is a little higher than that of zinc. It preserves its silvery lustre in dry air, but soon tarnishes in moist air owing to the formation of a film of hydrated oxide. It is readily malleable, but only ductile at high temperatures. On the large scale it is usually pressed into wire while in a state of semi-fluidity. This is then flattened into ribbon, in which form it is most employed. It burns when heated in a flame in air with an intense white light, very rich in the chemically active violet rays; hence its use in photography. According to Roscoe, a burning magnesium wire of 0·297 mm. thickness evolves as much light as 74 stearin candles of which five go to the pound. The light of burning magnesium is also employed in signalling and pyrotechny. For the production of the so-called 'Bengal lights,' the following mixtures are recommended. For white fire, 1 part shellac is fused with 6 parts barium nitrate, the fused mixture ground and mixed with 2·5 p.c. of powdered magnesium. For red fire, 1 part shellac is fused with 5 parts strontium nitrate, and the ground mass mixed with 2·5 p.c. of magnesium. These mixtures may either be made into ribbons about a finger's breadth or may be charged into thin zinc tubes so as to serve as torches. On burning the zinc case burns along with the mixture.

The strength of magnesium has been determined at the mechanical experimental station at Charlottenburg, and shown to be very considerable. Its breaking coefficient for tensile strain per square mm. is 23·2 kilos.; specific resistance to compression, 27·2 kilos. per square mm.; bending strength, 17·4 kilos. At a temperature of 450° it can be rolled, pressed, worked, and brought into complicated forms. Screws and threads of magnesium are considerably sharper and more exact than those of aluminium (J. Soc. Chem. Ind. 6, 730).

Magnesium has no action on pure water, but in presence of a trace of platinum chloride it decomposes water rather quickly, evolving hydrogen and forming magnesium hydroxide. Platinised magnesium constitutes a good deoxidising agent; it reduces nitrobenzene, for instance, completely to aniline (Ballo, Ber. 16, 694). Dilute acids rapidly dissolve it with violent evolution of hydrogen; with dilute hydrochloric acid it inflames when first thrown in. Strong sulphuric acid acts slowly, and a mixture of this acid with fuming nitric acid has no action upon it at ordinary temperatures. Solutions of caustic alkalis have no action upon it, but, heated with solutions of ammonium salts, it evolves hydrogen and dissolves, forming a double salt of ammonium and magnesium. Aqueous solutions, however, of acid sodium or potassium carbonates, as well as solutions of carbonic acid, dissolve the metal with evolution of hydrogen (Ballo, Ber. 15, 3003). Magnesium burns when heated in chlorine gas or bromine vapour, and especially brilliantly in the vapours of sulphur and iodine. It combines at determinate temperatures, when in a finely divided state, with sulphur, phosphorus, and arsenic, and at a red heat decomposes oxides of carbon, sulphur dioxide, and many hydrocarbons. Silica and boric acid are readily reduced by it. It combines directly with nitrogen, forming a crystalline nitride Mg_3N_2. It precipitates nearly all the metals from their neutral solutions in the metallic state; aluminium, uranium, and chromium as oxides.

Magnesium may be advantageously employed in place of zinc in toxicological investigations, owing to its freedom from arsenic. It may likewise be used instead of zinc in voltaic batteries, owing to its higher electromotive force (Roussin, J. Pharm. Chim. [iv.] 3, 413).

Alloys.—Magnesium forms malleable alloys with potassium and sodium, which decompose water at ordinary temperatures. 15 parts of magnesium form with 85 parts of tin a brittle lavender-coloured alloy, which also decomposes water. An alloy with 5 p.c. of thallium is stable and more malleable than pure magnesium. With mercury, it does not appear to form an amalgam at ordinary temperatures. Alloys with aluminium, zinc, cadmium, lead, bismuth, antimony, silver, gold, and platinum have also been prepared (Parkinson, Chem. Soc. Trans. 1867, 125) by fusing the metals together in a current of hydrogen, or by fusion in an earthen crucible under a flux of equal parts fluorspar and cryolite, or one part fluorspar with two parts of common salt. The magnesium was attached to the end of an iron rod and well stirred among the other metal, otherwise, being so light, it would float to the top. Triple alloys were also obtained with bismuth and copper, copper and gold, and with copper and nickel. All these alloys are brittle, showing a granular fracture, and are unfortunately too easily alterable for use in the arts.

Magnesium oxide. *Magnesia.* MgO. This is the product of the combustion of magnesium in air or oxygen. It is also formed when the carbonate or nitrate is heated in the air. As thus obtained, it is a white amorphous powder, but may be obtained crystallised in cubes and octahedra by heating the amorphous form in a current of hydrogen chloride. If ferric oxide be mixed with the magnesia, brilliant black octahedra of magnoferrite $MgO{\cdot}F_2O_3$ are formed, together with octahedra of MgO, slightly yellow in colour, due to oxide of iron, and identical with those of *periclase*, a mineral found at Monte Somma, near Vesuvius. Moissan obtained transparent crystals of magnesia, sp.gr. 3·654, by distillation of the oxide in the electric furnace. Ordinary magnesia is known in commerce as *magnesia usta* or calcined magnesia, and is much used for medicinal purposes. It is a fine bulky powder of sp.gr. 3·07 to 3·2. The sp.gr. is increased to 3·61 by heating in a pottery furnace.

It is only fusible at the temperature of the oxyhydrogen blowpipe flame, and on again solidifying forms a hard enamel, which scratches glass. It is alkaline to litmus, but is not caustic. It is almost insoluble in water; according to Fresenius, it requires 55,368 parts of either cold or boiling water to effect solution. This solution has an alkaline reaction. Magnesia containing 0·1 p.c. of chromic oxide becomes slightly fluorescent after ignition.

Manufacture.—Magnesia is generally obtained commercially by gentle but prolonged heating of the carbonate or by heating the hydoxide. Since the discovery, however, of the immense stores of carnallite, the double chloride of potassium and magnesium, in the saline deposits of Stassfurt, several processes have been patented for utilising the waste magnesium chloride liquor obtained as by-product in the manufacture of potassium chloride.

Schlœsing, in 1881 (Compt. rend. 93, 156, 215), describes the following process for obtaining cheap magnesia. A paste of slaked lime and water containing 34–36 p.c. of calcium oxide is allowed to run through perforations in a metallic plate into a solution of magnesium chloride containing 60–95 grams per litre. As soon as the lime paste reaches the solution it becomes coated with a layer of magnesium hydroxide, which acts like a shell, causing it to form long threads, which are entirely converted into magnesium hydroxide in about 6 days. The hydroxide thus obtained may be washed by diffusion, and, when triturated with water and dried, gives a compact, friable powder, which can of course be converted into calcined magnesia by heating in a suitable furnace. Presence of common salt has no effect on the value of the process, but if soluble sulphates are present, they must be removed by adding some of the calcium chloride solution from a previous operation, allowing to settle, and decanting from the more insoluble calcium sulphate.

Ramdohr, Blumenthal, & Co. in 1881 patented the following process (D. R. P. 19259, Sept. 1881). A solution of magnesium chloride is evaporated until it consists approximately of $MgCl_2,6H_2O$. About 4–10 p.c. of magnesite is added, and the mixture heated to redness in a current of air until the evolution of hydrogen chloride ceases. Magnesium oxychloride is left, which, on heating with water, splits up into magnesium hydroxide and chloride.

The United Chemical Works Joint Stock Co., Leopoldshall, in 1882, patented the following process (D. R. P. 20277, Feb. 1882). Burnt lime is treated with a solution of calcium chloride. After removal of the clear liquid, the paste is washed with a fresh solution of calcium chloride, whilst the clear solution in turn is repeatedly digested with fresh lime. A small portion of this solution is then mixed with the magnesium chloride solution in order to precipitate all the iron and sulphuric acid which it contains. The purified magnesium solution is then added to the bulk of the clear calcium solution, which contains calcium oxychloride $3CaO{\cdot}CaCl_2,16H_2O$, when pure hydrated magnesium oxide separates out.

On account of its infusibility, magnesia is now extensively used in the manufacture of firebricks, especially for use in the basic Bessemer steel process. The bricks are made of crushed dead-burnt magnesite mixed with sufficient gently calcined magnesite to give plasticity to the paste formed by mixing the materials with water to permit of moulding. The bricks are fired at a red heat before use.

Dolomite has also been extensively used for this purpose. Closson's plan was to mix calcined dolomite with a solution of magnesium chloride when calcium chloride and magnesia are formed; the calcium chloride can then be washed out. Many other wet methods for the recovery of magnesia have been employed, but, according to Wedding, magnesia prepared in the wet way, though obtained from cheap waste materials or by-products, is too expensive for the manufacture of bricks.

Magnesia, in combination with lime, also finds an extended use for mortar making in districts where only magnesium limestone is available. The dolomitic limestone is burnt at a lower temperature than ordinary limestone, otherwise its hydrating properties and consequently the quality of the mortar are impaired.

Magnesium suboxide. A substance of this nature appears to be formed when a solution of sodium or ammonium chlorides is electrolysed, using poles of magnesium wire, the positive pole becoming covered with a black deposit (Beetz, J. 1866, 172). The same substance is also obtained when magnesium is immersed in solutions of chlorides of the alkalis and alkaline earths, common salt giving the largest deposit. In a few days it disappears, being replaced by the ordinary white oxide. It turns white when heated just below redness. It dissolves in nitric acid with partial reduction of the acid. It readily dissolves in hydrochloric and sulphuric acids with effervescence, forming the ordinary chloride and sulphate (Gore, Chem. News, 50, 157).

Magnesium hydroxide $Mg(OH)_2$ occurs native as the mineral *brucite*, crystallising in the rhombohedral section of the hexagonal system. The hydroxide is precipitated as a white powder when the hydroxide of potassium or sodium is added to the solution of a magnesium salt. De Schulten (Compt. rend. 101, 72) obtained it in the form of flattened hexagonal prisms, of sp.gr. 2·36 at 15°, by heating a mixture of 12 grams crystallised magnesium chloride $MgCl_2,6H_2O$, 340 grams of potash, and 60 c.c. of water, at 210°–220°. The solid residue, after washing away the alkali, consisted of these small crystals of the hydroxide. They were readily soluble in acids and in a warm solution of ammonium chloride.

Magnesium hydroxide slowly absorbs carbon dioxide from the air. At a low red heat it loses its water, becoming converted into the oxide. This calcined magnesia is again capable of taking up water, with evolution of heat, to reform the hydroxide.

Magnesium hydroxide is much used upon the Continent for extracting sugar from molasses; it forms an insoluble granular crystalline magnesium saccharate, which when decomposed by carbon dioxide yields pure sugar.

In order to meet this demand, the Consolidated Alkali Company of Stassfurt manufacture large quantities of magnesium hydroxide by the following process. The 3 p.c. of sulphates contained in the last mother liquor from the extraction of potassium chloride from carnallite are first removed by means of a solution of calcium chloride. A quantity of milk of lime is then added rather less than sufficient to decompose the whole of the magnesium chloride; the precipitated magnesia is allowed to settle and then passed through filter presses, in which it is thoroughly washed. The magnesium hydroxide thus obtained contains only 0·1 p.c. of calcium sulphate, and is eminently suitable for the purpose of the sugar refiner (Hake, J. Soc. Chem. Ind. 2, 149).

Magnesia prepared by heating the nitrate is converted by prolonged immersion in water into a form of the hydroxide having the density of marble, but harder and more translucent. A similar form, but contaminated with oxide of iron and aluminium, magnesium carbonate and sand, is also obtained by action of water upon the product of the ignition of commercial magnesium chloride. This singular property of hardening is only possessed by magnesia prepared by ignition of the nitrate or chloride at a moderate red heat. After heating to whiteness it appears to lose it. Ignition of native magnesite at the lowest possible temperature also yields a product possessing the same hydraulic property, but the basic carbonates of commerce yield a perfectly soft hydroxide. The paste prepared from calcined magnesite and water hardens in about half a day, and afterwards not only withstands the action of water, but actually acquires in contact with it the hardness of the best Portland cement.

A mixture of magnesia with a concentrated solution of magnesium chloride of sp.gr. 1·16–1·26 hardens in a short time to a compact mass of basic chloride, which resists the action of water. The pasty mixture is very plastic, and is capable of binding more than twenty times its weight of sand.

Magnesium chloride $MgCl_2$ is one of the salts present in sea-water and the water of many springs. It also occurs combined with potassium chloride in large quantities as the mineral *carnallite* $MgCl_2{\cdot}KCl,6H_2O$ in the Stassfurt deposits. It is formed when magnesium burns in chlorine, or when a stream of chlorine is passed over a heated mixture of magnesia and carbon. It is also produced by dissolving the metal, oxide, or carbonate, in hydrochloric acid. On concentration of the solution monoclinic crystals of the composition $MgCl_2,6H_2O$ separate out. Crystals of this composition have also been discovered, associated with carnallite and rock salt, at Stassfurt, and named *bischofite*. On attempting to obtain the anhydrous chloride by ignition of these crystals, hydrochloric acid is evolved in addition to water, and a portion of the chloride becomes converted to oxide. If, however, the crystals be heated in a current of hydrogen chloride, the anhydrous chloride is obtained without the formation of any basic salt (Hempel, Ber. 21, 897). Another method of obtaining the anhydrous chloride is to add ammonium chloride to the solution, evaporate to dryness, and ignite in a platinum dish. The magnesium ammonium chloride thus formed loses its water without any decomposition of the magnesium chloride, and the ammonium chloride can then be sublimed out, leaving the anhydrous magnesium chloride as a clear fused mass, which on cooling solidifies to a crystalline solid. 100 parts of water at 0° dissolve 52·2 parts of the anhydrous chloride, with considerable evolution of heat, forming a solution of sp.gr. 1·3619 at 15° (Engel, Bull. Soc. chim. [ii.] 47, 318). At the ordinary temperature 100 parts of water dissolve about 130 parts, and at 100° about 366 parts. This solution on cooling again deposits the crystals. Magnesium chloride solution possesses a bitter taste. The solid, either anhydrous or crystals, is very deliquescent. It combines directly, with evolution of heat, with methyl and ethyl alcohols, the solutions yielding, on cooling with ice, crystals of $MgCl_2,6CH_3OH$ and $MgCl_2,6C_2H_5OH$, respectively.

Commercial preparation.—The last mother liquor obtained in the process of preparing potassium chloride from the carnallite at Stassfurt supplies as by-product large quantities of magnesium chloride. The liquor has a sp.gr. of 1·32, and contains no less than 35 p.c. of the chloride. It is first evaporated to sp.gr. 1·34, when potassium and sodium chlorides and magnesium sulphate separate out. The hot concentrated liquor is then run into casks, where on cooling it solidifies to a white translucent mass containing 50 p.c. of magnesium chloride. In this state it is largely exported to this country, being used by cotton-spinners as a thread lubricator (Hake, J. Soc. Chem. Ind. 2, 149).

Lanquetin, in 1881, patented (D. R. P. 20396) a process for preparing magnesium chloride by introducing burnt magnesite or dolomite into a solution of waste calcium chloride, and driving carbon dioxide through the mixture, when calcium carbonate separates out and magnesium chloride remains in solution.

Cochrane and Bramley, of Middlesbrough (Eng. Pat. 15498, Nov. 1886), charge hydrated magnesium carbonate into a series of closed vessels through which a solution of calcium chloride is circulated, carbon dioxide being at the same time injected. Magnesium chloride is in this case also gradually formed in solution and calcium carbonate precipitated.

Magnesium chloride may also be extracted from the mother liquor of the potassium chlorate manufacture (Muspratt and Eschellmann, Widnes, Eng. Pat. 1900, Feb. 1885).

Magnesium chloride unites with the alkaline chlorides to form crystalline double salts.

Magnesium potassium chloride $MgCl_2{\cdot}KCl,6H_2O$, the carnallite of Stassfurt, crystallises in colourless deliquescent rhombic prisms. On heating, the water is driven off without loss of chlorine, the anhydrous mixture fusing at a red heat. The native carnallite used at Stassfurt for the extraction of potassium and magnesium chlorides has the following average composition (Hake, J. Soc. Chem. Ind. 2, 149):

KCl	16·2	$CaCl_2$	0·2
$MgCl_2$	24·3	Clay and $CaCO_3$	2·1
$MgSO_4$	9·7	H_2O	28·8
NaCl	18·7		

Magnesium ammonium chloride

$$MgCl_2{\cdot}NH_4Cl,6H_2O$$

is deposited from mixed solutions of magnesium and ammonium chlorides in small rhombic crystals.

The corresponding sodium salt appears to contain only one molecule of water (Poggiale, Compt. rend. 20, 1130).

Magnesium calcium chloride, *Tachydrite*, $2MgCl_2{\cdot}CaCl_2,12H_2O$, is also found at Stassfurt in deliquescent yellowish masses.

Magnesium oxychlorides. When highly calcined magnesia is treated with a strong solution of magnesium chloride, it dries in a few hours to a hard mass of oxychloride, capable of receiving a polish. A sample prepared in this manner, and hardened by 6 months' exposure in the air, was found to consist of a mixture of $MgCO_3$ with a compound

$$MgCl_2{\cdot}5MgO,17H_2O.$$

On heating to 180° it was converted into $MgCl_2{\cdot}5MgO,6H_2O$. By prolonged treatment with water the whole of the magnesium chloride was extracted, and the compound $2MgO{\cdot}3H_2O$ left. This residual hydrate is a compact solid as hard as sandstone, possessing a brilliant surface, and taking a high polish; its cohesive power is not impaired by either cold or hot water (Bender, Annalen, 159, 341).

The crystalline deposit frequently found in bottles containing magnesia mixture (magnesium sulphate or chloride, ammonia and ammonium chloride) consists of a hydrated oxychloride $MgCl_2{\cdot}5MgO,13H_2O$. On washing the crystals with a large quantity of water the whole of the chloride may be removed, the residue consisting of hydrated oxide (Davis, Chem. News, 25, 258).

By mixing freshly calcined magnesia with a solution of magnesium chloride in a flask well corked and nearly filled with the liquid, and heating on a water-bath with frequent agitation, needle-shaped crystals of an oxychloride are formed. When washed and dried at 110° they consist of $MgCl_2{\cdot}10MgO,14H_2O$. The dry crystals are not attacked by carbon dioxide, but when moist are decomposed (Krause, Annalen, 165, 38).

When 20 grams of calcined magnesia are boiled with a solution of 400 grams magnesium chloride in 500 grams of water and the solution filtered, the filtrate deposits needles of $MgCl_2{\cdot}MgO,16H_2O$. When dried *in vacuô* they are converted into $MgCl_2{\cdot}MgO,6H_2O$. Both salts are decomposed by water and alcohol (André, Compt. rend. 94, 444).

When crystallised magnesium chloride is heated in air, an oxychloride of variable composition appears to be left, a portion of the chlorine passing away in the form of hydrochloric acid. If the chloride be heated to a sufficiently high temperature in a current of air a certain amount of free chlorine is evolved; and if a mixture of hydrogen chloride and air is passed over the heated chloride, especially in presence of a little free magnesia, a larger quantity of chlorine is obtained in the free state. This reaction forms the basis of the Weldon-Pechiney process of manufacturing chlorine, as worked at Salindres (Weldon, Eng. Pat. 9307, June, 1884; 11036, Aug. 1884). A solution of magnesium chloride is first evaporated down until it consists approximately of $MgCl_2,6H_2O$. This is then converted to oxychloride by addition of $1\frac{1}{3}$ equivalents of calcined magnesia. This oxychloride is crushed and sifted, solid pieces free from dust being eventually chosen not larger than the size of a walnut. It is next heated to remove a portion of its water, and finally decomposed by heating to a high temperature in a current of air. The furnace employed for the latter process is constructed upon the principle of a baker's oven. It consists of a series of vertical chambers, the thickness of the dividing walls of which is greater than the width of the spaces between them. Before charging these spaces with the small lumps of oxychloride, products of combustion are passed through them until the dividing walls are raised to a high temperature. After charging, the oxychloride becomes heated by contact with the walls, and a mixture of chlorine, nitrogen, excess of air, and hydrogen chloride is evolved. The hydrochloric acid is condensed in ordinary towers, and the remaining gases pass on to the bleaching powder chambers. The magnesium remains as oxide, the oxygen being furnished by a regulated supply of air, and is afterwards partly dissolved in the condensed hydrochloric acid for preparation of more oxychloride (Weldon, J. Soc. Chem. Ind. 4, 175). The reactions occurring in the process are probably as follows:

(1) $H_2O+MgCl_2=MgO+2HCl$.
(2) $2HCl+O=H_2O+Cl_2$.
(3) $MgCl_2+O=MgO+Cl_2$.

(Kingzett, J. Soc. Chem. Ind. 7, 286).

Nithack (D. R. P. May 29, 1884) decomposes magnesium chloride for the preparation of chlorine by injecting a fine spray of the solution into heated chambers, when the same reactions occur.

Mond (Brit. Assoc. 1896, 741) modified the process for recovering both ammonia and chlorine from the ammonium chloride produced in the ammonia soda process. Magnesia is mixed with a little china clay and potassium chloride to facilitate the production of a perfectly anhydrous chloride. The mixture is made into pills and placed in towers. These are heated from a previous operation to 300°; the ammonium chloride vapour is passed through, producing ammonia and magnesium chloride. Air at 600° is then circulated, when free chlorine is liberated and magnesia reformed. Hence the process becomes continuous.

Hermite (J. Soc. Chem. Ind. 7, 726, 737) prepares chlorine for bleaching purposes by the electrolysis of a solution of magnesium chloride.

Magnesium bromide $MgBr_2$ occurs in sea-water and many salt springs. It very much resembles the chloride, being deposited from a solution of magnesia in hydrobromic acid in needles of $MgBr_2,6H_2O$, which behave like the chloride on heating.

Magnesium iodide MgI_2 also occurs in sea-water and saline springs, and may be obtained by dissolving magnesia in hydriodic acid, when deliquescent crystals separate, which readily evolve iodine on warming.

Magnesium fluoride MgF_2 occurs native in the mineral *sellaïte* in colourless quadratic crystals, and may be prepared in an amorphous form by evaporating magnesia with excess of hydrofluoric acid. When the amorphous form is fused with sodium chloride and gradually cooled, it is obtained, after washing with water, in crystals resembling those of sellaïte.

Feldmann (Eng. Pat. 15295, Nov. 1887) patented a process for an industrial preparation of this salt. Magnesium chloride is treated with calcium fluoride in either the dry or the wet way. In the former the fluorspar is mixed with the anhydrous chloride in excess, and the mixture fused at a red heat, when $CaCl_2$ and MgF_2 are formed. After cooling, the mass is lixiviated, when the magnesium fluoride remains behind. In the wet method powdered fluorspar is suspended in a concentrated solution of magnesium chloride and heated till double decomposition occurs, water being added to make up the loss by evaporation. It is then allowed to cool, when the mass solidifies and is lixiviated as before. Any undecomposed calcium fluoride may be removed by elutriation from the specifically lighter magnesium fluoride.

A double fluoride of magnesium and sodium $MgF_2{\cdot}NaF$ is obtained in insoluble cubical crystals by fusing magnesium chloride with a large excess of sodium fluoride and chloride and allowing to cool slowly. Also in the amorphous state by boiling a solution of sodium fluoride with magnesia.

Magnesium carbide has not been isolated in the pure state. It is obtained mixed with carbon by heating magnesium powder to redness in the vapour of benzene (Parkinson) or acetylene (Berthelot). According to Moissan, it is completely decomposed in the electric furnace, which explains why magnesia can be fused in a carbon crucible without reaction (Ann. Chim. Phys. [vii.] 16, 151).

Magnesium carbonate $MgCO_3$ occurs native as *magnesite* in rhombohedral crystals isomorphous with those of calcite. It is also found in large compact or granular masses, and, combined with calcium carbonate, as *dolomite* $(MgCa)CO_3$, in immense quantities all over the world. The amorphous precipitate formed when an alkaline carbonate is added to a solution of a magnesium salt has the composition

$$MgCO_3,2H_2O,$$

but after standing an hour or two at a temperature below 16°, it becomes converted into tabular crystals of $MgCO_3,5H_2O$. If the temperature exceeds 22° it becomes converted into prismatic crystals of $MgCO_3,3H_2O$. Between 16° and 22° both these salts are formed. The amorphous precipitate is decomposed by water into a basic carbonate of the composition

$$5MgO{\cdot}4CO_2,11H_2O$$

or $5(MgCO_3,2H_2O)$, in which one molecule of $MgCO_3$ has been converted into $Mg(OH)_2$. This basic carbonate absorbs carbon dioxide from the air, and becomes $MgCO_3,2H_2O$ again (Engel, Compt. rend. 100, 911). According to Marignac, normal magnesium carbonate is also formed by the action of magnesium chloride on calcium carbonate.

When the precipitated carbonate is suspended in water and dissolved by the passage of a current of carbon dioxide, on evaporation of the solution the anhydrous carbonate is precipitated in minute crystals isomorphous with aragonite, the rhombic form of calcium carbonate. On the other hand, when mixed solutions of a soluble magnesium salt and an alkaline bicarbonate supersaturated with carbon dioxide are inclosed in a strong vessel closed by a cork, through which the carbon dioxide is slowly allowed to escape, microscopic rhombohedrons of the anhydrous carbonate resembling those of native magnesite and calcite are deposited.

Both the natural and artificial varieties of magnesium carbonate give an alkaline reaction with litmus solution. They dissolve slowly in acids with but little effervescence.

Magnesium carbonate dissolves in water saturated with carbon dioxide. According to Engel (Compt. rend. 100, 444, 1224) the solubility at constant temperature is proportional to the cube-root of the pressure of the carbon dioxide. The results of a large number of experiments agreed with those calculated from the general formula $x^{0{\cdot}333}=ky$ or $y=\frac{1}{k}\sqrt[3]{x}$, where x represents the pressure of carbon dioxide, y the quantity dissolved, and k a constant $=0{\cdot}03814$. At different temperatures under atmospheric pressure the amount of magnesium carbonate dissolved is proportional to the coefficient of solubility of carbon dioxide at the particular temperature. The following table is given by Engel and Ville (Compt. rend. 93, 340) showing the solubility first at constant temperature and second at constant pressure :

Atmospheres pressure	Temperature	$MgCO_3$ dissolved in a litre of water
1	19°5	25·79
2·1	19·5	33·11
3·2	19·7	37·30
4·7	19·0	43·50
5·6	19·2	46·20
6·2	19·2	48·51
7·5	19·5	51·20
9·0	18·7	56·59
mm. pressure		
751	13·4	28·45
763	19·5	25·79
762	29·3	21·94
764	46·0	15·70
764	62·0	10·35
765	70·0	8·10
765	82·0	4·90
765	90·0	2·40
765	100·0	0·00

When the solution in carbonic acid is left to evaporate spontaneously, or kept in a partially closed flask for some time at 50°, it deposits small hexagonal prisms of $MgCO_3,3H_2O$, which effloresce in air, becoming opaque. At a winter temperature the same solution deposits monoclinic prisms of $MgCO_3,5H_2O$. Warmed with water at 50°, they are converted into the trihydrate, whilst on boiling with water they lose carbonic acid and become converted eventually into the basic carbonate

$$2MgCO_3{\cdot}Mg(OH)_2,2H_2O.$$

Basic carbonates. A basic carbonate of the composition $3MgCO_3{\cdot}Mg(OH)_2,3H_2O$ occurs native as *hydromagnesite* in small white monoclinic crystals of sp.gr. 2·14–2·18. A salt of the same composition is also obtained by mixing magnesium sulphate with excess of a hot solution of potassium carbonate and boiling the precipitate with fresh quantities of water so long as acid carbonate dissolves out. Also by boiling a saturated solution of the acid carbonate, and twice boiling the precipitate produced with fresh quantities of water. When dried at 100° in the air it absorbs carbon dioxide, and is converted into $5MgO{\cdot}4CO_2,5H_2O$.

Another basic carbonate of the composition $2MgCO_3{\cdot}Mg(OH)_2,2H_2O$ is obtained as above from the solution of the normal carbonate in carbonic acid. Also, according to Fritzsche (Pogg. Ann. 37, 310), by precipitating magnesium sulphate with a very large excess of sodium carbonate and boiling till granular, then washing rapidly three times with fresh boiling water.

Commercial carbonates. The commercial preparation known as *magnesia alba* is a basic carbonate of slightly varying composition, according to the conditions of production. It is usually prepared by precipitation of either the commercial sulphate or chloride of magnesium with sodium carbonate. As thus obtained it is a very light bulky powder, and is distinguished as *magnesia alba levis.* If the precipitation is carried on at a higher temperature by the addition of one volume of a cold saturated solution of sodium carbonate to a boiling mixture of one volume of a saturated solution of magnesium sulphate with thirty volumes of water, the precipitate washed with hot water and dried at 100°, a denser form is obtained known as *magnesia alba ponderosa.* The composition of the light variety is generally given as the same as that of hydromagnesite $3MgCO_3{\cdot}Mg(OH)_2,3H_2O$. Beckurts (Arch. Pharm. [iii.] 18, 429; 19, 13), however, deduces the formula

$$5MgCO_3{\cdot}2Mg(OH)_2,7H_2O,$$

but also found several specimens of the hydromagnesite formula, but containing $4H_2O$. Kraut (Arch. Pharm. [iii.] 20, 180) gives $4MgCO_3{\cdot}Mg(OH)_2$ as the correct formula. Hence it appears likely that different samples vary somewhat in composition. As representing the composition of the heavy variety, Beckurts (*l.c.*) gives the formula $3MgCO_3{\cdot}Mg(OH)_2,4H_2O$, which only differs from that of hydromagnesite by one molecule of water.

Magnesia alba levis and *ponderosa* yield upon calcination corresponding light and heavy varieties of the oxide, known in commerce as *magnesia usta levis* and *magnesia usta ponderosa.*

Another method of preparing *magnesia alba* was patented by Pattinson. This consists in treating slightly ignited dolomite with water and carbon dioxide under a pressure of 5-6 atmospheres. So long as any magnesium carbonate remains undissolved, the calcium carbonate is unattacked, the acid magnesium carbonate being much more readily formed. This solution of hydrogen magnesium carbonate is decanted from the calcium carbonate and heated by injection of steam, when *magnesia alba* is precipitated as a white bulky powder of loose texture. Unignited dolomite does not yield any acid carbonate with carbonic acid.

Bramley and Cochrane, of Middlesbrough, patented a process (Eng. Pat. 13762, Oct. 1886) in which magnesia is added to the solution of an alkaline bicarbonate or sesquicarbonate and the mixture heated and agitated. The alkaline carbonate is converted to a normal carbonate, and hydrated magnesium carbonate formed. The operation is performed in closed vessels to prevent loss of carbon dioxide.

Magnesia alba can also be profitably prepared from sea-water (Gutzkow, Dingl. poly. J. 270, 30). The mother-liquor (bittern) obtained after extraction of common salt (bay-salt) is treated with milk of lime; the precipitated magnesium hydroxide is allowed to settle, the supernatant liquid removed by decantation, and the precipitate stirred up with water through which a stream of carbon dioxide is passed. The hydroxide is dissolved as acid carbonate. The clear solution is then heated rapidly to 70°, and afterwards more gradually to the boiling-point. The precipitated *magnesia alba* is filtered off and dried on plates heated by steam. If necessary, the original mother-liquor may first be freed from organic matter by treatment with alum.

Magnesia alba is almost insoluble in water, but dissolves readily in solutions of ammonium salts owing to the formation of soluble double salts of magnesium and ammonium and ammonium carbonate.

Magnesium ammonium carbonate

$$MgCO_3{\cdot}(NH_4)_2CO_3,4H_2O$$

separates in rhombohedral crystals from a mixture of cold aqueous solutions of magnesium sulphate or chloride and excess of ammonium carbonate and free ammonia.

Magnesium potassium carbonate

$$MgCO_3{\cdot}K_2CO_3,4H_2O$$

is obtained in small rhombic prisms when *magnesia alba* is digested with a solution of acid potassium carbonate for 15 hours at 60°–70°.

A salt of the composition

$$MgCO_3{\cdot}HKCO_3,4H_2O$$

is obtained in large crystals from a cold aqueous mixture of magnesium chloride or nitrate with excess of acid potassium carbonate. Engel (Compt. rend. 100, 1224) obtained the same salt by decomposing a solution of the acid magnesium carbonate with potassium bicarbonate, and also by direct action of the potassium bicarbonate upon normal magnesium carbonate.

Magnesium sodium carbonate $MgCO_3{\cdot}Na_2CO_3$ is similarly obtained in small anhydrous crystals by digesting *magnesia alba* with sodium bicarbonate.

Magnesium nitride Mg_3N_2. Magnesium combines directly with nitrogen when heated to redness. It is also one of the products of the incomplete combustion of magnesium in air. It is a greenish-yellow amorphous body which decomposes slowly in humid air, yielding ammonia and magnesia, rapidly in contact with water with elevation of temperature. Hydrochloric and nitric acids decompose it yielding ammonia and the magnesium salt. With sulphuric acid it yields sulphur dioxide and magnesium sulphate. Argon does not combine with magnesium.

Magnesium nitrate $Mg(NO_3)_2$ occurs in the mother-liquors of the saltpetre manufacture, and also frequently in well-water. It may readily be prepared by dissolving *magnesia alba* in nitric acid and evaporating to small bulk, when monoclinic prisms and needles of the hydrated salt $Mg(NO_3)_2,6H_2O$ separate out. These are soluble in half their weight of cold water, and also in nine times their weight of alcohol of sp.gr. 0·84, with which magnesium nitrate forms an alcoholate of the composition $Mg(NO_3)_2,6C_2H_6O$. When dried over sulphuric acid the hydrated salt loses four molecules of its water, and at the temperature of melting lead another molecule is evolved, leaving the salt $Mg(NO_3)_2,H_2O$. When this latter salt is heated to a still higher temperature the last molecule of water is given off, together with part of the nitric acid, and a trimagnesium nitrate $Mg_3(NO_4)_2$, analogous to the tri-orthophosphate, is left.

Magnesium borate. When magnesium oxide in slight excess is heated with a mixture of boric anhydride and potassium hydrogen fluoride in molecular proportions, the borate $3MgO,B_2O_3$ is obtained in transparent acicular crystals which are soluble in inorganic acids but not in acetic acid or water.

Magnesium phosphide Mg_3P_2 may be obtained by heating magnesium filings with red phosphorus (Parkinson) or by passing phosphorus vapour over magnesium filings, heated to redness, in a current of carbon dioxide. Gautier obtained it crystalline by heating red phosphorus and magnesium in a graphite boat, then driving off the excess of phosphorus in a current of hydrogen (Compt. rend. 128, 1167). It decomposes water, yielding phosphoretted hydrogen and magnesium hydroxide.

Trimagnesium orthophosphate $Mg_3(PO_4)_2$ is found in the ashes of plants and animals and occurs in nature as *wagnerite* $Mg(MgF)PO_4$ combined with fluorine. It may be prepared by adding magnesium sulphate in excess to a solution of trisodium phosphate and boiling. It is a white amorphous powder containing $5H_2O$, which on calcining loses water and becomes phosphorescent.

Di-magnesium orthophosphate $Mg_2H_2(PO_4)_2$ is formed by precipitating a solution of a magnesium salt with normal sodium phosphate. If the solution is dilute it separates in hexagonal needles containing seven molecules of water. It occurs in the fæces of man.

Ammonium magnesium phosphate

$$MgNH_4PO_4,6H_2O$$

is formed as a crystalline precipitate when sodium phosphate is added to an ammoniacal solution of a magnesium salt. The precipitate is almost insoluble in water and still less so in ammonia. It serves for the quantitative estimation of both magnesia and phosphoric acid. The compound occurs in nature in well-formed crystals known under the name of *struvite*.

Magnesium pyrophosphate $Mg_2P_2O_7$ is obtained by igniting either ammonium magnesium phosphate or the acid phosphate.

Magnesium sulphide MgS is formed by heating magnesium filings in the vapour of sulphur or sulphuretted hydrogen. So obtained it is a grey amorphous material which is difficultly fusible even in the electric furnace (Mourlot, Compt. rend. 127, 180). It is decomposed by cold water with the formation of magnesium hydrogen sulphide. In warm water it is said to form polysulphides, and on boiling, hydrogen sulphide is evolved leaving only hydrated magnesia.

Magnesium sulphite $MgSO_3$. When water containing magnesium hydroxide in suspension is saturated with sulphur dioxide, the solution concentrated *in vacuô* at a temperature below 100° and then allowed to cool, rhombohedral crystals of $MgSO_3,6H_2O$ are deposited (Hartog, Compt. rend. 104, 1793).

A basic magnesium sulphite of the composition $MgSO_3{\cdot}2Mg(OH)_2$, similarly prepared by passing sulphur dioxide into water holding magnesia in suspension, is used in sugar factories (Bergreen and Licht, Bied. Centr. 1884, 201).

Magnesium sulphate (*Epsom salts*) $MgSO_4$ occurs in the mineral *kieserite* $MgSO_4,H_2O$, in the Stassfurt salt beds; and as *epsomite*

$$MgSO_4,7H_2O$$

in the gypsum quarries of Montmartre, in Spain, Chile, and in the Mammoth Cave, Kentucky. Kieserite is occasionally found in rhombic prisms, but more generally occurs in granular masses. Epsomite is found both in the massive state and in silky fibrous crystals. Natural crystals of epsomite more than a centimetre long have also been found coating the walls of a gypsum quarry in the Department of Hérault, France. The sulphate was in a constant state of exudation, and as it solidified formed a lustrous coating of crystals upon the surface of the gypsum (De Rouville, Compt. rend. 87, 703).

Magnesium sulphate forms the purgative principle of bitter spring waters (hence its name of Bitter salt) such as those of Bath, and Seidlitz, Saidschütz, and Püllna in Bohemia. At the three latter places it is obtained by digging pits into which the bitter water runs, and allowing the solution thus collected to evaporate in shallow pans.

The magnesium sulphate of commerce is now chiefly obtained from the kieserite of Stassfurt.

The crude kieserite obtained from the upper layers (Abraumsalz) of the Stassfurt beds is first freed from magnesium and sodium chlorides by being placed in large sieves, standing in tanks of water. The two salts mentioned dissolve out, whilst the kieserite, which is very sparingly soluble in water, falls through the meshes of the sieves in a state of fine powder. Any gangue or other impurities such as anhydrite or larger lumps of rock salt remain behind in the sieves. The kieserite powder is then packed into conical wooden moulds, where it sets to a compact solid, owing to its combining with six more molecules of water to form epsomite. This solid 'stone' is then dried and afterwards powdered. In this condition it contains from 80 to 90 p.c. of $MgSO_4$ and about 1 to 2 p.c. of sodium chloride. A large quantity is brought into the market in this form. The rest is crystallised from water and brought into commerce as Epsom salts.

Another mode of manufacturing magnesium sulphate, which was almost universally employed before the working of the Stassfurt beds, consists in decomposing dolomite, magnesium limestone $(CaMg)CO_3$, with oil of vitriol. As calcium sulphate is only sparingly, while magnesium sulphate is readily soluble, the separation affords no difficulty.

The dolomite is first calcined, when on treatment of the hot mass with a small quantity of water it is readily broken up into powder. This powder is then suspended in water in large digesters constructed of wood lined inside with lead and Yorkshire flags. For a digester 6 feet square and 7 feet deep, about 3 tons of dolomite would form a convenient charge. Into this emulsion are then poured the contents of twelve carboys of sulphuric acid, and water added until the sp.gr. becomes 1·125 to 1·150. At the end of an hour, when the contents begin to cool down, steam is injected by a leaden pipe which completes the action. Excess of acid must be carefully avoided, as it causes loss in crystallising. The liquor is then run off into a settler made of lead or flags, but not of iron; after settling the clear solution is siphoned over into an iron evaporating pan, where it is evaporated down to 66° of Twaddell's hydrometer. The clear concentrated liquor stands for an hour or two to allow any suspended matter to settle, after which it is conveyed to the coolers, which are made of wood, flags, or, best of all, slate, where it is agitated so as to cause the salt to fall in small crystals. The crystals are then drained and finally dried on shelves in a stove room at a temperature not exceeding 80°F.

Magnesium sulphate is largely used in the Lancashire cotton trade in the process of warp-sizing; it is also employed for medicinal and agricultural purposes and for dyeing with the aniline colours.

The crystals have the composition of epsomite $MgSO_4,7H_2O$, and form right rhombic prisms, resembling those of the sulphates of zinc and nickel. They have a sp.gr. of 1·676 (Thorpe and Watts, Chem. Soc. Trans. 37, 106). On heating, they melt in their water of crystallisation, lose 6 molecules of water at 150° and the seventh at 200°.

A salt also having the composition $MgSO_4,7H_2O$ is occasionally deposited from cold supersaturated solutions in monoclinic prisms isomorphous with those of ferrous sulphate $FeSO_4,7H_2O$. By crystallisation of the ordinary salt above 40° monoclinic prisms of a hydrate $MgSO_4,6H_2O$, of sp.gr. 1·734, are obtained. By drying the heptahydrate over oil of vitriol to constant weight, $MgSO_4,5H_2O$, of sp.gr. 1·869 is obtained. A salt of the composition $MgSO_4,2H_2O$, sp.gr. 2·373, may also be prepared by boiling finely powdered Epsom salts with absolute alcohol. The sp.gr. of the monohydrate $MgSO_4,H_2O$ is 2·445 and that of the anhydrous salt 2·709 (Thorpe and Watts, *l.c.*).

Magnesium sulphate is readily soluble in water. According to Gay-Lussac 100 parts of water dissolve 25·76 parts of the anhydrous salt at 0° and 0·47816 parts for every degree beyond. One part of Epsom salts dissolves in 0·79 parts of water at 18·75°, forming a liquid of sp.gr. 1·2932.

The following table, due to Schiff (Annalen, 108, 336), shows the amounts of the sulphate in solutions of different specific gravities:—

Sp.gr. at 23°	Per cent of $MgSO_4,7H_2O$	Per cent. of $MgSO_4$
1·0048	1	0·488
1·0096	2	0·975
1·0193	4	1·951
1·0290	6	2·928
1·0387	8	3·904
1·0487	10	4·878
1·0587	12	5·854
1·0688	14	6·830
1·0790	16	7·806
1·0894	18	8·782
1·0997	20	9·756
1·1103	22	10·732
1·1209	24	11·708
1·1316	26	12·684
1·1426	28	13·660
1·1536	30	14·634
1·1648	32	15·610
1·1760	34	15·586
1·1875	36	17·562
1·1991	38	18·538
1·2108	40	19·512
1·2228	42	20·488
1·2349	44	21·464
1·2472	46	22·440
1·2596	48	23·416
1·2722	50	24·390
1·2850	52	25·366
1·2980	54	26·341

Magnesium sulphate also dissolves in dilute alcohol, but is insoluble in absolute alcohol.

Magnesium hydrogen sulphate $MgH_2(SO_4)_2$. If 2 parts of anhydrous magnesium sulphate are dissolved in 100 parts of boiling sulphuric acid of sp.gr. 1·7 and the solution evaporated at the boiling-point, $MgH_2(SO_4)_2$ is deposited in prisms. On cooling, an acid salt of the composition $MgSO_4{\cdot}3H_2SO_4$ crystallises out in small shining tables which fuse and decompose when heated.

Magnesium sulphate forms an isomorphous series of double salts with the sulphates of the alkali metals, of the general formula

$$MgSO_4{\cdot}M_2SO_4,6H_2O,$$

which crystallise in monoclinic prisms.

Magnesium potassium sulphate

$$MgK_2(SO_4)_2,6H_2O$$

is found in the Stassfurt salt deposits and is known as *schönite;* also as a volcanic product (*picromerite*). It is prepared by dissolving the salts in molecular proportions and crystallising. It forms monoclinic prisms.

Magnesium ammonium sulphate

$$Mg(NH_4)_2(SO_4)_2,6H_2O$$

is found in the fumeroles of Tuscany and is known as *cerbolite.* Prepared artificially it crystallises in monoclinic prisms and is isomorphous with the potassium double salt.

Magnesium silicates occur abundantly in nature and some of them have been prepared artificially. The more important silicates are the following :—

Forsterite Mg_2SiO_4 occurs in crystals in the volcanic ejections of Monte Somma. Ebelmen (Ann. Chim. Phys. [iii.] 33, 58) obtained the mineral artificially by fusing silica and magnesia in proper proportions with boric acid. The crystals obtained were similar to those from Vesuvius. Forsterite forms with the corresponding calcium orthosilicate (*monticellite*) an isodimorphous group of mixed crystals (V. Poschl, Tsch. Min. Mitt. 26, 413).

Olivine $nMg_2SiO_4+Fe_2SiO_4$ is a constituent of many basic rocks. It crystallises in the rhombic system. The olive green and bottle green crystals are used as gemstones under the name of peridote. Magnesium silicate forms isomorphous mixtures with iron orthosilicate, but there is a gap in the series (V. Poschl, *loc. cit.*).

Enstatite $MgSiO_3$ the metasilicate, occurs in nature crystallised in the rhombic system. Ebelmen (*loc. cit.*) obtained it by fusing magnesia and silica with boric acid in proportions corresponding to the metasilicate; Poschl (*loc. cit.*) has shown that it forms with diopside ($CaMgSi_2O_6$) an isodimorphous series similar to that given by magnesium sulphate and ferrous sulphate.

Sepiolite $2H_2O2MgO3SiO_2$ is a compact, earthy hydrated silicate, sometimes known as meerschaum.

Talc $H_2Mg_3(SiO_3)_4$ occurs as foliated masses, compact as steatite; the soft variety is known as soapstone or French chalk.

Serpentine $H_4Mg_3Si_2O_4$ forms large rock masses and usually contains ferrous oxide. The fibrous variety is known as *chrysotile* and comes into commerce under the general name of asbestos.

Magnesium titanate $MgTiO_3$ occurs in nature as *geikielite.*

Magnesium citrate $Mg_3(C_6H_5O_7)_2,14H_2O$ is obtained as a crystalline crust when magnesia is dissolved in slightly more than an equivalent quantity of a solution of citric acid, and the solution evaporated at about 50°. It is very soluble in water, and is often preferred to Epsom salts as a mild purgative on account of its pleasanter taste.

The citrate of magnesia of the shops, so popular as an effervescent salt, may be prepared by mixing 16 parts of sodium bicarbonate, 10½ of tartaric acid, 4 of citric acid, about 12 of sugar, ½ part of Epsom salts, and 2 parts of crystallised sodium bisulphate, and heating on an enamelled iron plate until it becomes spongy from the escape of carbon dioxide. The cooled mass is then put through sieves of four to six meshes per square inch. In this granular form it is again heated until quite dry. The solution of the granules in water, after the liberation of the carbon dioxide, contains principally citrate and tartrate of soda and sugar.

It may also be prepared by making a mixture of magnesium citrate, prepared by dissolving magnesia in citric acid solution and crystallising, with sodium bicarbonate, citric acid and sugar, and rendering granular by moistening with alcohol and drying.

The magnesia preparation called *sinodor*, used for removing unpleasant odours and for disinfecting and preserving purposes, is obtained by heating neutral magnesium acetate with magnesium oxide until the mass assumes a pasty consistency. It consists of basic magnesium acetate containing excess of magnesium hydroxide (Kubel, Pat. 18090, Nov. 1881).

Magnesium is usually estimated quantitatively by precipitating an ammoniacal solution with sodium or ammonium phosphate. The precipitate is washed with ammonia water, ignited and weighed as pyrophosphate.

G. S. B.

MAGNETIC IRON-ORE *v.* Magnetite; Iron.

MAGNETIC PYRITES *v.* Pyrrhotite.

MAGNETITE, or Magnetic iron-ore. A mineral of the spinel group, consisting of magnetic oxide of iron, Fe_3O_4 or $FeO{\cdot}Fe_2O_3$; an important ore of iron (Fe 72·4 p.c.). Sharply developed crystals with bright faces are not uncommon; these belong to the cubic system and usually have the form of the regular octahedron or the rhombic-dodecahedron. Granular to compact masses are, however, more abundant. The colour is iron-black with a dull, sub-metallic lustre and a black streak. Sp.gr. 5·18; hardness 6. The mineral may be always readily recognised by its strong magnetic character: small fragments are picked up by a magnetised knife-blade. Only occasionally are specimens magnetic with polarity (*v.* Loadstone).

As small grains and crystals, magnetite is of wide distribution in many kinds of igneous rocks, especially the darker coloured with a low silica percentage. In such rocks it sometimes forms rich segregations available for mining; as in the Ural Mountains, and at Kirunavara and Gellivara in Swedish Lapland. Other important deposits, *e.g.* some of those in southern Sweden and Norway, have been formed by the metamorphism of pre-existing iron-ores, where these have been subjected to the baking action of intrusive masses of igneous rock. Extensive deposits of magnetite are also mined in the crystalline Archæan rocks of the Adirondack region of New York and in Canada.

L. J. S.

MAGNOFERRITE *v.* Iron.

MAIZE. *Zea Mays* (Linn.). **'Indian corn'** or **'mealies.'** This plant was grown by the aborigines of America; it was introduced into Europe in the sixteenth century, and is now extensively grown in almost all countries possessing sufficiently warm climates. It grows to a height of from 5 to 12 or even 15 feet.

Many varieties of maize are known, differing greatly in size, shape, colour, and composition of the grain and in the arrangement of the grain around the cob.

The average composition of all varieties of maize has been given under Cereals.

South African, American, and Australian grown maizes contain distinctly less moisture than European samples. White and yellow are the commonest colours of the maize grain, but orange, red, blue, violet, and even black grains are known, as well as striped ones.

The separate parts of white American horsetooth maize have been analysed by Plagge and

Lebbin in 1897 (quoted by König). They obtained the following results :—

	P.c. of whole grain	In the dry matter, p.c.				
		Water	Protein	Fat	Carbohydrates	Ash
Germ . . .	11·78	6·70	13·75	29·36	46·99	7·23
Husks . . .	9·35	8·66	8·32	7·94	82·81	1·63
Horny part of starch	49·79	12·16	8·04	0·64	91·11	0·21
Mealy ,, ,,	29·08	9·68	6·46	0·93	92·97	0·34
Whole grain .		11·38	8·09	5·79	84·61	1·51

Hopkins, Smith and East (J. Amer. Chem. Soc. 1903, 25, 1166) determined the distribution of the proteids in maize grains of (*a*) low (9·89 p.c.), (*b*) medium (11·33 p.c.), and (*c*) high (12·64 p.c.) protein content. Their results were—

	(*a*)	(*b*)	(*c*)
Germ . .	19·31	20·14	18·45
Husks . .	2·75	2·07	1·85
Horny portion .	53·07	59·03	64·88
Mealy portion .	23·98	17·63	14·22
Tip caps . .	0·89	1·14	0·59

They found that the germ contained almost all the oil and about ten times the percentage of ash of the other parts of the grain. Hopkins, indeed (Bull. 55, Illinois Agric. Stat. 1899, 310), finds it possible to classify samples of maize according to their richness in protein or fat by mechanical examination only, the fat being mainly dependent upon the proportion of germ in the grain and the nitrogenous matter being largely determined by the proportion of horny or glutinous matter.

For proteids and oil of maize, *v.* Cereals.

The injurious effect of a diet consisting largely of maize upon animals has been ascribed to the absence of tryptophan among the products of hydrolysis of *zein*, the characteristic protein of maize (Willcock and Hopkins, J. Phys. Chem. 1906, 35, 88); also to the presence of much phenylalanine and tyrosine among such products, and the ease with which they split off phenolic compounds, thus producing phenolic poisoning (Baglioni, Atti. R. Accad. Lincei. 1908, 17, i. 109).

The 'non-nitrogenous extract' of maize consists mainly of starch and cellulose, but includes also cane sugar, dextrin, and gum.

As the average of several determinations of the soluble carbohydrates in various types of maize, König gives the following numbers:

Maize from		Number of determinations	In the original substance, p.c. Sugar	Dextrin and gum	Starch, etc.
South-eastern Europe		8	1·76	2·83	61·20
Italy . . .		22	2·22	1·09	64·41
America	Flint corn	23	2·29	2·30	64·04
	Dent corn	11	2·64	3·62	62·39
	Sweet corn	10	4·64	14·47	43·47

Stone (Bull. 34, O. Exp. St. 14) extracted 0·25 p.c. cane sugar from ordinary and 3·5 p.c. from sweet maize, but could not detect invert sugar in the former. Tollens and Washburn (J. Landw. 1889, 37, 503) found 9 p.c. of glucose and 7·8 p.c. of sucrose and dextrin in sweet maize, but only a trace of glucose and 1·78 p.c. of sucrose and dextrin in ordinary maize. Stone found about 5 p.c., Tollens 7·08 p.c. of pentosans in maize grain.

For ash of maize grain, *v.* Cereals.

An objection to the use of large quantities of maize as a cattle food is the effect which it has of lowering the melting-point of the fat produced by the animal (*e.g.* bacon in the case of the pig, butter in the case of dairy cows). Maize is too rich in fat and carbohydrates and too poor in ash constituents, especially lime, to form the sole diet of an animal.

Maize cob—the central portion of the ear—consists largely of cellulose and xylan (25 p.c. of the latter). American analyses show it to contain—

Water	Protein	Fat	N-free extract	Crude fibre	Ash
10·7	2·4	0·5	54·9	30·1	1·4

It is sometimes ground along with the grain, and the product, 'corn and cob meal,' is used as a cattle food.

Maize is also employed as a fodder plant, being cut green and either eaten fresh, or, in some cases, made into hay or ensilage. Though immature maize plants contain a cyanogenetic glucoside (Brünnich, Chem. Soc. Trans. 1903, 788), the quantity of hydrocyanic acid present —not exceeding 0·5 grain per 1 lb. of green material—is so small, that there is little or no danger of poisoning the animals fed upon them.

The following table gives the average composition of certain products from maize:

	Water	Protein	Fat	N-free extract	Crude fibre	Ash
Green fodder .	79·3	1·8	0·5	12·2	5·0	1·2
Silage . .	79·1	1·7	0·8	11·0	6·0	1·4
Straw . .	15·0	5·0	1·5	34·5	39·2	4·8
Bran . .	12·5	9·9	3·6	61·5	9·5	3·0
Maize germ cake	11·0	21·0	9·0	43·8	9·1	6·1
Corn & cob meal	15·1	8·5	3·5	64·8	6·6	1·5
Gluten meal .	9·6	29·4	6·8	52·4	1·6	0·7

H. I.

MAIZE OIL (Corn oil) is obtained from the germs of the maize plant, *Zea Mays*, L. The germs are recovered, in the process of manufacturing starch, by sifting and winnowing them from the starch granules in which they are imbedded. The oil is therefore a by-product of starch and glucose works using maize (corn) as their raw material.

Formerly maize oil was obtained as a by-product in alcohol distilleries. When the malted and crushed grain was allowed to ferment, the oil was laid bare and rose to the top in the fermentation vats. Before distilling off the alcohol, the oil was ladled off and purified in a crude fashion by washing, filtering, and 'settling.' Since, however, the presence of the germ imparts an unpleasant flavour to the spirit obtained by fermentation, and the oil so recovered was very impure, and had a different character from the oil expressed from the germs, the older process of fermenting the crushed grain has been abandoned. Nowadays, the corn is first malted, beaten up with water to a fine pulp, and the germs are separated from the starch by sieving. At present, maize oil is manufactured on a very large scale from the isolated germs by expression in hydraulic presses. In a dry condition, the germs contain 53 p.c. of oil, and yield in practice about 40 p.c. The whole grain contains 4·10 p.c. of oil.

Maize oil, if properly prepared, is clear in colour, and does not require refining for commercial purposes. If, however, the oil is badly prepared and allowed to stand in contact with albuminoid matter, so that it undergoes a process of fermentation, whereby considerable quantities of free fatty acids are produced, it acquires a dark colour and becomes unsuitable for light-coloured soaps. Such oil is therefore bleached in soap works in the same manner as linseed oil.

The freshly prepared maize oil is of a pale yellow or golden-yellow colour, and has a distinctive odour; its taste is pleasant at first, and is most characteristic in that it resembles that of newly ground corn-meal. It is therefore possible to identify the oil by its taste alone.

Maize oil is characterised by its high amount of unsaponifiable matter, amounting to as much as 1·55 and even 2·32 p.c. The unsaponifiable matter consists of lecithin, and of an alcohol which appears to be identical with sitosterol (phytosterol). The sp.gr. of maize oil is 0·925 to 0·927 at 15·5°. The saponification value is 190 to 192, and the iodine value varies between 120 and 130.

The saturated fatty acids in maize oil amount to about 5 p.c. and appear to consist of palmitic, stearic, and arachidic acids. As to liquid fatty acids, linolenic acid is absent, but the oil contains considerable amounts of linolic acid in addition to oleic acid. The oil has somewhat better drying powers than cotton-seed oil, but differs from the latter in that it is not oxidised with equal energy when finely subdivided on cotton waste.

Well-refined maize oil is used for edible purposes ('salad oil'). Since its 'grainy' taste is objectionable, the edible quality consists mostly of a mixture of maize oil with edible cotton oil and other edible oils. Maize oil is also used in the manufacture of margarine ('oleomargarine' of the United States), as also in the manufacture of compound lard (replacing cotton seed oil). Such maize oil as cannot be employed for edible purposes is used chiefly in the manufacture of soft soap, for which it is eminently suitable. A cotton 'softener' largely used in the United States contains maize oil soft soap. Maize oil is not suitable for hard soaps of acceptable quality. J. L.

MALACHITE. An ore of copper, crystallising in the monoclinic system, but usually occurring in mamillated and botryoidal forms, or in fibrous, compact, or earthy masses of a bright green colour. It is a basic copper carbonate $H_2Cu_2CO_5$ (or $CuCO_3+CuO_2H_2$), having a sp.gr. of 3·9 to 4·0, and hardness 3½ to 4. Heated in a tube, it evolves water and turns black, while on charcoal it yields metallic copper. Malachite is frequently found as an alteration-product of other copper-ores, and occurs as a pseudomorph after cuprite, &c. If derived from copper-pyrites it is generally accompanied by limonite. Malachite is not only important as an ore of copper (Cu, 57·4 p.c.), but is valued as an ornamental stone, since it takes a good polish and is prettily marked with light and dark green bands of colour. It is chiefly used for vases and small boxes, but its comparative softness stands in the way of its extensive use in jewellery. Large slabs are not generally attainable, but small pieces are skilfully joined together, the interstices being filled in with powdered malachite, and the whole polished; in this way it becomes easy to employ it for inlaid and encrusted furniture, especially for table-tops of considerable size. Malachite is also used to a limited extent as a green pigment, but the term 'malachite green' has been extended to certain organic dyestuffs. Malachite is widely distributed as a mineral, being found in greater or less quantity in most copper-deposits, but the finest examples occur near Nizhne-Tagilsk in the Ural Mountains, and in South Australia. L. J. S.

MALACHITE GREEN, VICTORIA GREEN, BENZAL GREEN *v.* TRIPHENYLMETHANE COLOURING MATTERS.

MALAKIN *v.* SYNTHETIC DRUGS.

MALARIN. Trade name for the citrate of acetophenone-phenetidide, prepared by heating equivalent proportions of acetophenone and *p*-phenetidine either alone or with addition of dehydrating agents. Crystallises in yellow needles, m.p. 88°, readily soluble in hot alcohol, ether, or glacial acetic acid.

MALAYAN CAMPHOR *v.* CAMPHORS.

MALE FERN *v.* FILIX-MAS.

MALEIC ACID *v.* FUMARIC ACID.

MALIC ACID, *Hydroxysuccinic acid* (*Acide malique*, Fr.; *Aepfel- säure*, Ger.)

$$\begin{array}{l}CH_2COOH\\ \,|\\ CH(OH)COOH.\end{array}$$

This acid contains an asymmetric carbon atom and hence can occur in three modifications, viz. a dextrorotatory form, a lævorotatory form, and an inactive variety. The lævo-rotatory variety occurs free or in the form of salts in many plant juices and hence is frequently termed *ordinary* malic acid. *l*-Malic acid was discovered by Scheele in 1785 in sour apples and Liebig in 1832 ascertained its composition. The inactive acid was first obtained by Pasteur in 1852 from inactive aspartic acid, and by Kekulé in 1861 from bromosuccinic acid. The *d*-acid was first obtained by Bremer in the reduction of *d*-tartaric acid.

Preparation.—*l-Malic acid* occurs free in unripe grapes, apples, gooseberries, &c., and in mountain ash berries (*Pyrus Aucuparia*) (Ehrh.), in the berries of *Hippophaë rhamnoides* (Linn.), and in *Berberis vulgaris* (Linn.) (Muttelet, Chem. Zentr. 1910, i. 376; Kunz and Adam, *ibid.* 1906, i. 1849; Farnsteiner, Zeitsch. Nahr. Genussm. 15, 598; Jörgensen, *ibid.* 17, 396; Adam. Chem. Zentr. 1905, ii. 1042; Erdmann, Ber. 1891, 3351; Pharm. Centralh. 41, 200; Hilger, Zeitsch. Nahr. Genussm. 8, 110; Kremla, Bied. Zentr. 1895, 24, 498). Suint contains potassium malate to the extent of 2½ p.c. of the solid residue and it is a product of excretion (A. and P. Buisine, Compt. rend. 106, 1426); *l*-malic acid is also found in the calcium precipitate formed in the treatment of beetroot (Lippmann, Ber. 1891, 3299). It can be prepared from the unripe berries of *Pyrus Aucuparia* (Ehrh.) (Hagen, Annalen, 38, 257), or of *Berberis vulgaris* (Linn.) (Lennsen, Ber. 1870, 966) in the following manner. The expressed juice is evaporated, filtered, heated to boiling, and saturated with milk of lime. The calcium malate which separates is dissolved in hot dilute nitric acid (1 : 10); on cooling, the solution deposits the acid malate, which is purified by recrystallisation from water. In order to obtain malic acid from it, its solution is precipitated with lead acetate and the lead salt is decomposed with sulphuretted hydrogen (Brœksmit, Pharm. Weekbad. 42, 637). It may be obtained from the juice of cherries or grapes by means of the cinchonine salt, which is very insoluble, the cinchonine salts of the other acids remaining in solution (Lindet, Bull. Soc. chim. 1896, 15, 1160). Castoro recommends separating malic acid from the expressed juice of the rhubarb, in which it occurs as the acid potassium salt, by means of its strontium salt (Chem. Soc. Abstr. 1902, i. 259).

l-Malic acid can be obtained from *l*-chloro- or *l*-bromosuccinic acid through the action of moist silver oxide, mercuric oxide, &c., or from *d*-chloro- or *d*-bromosuccinic acid by the action of potassium hydroxide, or hydroxides of the other alkali metals (Walden, Ber. 1896, 135; 1897, 2795, 3148; 1899, 1833, 1853). It can also be obtained by the action of nitrous acid on *l*-asparagine or *l*-aspartic acid (Walden, *l.c.*). By heating the ammonium salt of inactive malic acid to 80°, the active salt crystallises out from the solution of the inactive salt (Kenrick, Ber. 1897, 1749; Van't Hoff and Dawson, *ibid.* 1898, 528).

d-Malic acid occurs naturally in *Crassulaceæ* (Aberson, Ber. 1898, 1432; Walden, *ibid.* 1899, 2706). It can be obtained synthetically by methods similar to those for obtaining *l*-malic acid (Walden, *l.c.*; Piutti, Ber. 1886, 1693; Bremer, *l.c.*). Racemic acid can be reduced to inactive malic acid, which can be resolved into *d*- and *l*-malic acids by cinchonine (Bremer, Ber. 1880, 351; Rec. trav. chim. 4, 180).

Inactive malic acid can be prepared by methods similar to those above (Tanatar, J. Russ. Phys. Chem. Soc. 1891, i. 339; Annalen, 273, 37; Van't Hoff, Ber. 1885, 2170, 2173). It is also obtained by heating fumaric or maleic acids with caustic soda to 100° (Van't Hoff, *l.c.*; Lloyd, Annalen, 192, 80; Bremer, *l.c.*; Skraup, Monatsh. 12, 113); by heating chloral and malonic acid with acetic acid and treating the γ-trichloro-β-hydroxybutyric acid thus formed with potassium hydroxide (Garzarolli-Thurnbackh. Monatsh. 12, 556); and by reducing oxalacetic acid with sodium amalgam in acid solution (Wislicenus, Ber. 1891, 3416; 1892, 2448).

Properties.—Inactive malic acid. Melts at 130°–131°; sp.gr. 20°/4° 1·611. Affinity constant (Walden, Ber. 1896, 1698). The diethyl ester is obtained by reducing ethyloxalacetate with aluminium amalgam (Wislicenus, J. pr. Chem. 1896, [ii.] 59, 18). Dielectric constant *v.* Drude, Zeitsch. physikal. Chem. 23, 310).

d-Malic acid. Physical properties, *v. l-malic acid.*

l-Malic acid. Crystallises in colourless needles, m.p. 100°. Very soluble in water or alcohol. Rotation of acid (*v.* Nasini and Gemari, Gazz. chim. ital. 25, i. 422; Zeitsch. physikal. Chem. 1896, 19, 113; Winther, Chem. Zentr. 1896, ii. 22; Woringer, Zeitsch. physikal. Chem. 1901, 36, 336). Thermal constants, *v.* Massol. Compt. rend. 113, 800. The esters are prepared by adding dry silver malate in small quantities at a time to an excess of alkyl iodide and completing the reaction by heating on the water-bath; or by treating malic acid and an alcohol with hydrochloric acid or sulphuric acid. When the former method is used, a small quantity of a more active substance is always present, *e.g.* in the preparation of ethyl malate, ethyl ethoxysuccinate is also produced (Purdie and Lander, Chem. Soc. Trans. 1898, 293; Purdie and Pitkeathly, *ibid.* 1899, 154). The dimethyl ester boils at 129° (16 mm.) and has sp.gr. 1·2301 at 20°/4°; the diethyl ester boils at 138° (25 mm.) and has sp.gr. 1·1340 at 20/4° (Purdie, *l.c.*; Walden, Zeitsch. Physikal. Chem. 1895, 17, 245; Frankland and Wharton, Chem. Soc. Trans. 1899, 338). Rotation, *v.* also Anschutz and Reitter, Zeitsch. physikal. Chem. 1895, 16, 493. Dielectric constant, v. Walden, *ibid.* 46, 103. According to H. Traube (Zeitsch. Kryst. Min. 1899, 31, 160), the best method for the preparation of the salts of malic acid is by the interaction of strontium hydrogen malate with the sulphate of the metal. A detailed account of the composition and crystallographic properties of the salts is given.

On heating malic acid to 100° for 24 hours, there results malomalic acid $C_5H_7O_3(CO_2H)_3$, and on heating *in vacuô* at 180° there is formed an anhydride, *malide* $C_8H_8O_8$ and small quantities of fumaric acid and maleic anhydride (Walden, Ber. 1899, 2716). Prolonged heating at 140°–150° yields fumaric acid as the main product, and at 180°, fumaric acid, maleic anhydride, and water are formed. Oxidation with hydrogen peroxide in the presence of a ferrous salt yields oxalacetic acid (Fenton and Jones, Chem. Soc. Trans. 1900, 77); with hydrogen peroxide in a sealed tube at 120°, tartaric acid (Zinno, Mon. Scient. 16, ii. 493); with potassium permanganate, oxalacetic acid (Deniges, Compt. rend. 130, 32); with nitric acid, oxalic acid; with potassium dichromate, malonic acid. Reduction with hydriodic acid yields succinic acid. By heating malic acid with sulphuric acid, the half aldehydes of malonic acid and formic acid are produced, the former of which is changed into coumalic and trimesic acids (Von Pechmann, Annalen, 264, 261): heating with glycerol gives rise to carbon dioxide and acrolein (de Coninck and Raynaud, Compt. rend. 135, 1351). Carbon dioxide, acetaldehyde, and crotonic aldehyde are formed by the electrolysis of a concentrated aqueous solution of the sodium salt (Miller and Hafer, Ber. 1891, 470). The coumarins are produced when malic acid is heated with phenols and sulphuric acid (Pechmann, Ber. 1884, 929, 1646). Benzaldehyde and malic acid in piperidine at 150°–160° react to form β-benzoylpropionic acid (Mayrhofer and Nemeth, Monatsh. 1903, 24, 80). Heated with hydrobromic acid, malic acid yields bromosuccinic acid and with phosphorus pentachloride chlorosuccinic acid. A concentrated solution of an alkaline malate gives with calcium chloride on boiling a precipitate of calcium malate. Ammonium salts prevent the precipitation; addition of alcohol aids it. Piñuera (Compt. rend. 1897, 124, 291) uses as a reagent a solution containing 0·02 gram β-naphthol per c.c. strong sulphuric acid. If 0·05 gram of dry substance is added to 15 drops of the reagent in a porcelain dish and malic acid is present, a yellow green colouration is produced, changing to light yellow on heating and orange on dilution. Details as to estimation, *v.* Clowes, J. Amer. Chem. Soc. 1908, 30, 1285; Pozzio-Escot, Bull. Soc. chim. Belg. 1908, 22, 413.

Malic acid is present in wines. When fermentation is carried out with pure yeast on sterile musts, no decomposition of malic acid occurs until the wines become contaminated with micro-organisms in the ordinary cellar operations. Then gradual fermentation sets in and thus liberates the carbon dioxde necessary to prevent premature decay (Rosenstiehl, Compt. rend. 1908, 147, 150; *cf.* Mestregat, *ibid.* 1907, 145, 260; Emmerling, Ber. 1899, 1915). Seiffert (Chem. Zentr. 1903, ii. 257) has shown that malic acid is gradually converted into lactic acid by an anærobic micrococcus (*Micrococcus malolacticus*); this is also brought about by *Bacillus lactis aërogens* (Emmerling, *l.c.*).

Detection and estimation in wines and fruit juices, v. Schneider (J. Soc. Chem. Ind. 1890, 1068); Micko (Zeitsch. anal. Chem. 31, 465; 32, 481; Chem. News. 68, 286); Hilger (Chem. Zentr. 1900, ii. 597; Zeitsch. Nahr. Genussm. 1903, 6, 721); Kunz (Apoth. Zeit. 1905, 20, 677); Mestzerat (Compt. rend. 1906, 143, 185; Ann. Chim. anal. 1907, 173; 12, 194); Jörgensen (Zeitsch. Nahr. Genussm. 13, 241); Heide and Steiner, *ibid.* 1909, 17, 307). *In tobacco,* Kissling (Chem. Zeit. 1898, 22, 1; 1899, 23, 2). *In cider vinegar,* Leach and Lythgoe (J. Amer. Chem. Soc. 1904, 25, 375).

isoMalic acid. Methyltartronic acid, *v.* TARTRONIC ACID).

β-isoMalic acid. β-Hydroxyisosuccinic acid $CH_2(OH)CH(CO_2H)_2$. The ethyl ester is obtained by treating formaldehyde with hydrogen chloride and adding to the solution ethylsodiomalonate; the product is hydrolysed with potash and the acid so obtained is a syrup decomposing into acrylic acid on heating (Coops, Rec. trav. chim. 1901, 20, 430; Chem. Weekbad. 1, 535; *cf.* Tanatar, Annalen, 273, 44).

Citramalic acid. α-Methylmalic acid

$$CO_2H{\cdot}CH_2(CH_3)C(OH)CO_2H.$$

Prepared from acetoacetic ester by means of prussic acid and hydrochloric acid (Michael, J. pr. Chem. [ii.] 46, 287; Demarcy, Bull. Soc. chim. [ii.] 27, 120; Morris, Chem. Soc. Trans. 1880, 6); by the reduction of chlorocitramalic acid, which is formed from citraconic acid (Carius, Annalen, 129, 160; Morawski, J. 1878, 721); by the action of N_2O_3 on methylaspartic acid (Piutti, Ber. 1893, 2046); by the action of caustic soda on β-bromopyrotartaric acid (Ssemenoff, J. Russ. Phys. Chem. Soc. 31, 289). Melts at 115°–117° and on heating to 200° decomposes into water and citraconic anhydride (Wislicenus, Ber. 1892, 196).

β-Methylmalic acid

$$CO_2H{\cdot}CH(OH)CH(CH_3)CO_2H.$$

Prepared by heating the ester of methyloxalacetic acid with sodium amalgam in aqueous solution (Wislicenus, Ber. 1892, 199). Colourless syrup.

MALLEABLE CAST IRON *v.* IRON.

MALLET BARK. The bark of *Eucalyptus occidentalis* (Endl.), found in Queensland. Employed in tanning; contains from 30 to 50 p.c. of tanning substance. The commercial extract has a density of 22°–24°B. and contains 30–36 p.c. of tanning substance.

MALLOTOXIN *v.* RESINS.

MALONIC ACID $CH_2(COOH)_2$, the second member of the oxalic acid series, was first prepared by Dessaignes by oxidising malic acid with potassium dichromate (Annalen, 1858, 107, 251), and was found by Lippmann among the calcium salts formed in beet-sugar manufacture (Ber. 1881, 14, 1183). Malonic acid can be obtained by oxidising crude sarcolactic acid with potassium dichromate (Dossois, Zeitsch. Chem. 1866, 449); or allylene or propylene with potassium permanganate (Berthelot, Annalen (Supl.) 1867, 5, 97); by the action of fuming nitric acid on hexabromomethylethyl ketone (Demole, Ber. 1878, 11, 1714); or of boiling baryta water on ethyl chloracrylate (Pinner, *ibid.* 1875, 8, 963); or of silver oxide at 125° on ethyl dichloroacrylate (Wallach, Annalen, 1878, 193, 25); by boiling bromomucic acid with baryta water (Jackson and Hill, Ber. 1878, 11, 289); or by boiling barbituric acid with alkali (Baeyer, Annalen, 1864, 130, 143). Malonic acid is best prepared by the hydrolysis of cyanacetic acid (Conrad, Ber. 1879, 12, 749; Bourgoin, Compt. rend. 1880, 90, 1289). Endemann (D. R. P. 183328, 1907) has devised a method for preparing malonic acid from abietic acid and the accompanying resins, by hydrolysing the resin or abietic acid with sodium hydroxide, oxidising the product with permanganate at 0°, and separating the malonic acid from the mixture of acids by means of its sparingly soluble calcium salt. Malonic acid also occurs among the decomposition products obtained by hydrolysing cellulose nitrate with concentrated alkali solution (Berl and Fodor, Chem. Zentr. 1911, ii. 1039).

Properties and reactions. Malonic acid crystallises in large triclinic plates, m.p. 133°–134°, decomposing at a higher temperature into carbon dioxide and acetic acid; when heated under a pressure of 8–10 mm. it sublimes unchanged (Krafft and Noerdlinger, Ber. 1889, 22, 816). For its solubility in alcohol and in ether *v.* Lamouroux, Compt. rend. 1899, 128, 999; Klobbie, Zeitsch. physikal. Chem. 1897, 24, 615.

Malonic acid dissolves in hot acetic anhydride to give a yellowish-red solution with a strong yellowish-green fluorescence, intensified by the addition of glacial acetic acid: the reaction is sensitive, being produced by a milligram of the acid (Kleemann, Ber. 1886, 19, 2030).

When malonic acid or its sodium salt is administered internally it passes only in small quantity into the urine, and leads to an increase of urinary carbonates and to the formation of barbituric acid (Marjori, Chem. Zentr. 1896, ii. 106).

Estimation. Malonic acid or its salts may be estimated by oxidation with permanganate at 80°–90° first in acid and then in alkaline solution, and titrating the excess of permanganate (Durand, Ann. Chim. anal. 1903, 8, 330; Cameron and McEwan, Chem. Soc. Proc. 1910 26, 144).

The malonic acid contained in maple products is estimated by precipitation with normal lead acetate and converting the washed precipitate into lead sulphate by evaporation with nitric and sulphuric acids (Albert P. Sy, Chem. Zentr. 1906, ii. 714).

Salts. Malonic acid is a strong dibasic acid forming both acid and normal salts, and the following salts are described: ammonium, barium, cadmium, calcium, cerium, chromium, cobalt, copper, iron, lead, lithium, magnesium, manganese, nickel, potassium, silver, sodium, strontium, uranium, zinc, and brucine (Massol, Ann. Chim. Phys. 1894, [vii.], 1, 184; Finkelstein, Annalen 133, 338; Miczynski, Monatsh. 7, 260; Rimbach, Kilian, Annalen, 1909, 368, 110; Howe, J. Amer. Chem. Soc. 1903, 25, 444; Werner, Chem. Soc. Trans. 1904, 144; Lord, J. Phys. Chem. 1907, 11, 173; Motooki Malsui, J. Coll. Sci. Tōkyō, 1908, 25, ii. 1; Heintzel, Annalen, 139, 129; Mulder, Bull. Soc. chim. [ii.] 29, 532; Fay, Amer. Chem. J. 18, 281; Hilditch, Chem. Soc. Trans. 1909, 1580).

Esters. The *ethyl ester* $CH_2(CO_2Et)_2$, can be prepared from malonic acid by the ordinary processes of esterification (Finkelstein, Annalen, 1864, 133, 338; Conrad, Ber. 1879, 12, 749; Phelps and Tillotson, Amer. J. Sci. 1908, [iv.] 26, 243); but it is more usually prepared by heating cyanoacetic acid with absolute alcohol in the presence of sulphuric acid or in a current of hydrogen chloride (Venable and Claisen, Annalen, 1883, 218, 131; Noyes, J. Amer. Chem. Soc. 1896, 18, 1105; Phelps and Tillotson, *l.c.*), and commonly contains small quantities of ethyl cyanoacetate (Crossley and Gilling, Chem. Soc. Trans. 1909, 95, 27 *f.n.*). *Diethyl malonate* is a colourless liquid, b.p. 197·7°–198·2° (corr.), sp.gr. 1·06104 at 15°, 1·05284 at 25° (Perkin, *ibid.* 1884, 45, 508), 1·07607 at 0° (Wiens, Annalen, 1889, 253, 298); m.p. —49·8° (von Schneider, Zeitsch. physikal. Chem. 22, 233). *Ethyl hydrogen malonate* $HO_2C{\cdot}CH_2{\cdot}CO_2Et$ (Hoff, Ber. 1874, 7, 1572), has sp.gr. 1·201 at 0° n_D 1·337 at 22° (Massol, Ann. Chim. Phys. 1894, [vii.] 1, 184); b.p. 147°/21 mm., sp.gr. 1·1759 at 19°/19°, n_D 1·4275 at 19° (Marguery, Bull. Soc. chim. 1905, [iii.] 33, 541).—*Dimethyl malonate* $CH_2(CO_2Me)_2$, a colourless liquid, b.p. 181·5° (corr.), sp.gr. 1·16028 at 15°; 1·15110 at 25° (Perkin, Chem. Soc. Trans. 1884, 45, 509); b.p. 180·7 (corr.°), sp.gr. 1·1753 at 0° (Wiens, Annalen, 1889, 253, 297); solidifies to a vitreous mass at —80° (von Schneider, Zeitsch. physikal. Chem. 22, 233). Mercuri salts of possible therapeutic value are obtained by shaking mercuric oxide (1 mol.) and methyl malonate ($2\frac{1}{3}$ mols.) in water at 37°; when the *mono-mercuri-dimalonic ester* $Hg[CH(CO_2Me)_2]_2$ thus formed is hydrolysed the acid loses CO_2 and forms the *anhydride* of *oxymercuri-acetic acid* $\begin{array}{l}CH_2{\cdot}Hg\\ |\quad\ \ |\\ CO{-}O\end{array}$. The methyl esters of methyl, ethyl and propyl malonic acid, or the alkali salts of the acid yield similar compounds (Schoeller and Schrauth, D.R.P. 208634, 1909; 213371, 1909).—*Ethyl propyl malonate* $(CO_2Et)CH_2{\cdot}CO_2Pr$, b.p. 211° (corr.), sp.gr. 1·04977 at 0° (Wiens, *l.c.*).—*Dipropyl malonate* $CH_2(CO_2Pr)_2$, b.p. 228°–229° at 770·3 mm. or 228·3° (corr.); sp.gr. 1·02705 at 0° (Wiens, *l.c.*). *Dibutyl malonate* $CH_2(COOC_4H_9)_2$, b.p. 251·5° (corr.), sp.gr. 1·0049 at 0° (Wiens, *l.c.*). *Di*-l-*amyl malonate* $CH_2(COOC_5H_{11})$, has $[M]_D$ 8·09° (Walden, Chem. Zentr. 1899, i. 327). *Diphenyl malonate* $CH_2(CO_2Ph)_2$, has m.p. 50°, b.p. 210°/15 mm. *Dibenzyl malonate*

$$CH_2(CO{\cdot}OCH_2Ph)_2,$$

b.p. 234·5°/14 mm. (Bischoff and Hendenström, Ber. 1902, 35, 3452; Auger and Billy, Compt. rend. 1903, 136, 555). *Dimenthyl malonate* $CH_2(CO{\cdot}OC_{10}H_{19})_2$, m.p. 62°, $[\alpha]_D$ 79·24° (Hilditch, Chem. Soc. Trans. 1909, 95, 1579).

Amides and substituted amides. *Ethyl malonamate* $EtO{\cdot}OC{\cdot}CH_2{\cdot}CONH_2$, m.p. 50°, (Pinner, Ber. 1895, 28, 473); *malonamide* $CH_2(CONH_2)_2$, m.p. 170°, soluble in 12 parts of water at 8° (Henry, Compt. rend. 1885, 100, 943).

Malonylmalonamide

$$CH_2{<}\begin{array}{c}CO{\cdot}NH{\cdot}CO\\ CO{\cdot}NH{\cdot}CO\end{array}{>}CH_2$$

m.p. 252°–253°, prepared by condensing malonamide and ethyl malonate, and the alkyl substituted derivatives in which one or more of the methylene hydrogen atoms are replaced by alkyl groups, have no hypnotic properties (Remfry, Chem. Soc. Trans. 1911, 99, 610).

Malondimethylamide $CH_2(CONHMe)_2$, m.p. 135° (Whiteley, Chem. Soc. Trans. 1903, 83, 24). *Malondiisobutylamide* $CH_2(CONH{\cdot}C_4H_9)_2$, m.p. 126°–127° (Whiteley). *Malonanilic acid* $HOOC{\cdot}CH_2{\cdot}CONHPh$, m.p. 132° with decomposition (Rügheimer, Ber. 1884, 17, 235; Seifert, Ber. 1885, 18, 1358); *ethyl malonanilate*

$$EtO{\cdot}OC{\cdot}CH_2{\cdot}CONHPh,$$

m.p. 38°–39° (Rügheimer and Hoffmann, *ibid.* 1884, 17, 739); *malonmonophenylamide*

$$PhHN{\cdot}CO{\cdot}CH_2{\cdot}CONH_2,\tfrac{1}{2}H_2O,$$

m.p. 153°–154° (Whiteley, Chem. Soc. Proc. 1904, 93); *malonanilide* $CH_2(CONHPh)_2$, m.p, 225° (Whiteley, Chem. Soc. Trans. 1903, 83. 24); *dithiomalonanilide* $CH_2(CSNHPh)_2$, m.p. 149° (Reissert and Moré, Ber. 1906, 39, 3298). *o-*, *m-* and *p-Malonamidobenzoic acids*

$$CH_2(CONH{\cdot}C_6H_4{\cdot}CO_2H)_2,$$

melt and decompose at 242°, 258°–259° and 270° respectively (von Pollack, Monatsh. 1905, 26, 327); the *ethyl ester* of *p-malonamidobenzoic acid*, $CO_2Et{\cdot}CH_2{\cdot}CONH{\cdot}C_6H_4{\cdot}CO_2H$, has m.p. 172°–173° (Schiff, Annalen, 1886, 232, 129; Gazz. chim. ital. 1885, 15, 534); *malonyldiphenetidide*

$$CH_2(CONH{\cdot}C_6H_4{\cdot}OEt)_2,$$

has m.p. 226° (Bischoff, Ber. 1898, 31, 3248). The chloro and bromo substituted derivatives of malonanilide and malonanilic acid are described by Chattaway and Mason (Chem. Soc. Trans. 1910, 97, 340). Certain of the salts and ethyl esters of the three isomeric *malontoluidic acids* $CO_2H{\cdot}CH_2{\cdot}CONHC_7H_7$, were prepared by Rügheimer and Hoffmann (Ber. 1885, 18, 2971). The *o-*, *m-* and *p-* acids melt at 138°–143°, 99°–101°, and 156° respectively; compare also Chattaway and Olmsted (*l.c.* 938). *Malondi-*p*-tolylamide* $CH_2(CONH{\cdot}C_7H_7)_2$, has m.p. 250° *malonmono-*p*-tolylamide* has m.p. 144°; *malondi-*o*-tolylamide* has m.p. 193° (Whiteley, *l.c.*); *dithiomalondi-*o*-toluidide* $CH_2(CSNHC_7H_7)_2$, and the corresponding *p-* isomeride melt at 122°–123° and 145° respectively (Reissert and Moré, Ber. 1906, 39, 3298). *Malondi-α-naphthylamide* $CH_2(CONH{\cdot}C_{10}H_7)_2$, melts at 225°; the β-isomeride melts at 235° (Whiteley, *l.c.*). *α-Malonnaphthil* $C_{10}H_7N{<}\begin{array}{c}CO\\ CO\end{array}{>}CH_2$, has m.p. above 300°, (Meyer, Annalen, 1906, 347, 17). *Malondimethylanilide* $CH_2(CONMePh)_2$, m.p. 109° (Freund, Ber. 1884, 17, 133); *malontetraphenyl-*

amide $CH_2(CO{\cdot}NPh_2)_2$, m.p. 219°–220° with decomposition; *malonmonomethylanilide*

$NHPhCO{\cdot}CH_2{\cdot}CONMePh$,

m.p. 112° (Whiteley, Chem. Soc. Proc. 1904, 93). *Malondibenzylamide* $CH_2(CONH{\cdot}CH_2Ph)_2$, m.p. 142° (Whiteley).

Malonyldiurethane $CH_2(CONH{\cdot}CO_2Et)_2$, m.p. 124° (Conrad and Schulze, Ber. 1909, 42, 729). *Malonylpiperidide* $C_{13}H_{22}O_2N_2$, m.p. 57° (Franchimont, van Rijn and Friedmann, Rec. trav. chim. 1907, 26, 228). *Malonylazoimide* $CH_2(CO{\cdot}N_3)_2$, an explosive oil, is converted into methylenediurethane, $CH_2(NHCO_2Et)_2$, on treatment with alcohol (Curtius, J. pr. Chem. 1895, [ii.] 52, 210).

Ethylenemalonamide $CH_2{<}\begin{smallmatrix}CO{\cdot}NH\\CO{\cdot}NH\end{smallmatrix}{>}C_2H_4$, from ethylenediamine and malonamide at 170°–180° (Freund, *l.c.*); o-*phenylenemalonamide* and o-*tolylenemalonamide* melt above 300° (Meyer, Annalen, 1906, 347, 17).

Malonylcarbamide, barbituric acid (2 : 4 : 6-di-ketohexahydropyrimidine), *v. Pyrimidines.*

Hydrazides. *Malonhydrazide*

$CH_2(CONH{\cdot}NH_2)_2$

crystallises in needles, m.p. 154°; for condensation products with aldehydes and alkyl acetoacetates, see Curtius, Schöfer and Schwan (J. pr. Chem. 1895, [ii.] 51, 180); Ruhemann (Ber. 1894, 27, 1658); Bülow and Bozenhardt, (Ber. 1909, 42, 4784; 43, 234; 551). *Malonphenylhydrazide* $CH_2(CONH{\cdot}NHPh)_2$, m.p. 187° (Goldsmith, *ibid.* 1888, 21, 1240; Asher, *ibid.* 1897, 30, 1018). The phenylhydrazine salt of *phenylhydrazidemalonic acid*

$PhNH{\cdot}NH_2{\cdot}HO_2C{\cdot}CH_2{\cdot}CONH{\cdot}NHPh$

melts at 141°–143°, and yields the *acid*

$CO_2H{\cdot}CH_2{\cdot}CONH{\cdot}NHPh$,

m.p. 154° on treatment with acid, and *malonylphenylhydrazide*, $CH_2{<}\begin{smallmatrix}CO\\CO\end{smallmatrix}{>}N_2HPh$, m.p. 128°, when heated at 200° (Fischer and Passmore, Ber. 1889, 22, 2728).

Malondihydroxamic acid $CH_2(C(OH){:}NOH)_2$, m.p. 160°, *ammonium malonylhydroxamate*

$(NH_4)O_2C{\cdot}CH_2{\cdot}C(OH){:}NOH$,

m.p. 181° (Hantzsch, Schatzmann, and Urbahn, Ber. 1894, 27, 804; Pickard, Allen, Bowdler and Carter, Chem. Soc. Trans. 1902, 81, 1572).

Nitriles of malonic acid. The *seminitrile* or *cyanacetic acid* $CN{\cdot}CH_2{\cdot}CO_2H$, prepared by the action of potassium cyanide on chloroacetic acid (Fiquet, Ann. Chim. Phys. 1893, [vi.] 29, 438; Phelps and Tillotson, Amer. J. Sci. 1908, iv. 26, 267, 278), forms well-defined large prisms, m.p. 69°–70°. The salts of cyanacetic acid are either amorphous or crystallise with difficulty (Engel, Bull. Soc. chim. [ii.] 44, 425; Meves, Annalen, 1867 143, 201).

Ethyl cyanacetate $CN{\cdot}CH_2{\cdot}CO_2Et$, b.p. 207° (Phelps and Tillotson, *l.c.* 264, 257); condenses with carbamide to form the ester,

$CO{<}\begin{smallmatrix}NH\\NH\end{smallmatrix}{>}C{\cdot}CH_2{\cdot}CO_2Et$,

m.p. 162° (decomp.), soluble in 8333 parts of water at 24°. It gives *m*-toluidine, strychnine, bromine and metallic derivatives. The corresponding *methyl ester* crystallises with 1½ mols. H_2O, m.p. 116° (anhydrous has m.p. 128°) and gives similar derivatives to the ethyl ester (Frerichs and Hartwig, J. pr. Chem. 1905, [ii.] 72, 489; *ibid.* 1906, [ii.] 73, 21).

The *sodium* compound of ethyl cyanacetate, $CN{\cdot}CHNa{\cdot}CO_2Et$ or $CN{\cdot}CH{:}C{<}\begin{smallmatrix}ONa\\OEt\end{smallmatrix}$, forms a neutral solution in water which is not decomposed by hydrochloric acid in the cold. It absorbs iodine rapidly, forming the compound $C_5H_6O_2NI$, and also ethyl dicyanosuccinate, m.p. 120°, as the result of a secondary reaction.

Methyl cyanacetate $CN{\cdot}CH_2{\cdot}CO_2Me$ is a colourless liquid, b.p. 177° (Fenton, Chem. Soc. Trans. 1900, 1297). *Menthyl cyanacetate*

$CN{\cdot}CH_2{\cdot}CO_2{\cdot}C_{10}H_{19}$,

flattened needles, m.p. 83°–84°, $[\alpha]_D$—81·12° (2 p.c. solution in benzene); the monobromo-derivative has m.p. 134°–135° (Bowack and Tapworth, Chem. Soc. Proc. 1903, 22). o-*Tolylcyanacetate* $CN{\cdot}CH_2{\cdot}CO_2{\cdot}C_6H_4Me$, prisms, m.p. 70·4° (Haller, Compt. rend. 1889, 108, 1116).

Cyanacetamide $CN{\cdot}CH_2{\cdot}CONH_2$ forms hexagonal tablets, m.p. 120° (Hesse, Amer. Chem. J. 18, 724; Errera, Gazz. chim. ital. 27, ii. 412; Sachs, Ber. 1900, 33, 964; Fiquet, *l.c.*). *Cyanacetanilide*, $CN{\cdot}CH_2{\cdot}CONH{\cdot}C_6H_5$, m.p. 198·5°–200°. The fluorine derivative

$CN{\cdot}CH_2{\cdot}CONH{\cdot}C_6H_4F$

has m.p. 150°–151° (Wallach and Heusler, Annalen, 1888, 243, 223). *Cyanacetdiphenylamide* $CN{\cdot}CH_2{\cdot}CO{\cdot}N(C_6H_5)_2$, has m.p. 153°–154° (Guareschi). *Cyanacet*-p-*tolylamide*,

$CN{\cdot}CH_2{\cdot}CONH{\cdot}C_7H_7$,

m.p. 180° (Grothe, Arch. Pharm. 238, 608).

Cyanacetxylylamide

$CN{\cdot}CH_2{\cdot}CONH{\cdot}C_6H_3(CH_3)_2$,

has m.p. 167°.

Cyanacetpiperidide, $CN{\cdot}CH_2{\cdot}CONC_5H_{10}$, forms large prisms, m.p. 88°–89° (Guareschi).

Cyanacetphenocoll

$OEt{\cdot}C_6H_4{\cdot}NH{\cdot}CO{\cdot}CH_2{\cdot}NHCO{\cdot}CH_2{\cdot}CN$,

white crystals, m.p. 28°.

Cyanacetylanisidine

$OMe{\cdot}C_6H_4{\cdot}NH{\cdot}CO{\cdot}CH_2{\cdot}CN$,

m.p. 136°, and *Cyanacetyl*-p-*aminophenetole* $OEt{\cdot}C_6H_4{\cdot}NH{\cdot}CO{\cdot}CH_2{\cdot}CN$, m.p. 180°–181°, yield the corresponding oxamic acid on oxidation (Nicola, Ann. Chim. Farm. 18, 353).

Cyanoacetylhydrazine $CN{\cdot}CH_2{\cdot}CO{\cdot}NH{\cdot}NH_2$, m.p. 114·5°–115°. With aldehydes it yields the compounds $CN{\cdot}CH_2{\cdot}CONH{\cdot}N{:}CHR$, with ketones, the compounds $CN{\cdot}CH_2{\cdot}CONHN{:}CRR'$.

Cyanacetylacetylhydrazine,

$CN{\cdot}CH_2{\cdot}CONH{\cdot}NH{\cdot}CO{\cdot}CH_3$,

has m.p. 172°.

Cyanacetyl phenylsulphonylhydrazine

$CN{\cdot}CH_2{\cdot}CONH{\cdot}NH{\cdot}SO_2C_6H_5$,

is formed by the action of benzenesulphonic chloride on cyanacetylhydrazine (Rothenberg, Ber. 1894, 27, 1894).

Cyanacetylcyanamide $CN{\cdot}CH_2{\cdot}CO{\cdot}NH{\cdot}CN$, m.p. 93° (D. R. P. 167138, Chem. Zentr. 1906, i. 797).

Cyanacetylcarbamide $CN{\cdot}CH_2{\cdot}CONH{\cdot}CO{\cdot}NH_2$, m.p. 212° (decomp.). The *methyl carbamide*, m.p. 206°, the *phenyl*, m.p. 216°, and other alkyl derivatives are described (D. R. P. 175415; Chem. Zentr. 1906, ii. 1590; Baum, Ber. 1908, 41, 532; Conrad and Schulze, Ber.

1909, 42, 735.) They are employed technically in the production of the purine bases.

Cyanacetylurethane

$$CN{\cdot}CH_2{\cdot}CO{\cdot}NH{\cdot}CO_2Et,$$

m.p. 167°–168° (Conrad and Schulze, *l.c.*).

Malonodinitrile $CH_2(CN)_2$ (Henry, Compt. rend. 1886, 102, 1394; Hesse, Amer. Chem. J. 1896, 18, 726) is a colourless crystalline compound, m.p. 29°–30°, b.p. 218°–219°/760 mm. (Henry); b.p. 99°/11 mm. or 109°/20 mm., soluble in 7·5 parts water, 2·5 parts alcohol, 5 parts ether, 10 parts chloroform, or 15 parts benzene (Hesse); forms the mono- and di- silver salts $CHAg(CN)_2$ and $CAg_2(CN)_2$ (Hesse), and reacts with hydroxylamine (1 mol.) to form *cyanethenylamidoxime*

$$CN{\cdot}CH_2{\cdot}C(NH_2):NOH,$$

m.p. 124°–127° with decomposition, and yields an *acetyl* and *benzoyl* derivative, m.p. 142° and 184°–192° respectively; *malonodiamidoxime* $CH_2[C(NH_2):NOH]_2$ melts and decomposes at 163°–167°, and yields a *diacetyl* and *dibenzoyl* derivative, m.p. 153°–159° and 183°–185° respectively (Schidtmann, Ber. 1896, 29, 1168).

Aldehydes of malonic acid. The *semialdehyde*, $CHO{\cdot}CH_2{\cdot}CO_2H$, obtained by Wohl and Emmerlich (Ber. 1900, 33, 2760) from β-chloropropionacetal $CH_2Cl{\cdot}CH_2{\cdot}CH(CO_2Et)_2$ is not stable and its physical constants have not been determined. The *amide* $(CHO{\cdot}CH_2{\cdot}CONH_2)$ obtained by Langheld (Ber. 1909, 42, 2360) by the action of sodium hypochlorite on asparagine, is not a stable compound but yields a *phenylhydrazone* $C_9H_{11}ON_3$, m.p. 239°–240°. The *nitrile* or *cyanacetaldehyde* $CN{\cdot}CH_2{\cdot}CHO$ is a colourless, limpid, volatile inflammable liquid of b.p. 71·5° (Chautard, Ann. Chim. Phys. 1889, [vi.] 16, 176).

The dialdehyde and semialdehyde of malonic acid are stated to be among the products formed when the ozonide peroxides of α- or β-linolenic acids are decomposed by boiling with water (Erdmann, Bedford and Raspe, Ber. 1909, 42, 1334).

Malonic acid halides. *Malonic semichloride* $CO_2H{\cdot}CH_2{\cdot}COCl$, m.p. 65° with decomposition, obtained by the action of thionyl chloride on an ethereal solution of malonic acid, is unstable (Staudinger and Ott, Ber. 1908, 41, 2208); the *ethyl ester* $COCl{\cdot}CH_2{\cdot}CO_2Et$, has b.p. 170°–180°, (Van 't Hoff, Ber. 1874, 7, 1572), or 68°–70°/13 mm., loses HCl at 125°–130°, and yields the *compound* $C_{13}H_{12}O_8$, yellow prisms, m.p. 170°–180° (corr.) (Marguery, Bull. Soc. chim. 1900, [3] 33, 541: Leuchs, Ber. 1906, 39, 2641). The *nitrile* or *cyanacetylchloride* $CN{\cdot}CH_2{\cdot}COCl$, was prepared by Mulder (Bull. Soc. chim. [ii.] 29, 533). *Malonyl chloride* $CH_2(COCl)_2$, obtained when malonic acid is mixed with an excess of thionyl chloride and distilled under reduced pressure (Staudinger and Bereza, Ber. 1908, 41, 4461), and yields carbon suboxide (*q.v.*) when treated with silver or lead oxide (Staudinger and Bereza, *l.c.*), is a colourless liquid, b.p. 58°/27 mm. (Auger, Ann. Chim. Phys. 1891, [vi.] 22, 325).

The *seminitrile* of *malonyl bromide*, *cyanacetylbromide*, crystallises in the monoclinic system, and has m.p. 77°–79° (Hübner, Annalen, 1864, 131, 66).

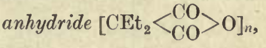
Substituted Malonic Acids and Derivatives.

Alkyl malonic acids. The hydrogen atoms of the methylene group in ethyl malonate can be replaced by sodium (Conrad, Annalen, 1880, 204, 129; Ballo, Ber. 1881, 335); ethyl sodiomalonate, $CHNa(CO_2Et)_2$, is a colourless crystalline compound; it does not undergo dissociation in alcoholic solution (Vorländer and Schilling, *ibid.* 1899, 32, 1876); is not stable in the presence of water, and yields no colour with ferric chloride (Vorländer, *ibid.* 1903, 36, 268). It condenses with alkyl and aryl halides to form the alkyl or aryl substituted malonic ester, the sodio-derivative of which yields on similar treatment the di-substituted ester (Bischoff, *ibid.* 1895, 28, 2616). The corresponding substituted malonic acids can be obtained by hydrolysis of the esters, and these lose carbon dioxide when heated above their melting-point with the formation of the corresponding acid of the acetic series:

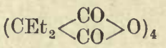
$$CH_2(CO_2Et)_2 \rightarrow CHR(CO_2Et)_2 \rightarrow CRR'(CO_2Et)_2$$
$$\rightarrow CRR(COOH)_2 \rightarrow CHRR'{\cdot}COOH.$$

With the exception of diethylmalonic acid, which is employed in the synthetic preparation of certain pyrimidines of therapeutic value, a description of the numerous alkyl malonic acids does not come within the scope of this article.

Diethylmalonic acid $CEt_2(CO_2H)_2$, m.p. 112°; the *anhydride*



$[CEt_2{<}^{CO}_{CO}{>}O]_n$, has m.p. 95°–97° (Staudinger and Ott, Ber. 1908, 41, 3829); the *quadrimolecular anhydride*



$$(CEt_2{<}^{CO}_{CO}{>}O)_4$$

has m.p. 220° (Einhorn and Diesbach, Ber. 1906, 39, 1222); the *ethyl ester* has b.p. 228·5°–229·5° (corr.) (Michael, J. pr. Chem. 1905, [ii.] 72, 537); *methyl ester* has b.p. 204°–205° (Meyer, Ber. 1906, 39, 198); *diethylmalonate* of *glycollamide*

$$CEt_2(CO{\cdot}O{\cdot}CH_2{\cdot}CO{\cdot}NH_2)_2,$$

has m.p. 126°; *diethylaminoethyl diethylmalonate* $CEt_2(CO{\cdot}OCH_2{\cdot}CH_2{\cdot}NEt_2)_2$ (Einhorn, Annalen, 1908, 359, 145); *ethyl diethylmalonamate*, has m.p. 79°, b.p. 263° (D. R. P. 182045); *diethylmalonamic acid*, m.p. 146°, *diethylmalondiethylamic acid* $NEt_2CO{\cdot}CEt_2{\cdot}CO_2H$, m.p. 88°–90° (Einhorn and Diesbach, Ber. 1906, 39, 1222); *diethylmalonamide*, m.p. 224° (corr.) (Fischer and Dilthey, *l.c.*), forms a crystalline compound, $CEt_2(CONH_2)_2{\cdot}CCl_3{\cdot}CHO$, m.p. 178° with chloral hydrate (Burrows and Keane, Chem. Soc. Trans. 1907, 91, 269). *Diethylmalonylmalonamide* has m.p. 175°–176°, *diethylmalonylmethylmalonamide* has m.p. 118°–119°; *diethylmalonylethylmalonamide*, m.p. 88°–89°; *diethylmalonylbenzidine*, m.p. 224° (Remfry, *l.c.*). *Diethylmalonylmonophenylamide* $NH_2{\cdot}CO{\cdot}CEt_2{\cdot}CO{\cdot}NHPh$, m.p. 132° the *sulphanilide* $NH_2{\cdot}CO{\cdot}CEt_2{\cdot}CO{\cdot}NH{\cdot}C_6H_4{\cdot}SO_3H$, has a strong acid reaction and decomposes carbonates, *diethylmalonanilic acid*

$$NHPh{\cdot}CO{\cdot}CEt_2{\cdot}CO_2H,$$

m.p. 105° (Conrad and Zart, Annalen, 1905, 340, 335). *Diethylmalonyl*-p-*phenetidine*

$$CEt_2(CO{\cdot}NH{\cdot}C_6H_4{\cdot}OEt)_2,$$

m.p. 143°, has antipyretic properties and exerts a soporific action (D. R. P. 165311). *Diethylmalonyldiurethane* $CEt_2(CO{\cdot}NH{\cdot}CO_2Et)_2$, a thick oil (Traube, D. R. P. 179946); *ureide of diethylmalonic acid* $CO_2H{\cdot}CEt_2{\cdot}CO{\cdot}NH{\cdot}CO{\cdot}NH_2$, m.p. 162° (corr.) (Fischer and Dilthey, Annalen, 335, 334); *ethyl diethylmalonylureide*

$$CO_2Et{\cdot}CEt_2{\cdot}CO{\cdot}NH{\cdot}CO{\cdot}NH_2,$$

m.p. 85°; *methyl diethylmalonylureide*, m.p. 115° (Boehringer and Söhne, D. R. P. 193447); *diethylmalonyluramide*

$$NH_2{\cdot}CO{\cdot}CEt_2{\cdot}CO{\cdot}NH{\cdot}CO{\cdot}NH_2,$$

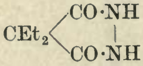
m.p. 199° (Conrad and Zart, *l.c.*); *diethylmalonyltetramethyldicarbamide*

$$CEt_2(CO{\cdot}NH{\cdot}CO{\cdot}NMe_2)_2,$$

m.p. 158°; *diethylmalonyltetraethyldicarbamide*, m.p. 123°–126° (Einhorn, D. R. P. 193446). *Diethylmalonylanthranilamide*

$$CEt_2(CO{\cdot}NH{\cdot}C_6H_4{\cdot}CONH_2)_2,$$

m.p. 215°. cyclo*Diethylmalonylhydrazide*



m.p. 256° (Einhorn, Annalen, 1908, 359, 145). *Diethylmalonodinitrile* $CEt_2(CN)_2$, m.p. 44°, b.p. 195°–195·5° (Hesse, Amer. Chem. J. 1896, 18, 723; Errera and Berté, Gazz. chim. ital. 1896, 26, ii. 220). The *seminitrile of diethylmalonic acid* (*diethylcyanacetic acid*)

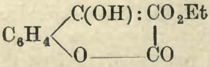
$$CN{\cdot}CEt_2{\cdot}CO_2H,$$

has m.p. 57°, b.p. 162°–164°/18 mm., the *ethyl ester*, b.p. 215°–216°, 100°–101°/14 mm. (Hesse, Amer. Chem. J. 1896, 18, 723; Hessler, *l.c.* 171). *Diethylcyanacetamide* $CN{\cdot}CEt_2{\cdot}CONH_2$, colourless plates, m.p. 120°, (Hesse). *Diethylmalonic semichloride* is an oil (Staudinger and Ott, Ber. 1908, 41, 2208); *diethylmalonyl chloride* $CEt_2(COCl)_2$, has b.p. 196·5°–197·5° (Fischer and Dilthey, Ber. 1902, 38, 844).

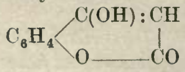
Acyl malonic esters. The acyl derivatives of malonic esters are prepared by the condensation of the sodiomalonic ester with the acyl chloride: the corresponding acids are not known.

The acetyl, diacetyl, phenacetyl, diphenacetyl, propionyl, butyryl, benzoyl, nitrobenzoyl, succinyl, adipyl, phthalyl, and camphoryl malonic esters and derivatives have been prepared, *see* Michael, Amer. Chem. J. 1892, 14, 481; Schott, Ber. 1896, 29, 1985; Guinchant, Bull. Soc. chim. 1895, [iii.] 13, 1029; Held, Compt. rend. 116, 720; Lang, Ber. 1887, 20, 1326; Knoevenagel and Faber, Ber. 1898, 31, 2771; Claisen, Annalen, 1896, 291, 72; Bischoff and Rach, Ber. 1884, 17, 2793; Haller, Bull. Soc. chim. [ii.] 45, 271; Barthe, *ibid.* [ii.] 21, 529; Scheiber, Ber. 1909, 42, 1318; Wislicenus, Annalen, 1887, 242, 23; Wislicenus and Winzer, Annalen, 1890, 257, 298; Baeyer, Ber. 1892, 25, 1039; Ingle, Ber. 1894, 27, 2526).

Ethyl sodiomalonate condenses with acetyl salicylyl chloride or ortho-substituted salicylylchlorides to form ethyl β-hydroxycoumarin-α-carboxylate



or the corresponding ortho-substituted derivatives; the acids obtained from these compounds by hydrolysis lose carbon dioxide and yield the β-hydroxycoumarin



or an ortho-substituted derivative, substances of potential therapeutic value.

Ethyl β-hydroxycoumarin-α-carboxylate has m.p. 93°; *β-hydroxycoumarin* has m.p. 206°; *ethyl 3:5-dichloro-β-hydroxycoumarin-α-carboxylate* has m.p. 135°, and *3:5-dichloro-β-hydroxycoumarin* has m.p. 275° (Aktien Gesellschaft für Anilinfabrikation, D. R. P. 102096, 1899; compare Anschütz, Ber. 1903, 36, 463).

Chloro, bromo, and iodo malonic acids. Malonic acid, its esters, amides and substituted amides react readily with chlorine or bromine, forming under suitable conditions the mono- and di-halogen derivatives. The halogen in certain of these compounds is highly reactive and liberates iodine from hydrogen iodide with the regeneration of the malonic compound according to the equation

$$(CONH_2)_2CBr_2+4HI\\=(CONH_2)_2CH_2+2HBr+2I_2.$$

The reaction is in most cases quantitative and affords a rapid means of estimating the halogen in the compound (Whiteley, Chem. Soc. Proc. 1908, 24, 278).

Chloromalonic acid $CHCl(CO_2H)_2$, m.p. 133°, (Conrad and Guthzeit, Ber. 1882, 15, 605), the *ethyl ester*, b.p. 137°–139°/50 mm., sp.gr. 1·1776 at 20°/4°, n_D 1·4327 at 20° (Brühl, J. pr. Chem. [ii.] 50, 140); b.p. 91°/2 mm. (Forster and Müller, Chem. Soc. Trans. 1910, 97, 126); the *seminitrile* or *ethyl chlorocyanacetate*

$$CN{\cdot}CHCl{\cdot}CO_2Et,$$

b.p. 190°, (Henry, Compt. rend. 1887, 104, 1618). *Chloromalonamide* $CHCl(CONH_2)_2$, m.p. 170° (Conrad and Bischoff, Annalen, 209, 231): *chloromalondimethylanilide* $CHCl(CONMePh)_2$, m.p. 184°, and *chloromalontetraphenylamide* $CHCl(CONPh_2)_2$, m.p. 213° (Whiteley). *Chlormalonaldehyde* $OH{\cdot}CH{:}CCl{\cdot}CHO$, m.p. 144°, gives with aniline, the *monoanilide*

$$NHPh{\cdot}CH{:}CCl{\cdot}CHO,$$

m.p. 193° (Dieckmann and Platz, Ber. 1904, 37, 4638).

Dichloromalonic acid $CCl_2(CO_2H)_2$ (Dootson, Chem. Soc. Trans. 1899, 169); the *aniline salt* has m.p. 105° (Conrad and Reinbach, Ber. 1902, 35, 1813); the *ethyl ester*, b.p. 231°–234°, sp.gr. 1·268 at 17°/15° (Conrad and Brückner, *ibid.* 24, 2993); the *methyl ester*, b.p. 110°–120°/20 mm., (Zincke, Kegel, *ibid.* 1890, 23, 244). *Dichloromalonamide*, m.p. 204° (Conrad and Brückner, *l.c.*; Zincke and Kegel, *l.c.*).

Bromomalonic acid $CHBr(CO_2H)_2$ (Petrieff; Ber. 1878, 11, 414; Conrad and Reinbach, Ber. 1902, 35, 1813; Lutz, Ber. 1902, 35, 2549) crystallises in plates, m.p. 113°; the *barium salt*, and the *silver salts* are crystalline. *Ethyl bromomalonate*, $CHBr(CO_2Et)_2$, b.p. 233°–235° with slight decomposition (Knoevenagel, Ber. 1888, 21, 1356), 118°–119°/11 mm. (private communication); 150°–152°/25 mm. (Bischoff, Ber. 1907, 40, 3134); sp.gr. 1·426 at 15° (Conrad and Brückner, Ber. 1891, 24, 2997); *methyl bromomalonate*

$CHBr(CO_2Me)_2$, b.p. 112·5°–113°/15 mm. (Bischoff, *l.c.*). *Bromomalondiurethane*

$CHBr(CO{\cdot}NH{\cdot}CO_2Et)$

m.p. 148° (Whiteley, private communication).

The *seminitrile* or *bromocyanacetic acid* $CN{\cdot}CHBr{\cdot}CO_2H$ (Petrieff, J. Russ. Phys. Chem. Soc. 10, 160). *Ethylbromcyanacetate*, b.p. 116°/25 mm. (Nef, Annalen, 1897, 298, 202).

Bromomalonitrile, $CHBr(CN)_2$, has m.p. 65°–66° (Hesse, Amer. Chem. J. 1896, 18, 723).

Bromomalonaldehyde $OH{\cdot}CH : CBr{\cdot}CHO$, m.p. 140°; the *anilide* $NHPh{\cdot}CH : CBr{\cdot}CHO$, has m.p. 184°; the *dianilide hydrobromide*

$NHPh{\cdot}CH : CBr{\cdot}CH : NHPh,HBr$,

crystallises with EtOH and has m.p. 217° (Lespieau, Compt. rend. 1901, 133, 538).

Dibromomalonic acid $CBr_2(CO_2H)_2$ (Petrieff, Ber. 1874, 7, 400; Willstätter, Ber. 1902, 35, 1374; Conrad and Reinbach, Ber. 1902, 35, 1813) has m.p. 130°–131° (Willstätter), or 147° (Conrad and Reinbach); the heat of solution is +2·02 cal. *Potassium hydrogen dibromomalonate* forms brilliant anhydrous crystals, heat of dissolution −5·60 cal.; the *potassium salt* becomes anhydrous at 100°, decomposes at 200°, and has heat of dissolution −9·94 cal. (Massol, Compt. rend. 1892, 114, 1200); the crystalline *aniline* salt melts at 113° (Conrad and Reinbach, *l.c.*). *Methyl dibromomalonate*, $CBr_2(CO_2Me)_2$, m.p. 63°–65°; *ethyl dibromomalonate* has b.p. 145°–155°/25 mm. (Conrad and Brückner, Ber. 1891, 24, 3001), b.p. 126°–131°/14 mm. (Reitter and Weindel, *ibid.* 1907, 40, 3358); 135°–137°/13 mm. (Ruhemann and Orton, Chem. Soc. Trans. 1895, 67, 1003); b.p. 134°/12 mm. (private communication). *Dibromomalonamide*

$CBr_2(CONH_2)_2$,

m.p. 206°, *dibromomalondimethylamide*

$CBr_2(CONHMe)_2$,

m.p. 162° (Freund, Ber. 1884, 17, 780); *dibromomalonanilide* $CBr_2(CONHPh)_2$, m.p. 143°–144° (Staudinger and Klaver, Ber. 1908, 41, 906). *Dibromomalonitrile* $CBr_2(CN)_2$, m.p. 123·5°–124° (Hesse, Amer. Chem. J. 1896, 18, 723). *Dibromomalonylchloride* $CBr_2(COCl)_2$, has b.p. 75°–77°/15 mm., and solidifies at the ordinary temperature (Staudinger and Bereza, Ber. 1908, 41, 4461); *dibromomalonyldibromide*

$CBr_2(COBr)_2$

has b.p. 91°–92°/13 mm. (Staudinger and Klever, *ibid.* 1908, 41, 906).

Iodomalondimethylanilide

$CHI(CONMePh)_2$,

has m.p. 164° (Vorländer and Herrmann, Ber. 1898, 31, 1826).

Di-iodomalonic acid $CI_2(CO_2H)_2$, is very unstable; it crystallises in pale yellow leaflets, m.p. 119°–120°. The *methyl ester* crystallises in pale yellow needles, m.p. 79°–80° (Willstätter, Ber. 1902, 35, 1374).

Ethyl chlorobromomalonate $CClBr(CO_2Et)$, has b.p. 136°–139°/35 mm., sp.gr. 1·467 at 16°/15° (Conrad and Brückner, Ber. 1891, 24, 2993); the *methyl ester* is crystalline, m.p. 40°–42° (Bischoff, Ber. 1907, 40, 3150).

Derivatives of cyanomalonic acid. *Ethyl cyanomalonate* $CN{\cdot}CH(CO_2Et)_2$, is a colourless oil, b.p. 120°–130°/25 mm., with a pungent smell and acid reaction, and forms crystalline soluble salts. *Methyl cyanomalonate* also yields crystalline metallic derivatives (Haller, Compt. rend. 1882, 95, 142; Ann. Chim. Phys. 1889, [vi.] 16, 403). The *ethyl ester* of the *seminitrile* (*ethyl dicyanacetate*) $(CN)_2CH{\cdot}CO_2Et$ is crystalline, and forms crystalline sodium, silver and copper salts. The methyl ester is also known (Haller, Compt. rend. 1890, 111, 53).

Ethyl dicyanomalonate or *ethyl cyanimino*iso*succinate* $NH{:}C(CN){\cdot}CH(CO_2Et)_2$, colourless needles, m.p. 93°.

Derivatives of triazomalonic acid. *Ethyl methyltriazomalonate* $CH_3{\cdot}CN_3(CO_2Et)_2$, is a colourless liquid, b.p. 69°/0·6 mm., sp.gr. 1·11695 at 16°/16°; *methyltriazomalonamide* $CH_3{\cdot}CN_3(CONH_2)_2$, m.p. 137·5°; *methyltriazomalonic acid* $CH_3{\cdot}CN_3(CO_2H)_2$, m.p. 87·5°; *ethyl triazomalonic acid* $C_2H_5{\cdot}CN_3(CO_2H)_2$, melts and decomposes at 105°–107°; the *ethyl ester* has b.p. 83·5°/0·7 mm., sp.gr. 1·1161 at 16°/10°; the *amide* has m.p. 167°.

Phenyltriazomalonic acid $C_6H_5{\cdot}CN_3(CO_2H)_2$, m.p. 99°; the *ethyl ester* decomposes on attempted distillation, the *amide* has m.p. 189°. *Ethyl bistriazomalonate* $C(N_3)_2(CO_2Et)_2$, has b.p. 115°–115·5°/0·81 mm., sp.gr. 1·2136 at 20°, and is violently decomposed by sulphuric acid; the *amide* melts at 162° with vigorous decomposition (Forster and Müller, Chem. Soc. Trans. 1910, 97, 126).

Aminomalonic acid and derivatives. *Aminomalonic acid* $H_2N{\cdot}CH(CO_2H)_2,H_2O$, m.p. 109° (Baeyer, Annalen, 131, 291; Ruhemann and Orton, Chem. Soc. Trans. 1895, 67, 1007; Lutz, Ber. 1902, 35, 2549); *ethyl aminomalonate hydrochloride*, $H_2N{\cdot}CH(CO_2Et)_2,HCl$, forms colourless needles, m.p. 162° (decomp.). The hydrochloride of the *methyl ester* melts and decomposes at 159°. *Aminomalonamide* $H_2N{\cdot}CH(CONH_2)_2$, m.p. 192° (Conrad and Guthzeit, Ber. 1882, 15 605; Piloty and Neresheimer, *ibid.* 1906, 39, 514). *Aminomalonanilide* $(CO{\cdot}NHPh)_2CH{\cdot}NH_2$, m.p. 141°–142°; *aminomalondimethylanilide* $(CONMePh)_2CH{\cdot}NH_2$, m.p. 108°; *aminomalontetraphenylamide* $(CONPh_2)_2CH{\cdot}NH_2$, m.p. 200°–201°, are obtained by reducing the corresponding *iso*nitroso derivatives (Whiteley, Chem. Soc. Proc. 1904, 92).

Methyl formylaminomalonate

$CHO{\cdot}NH{\cdot}CH(CO_2Me)_2$,

m.p. 85°, b.p. 250° (decomp.); the *ethyl ester* has m.p. 48°; the *amide* has m.p. 206° (decomp.) (Conrad and Schulze, Ber. 1909, 42, 729).

Diaminomalonamide $C(NH_2)_2(CO{\cdot}NH_2)_2$ (Conrad and Brückner, Ber. 1891, 24, 2993; Ruhemann and Orton, Chem. Soc. Trans. 1895, 67, 1002) loses ammonia and yields *iminomalonamide* $NH{:}C(CO{\cdot}NH_2)_2$ when carefully heated at 90°–100°. *Methyl tetramethyldiaminomalonate* $C(NMe_2)_2(CO_2Me)_2$, has m.p. 83°–85°, and yields on hydrolysis *tetramethyldiaminomalonic acid*, m.p. 133° (Willstätter, Ber. 1902, 35, 1378).

Iminodimalonamide

$(H_2N{\cdot}OC)_2CH{\cdot}NH{\cdot}CH(CONH_2)_2$,

decomposes without fusion (Conrad and Guthzeit, Ber. 1882, 15, 605).

Anilinomalonic acid $NHPh{\cdot}CH(CO_2H)_2$, m.p. 118°–119° (Reissert, Ber. 1898, 31, 382; Conrad and Reinbach, *ibid.* 1902, 35, 511). *Ethyl* *anilinomalonate* NHPh·CH(CO_2Et)$_2$, m.p. 44°–45° (Curtiss, Amer. Chem. J. 1897, 19, 691), yields indoxylic acid when heated (Blank, Ber. 1898, 31, 1812).

Methyl anilinomalonate, m.p. 68°; the *hydrochloride* has m.p. 133°–135°; the *amide*, m.p. 156°.

Ethyl p-*toluidinomalonate* and *ethyl β-naphthylaminomalonate* melt at 55° and 88° respectively and yield indoxylic acid derivatives when heated (Blank, Ber. 1898, 31, 1812).

Anilinomalonanilic acid

NHPh·CH(CO_2H)(CO·NHPh),

melts and decomposes at 157° (Reissert, *l.c.*). *Anilinomalonanilide*, m.p. 246°–247° (Wislicenus and Münzesheimer, Ber. 1898, 31, 551).

Ethyl dianilinomalonate (NHPh)$_2$C(CO_2Et)$_2$, m.p. 117°–118° (Curtiss, Amer. Chem. J. 1897, 19, 691); *methyl dianilinomalonate*, m.p. 124°–125° (Conrad and Reinbach, Ber. 1902, 35, 511).

Aniline dianilinomalonate melts and decomposes at 120° (Conrad and Reinbach, Ber. 1902, 35, 1813).

Methyl phenyliminomalonate

PhN:C(CO_2Me)$_2$,

is a thick yellow oil, reacting vigorously with water, alcohols, ammonia, amines and acids to form substituted anilinomalonates (Curtiss and Spencer, J. Amer. Chem. Soc. 1911, 33, 985).

Alkyl- and aryl-oxy-malonic acids. *Ethyl ethoxymalonate* CH(OEt)(CO_2Et)$_2$ has b.p. 228° and yields on hydrolysis *ethyl ethoxymalonic acid*, m.p. 123°–125°.

Ethyl diethoxymalonate C(OEt)$_2$(CO_2Et)$_2$, m.p. 43°–44°, b.p. 228° (Bischoff, Ber. 1897, 30, 487; Curtiss, Amer. Chem. J. 1897, 19, 691).

Ethyl diphenoxymalonate C(OPh)$_2$(CO_2Et)$_2$, b.p. 250°–260°/60 mm.; the *acid* has m.p. 173°.

Nitrophenoxymalonates. Sodium *o*-, *m*- and *p*-nitrophenoxides react with bromo-malonic esters in benzene or xylene solution according to the equation

$$NO_2{\cdot}C_6H_4{\cdot}ONa + CXBr(CO_2Y)_2 = NaBr + NO_2{\cdot}C_6H_4{\cdot}O{\cdot}CX(CO_2Y)_2$$

where X=H, Me, Et; Y=Me, Et: and sodium nitrophenoxides condense with methyl and ethyl dibromomalonates yielding bisnitrophenoxymalonic esters $(COOR)_2C(O{\cdot}C_6H_4{\cdot}NO_2)_2$ (Bischoff, Ber. 1907, 40, 3134, 3150).

Nitromalonic Esters and Derivatives. *Ethyl nitromalonate* $NO_2{\cdot}CH(CO_2Et)_2$ is a colourless liquid, b.p. 127°/10 mm., sp.gr. 1·1988 at 20°, 1·220 at 0°: the alkali salts are bright yellow and probably have the *iso*nitro structure $(CO_2Et)_2C{:}NO{\cdot}OR$ (Wahl, Compt. rend. 1901, 132, 1050; *cp.* Franchimont and Klobbie, Rec. trav. chim. 1889, 8, 283); *methyl nitromalonate* $NO_2{\cdot}CH(CO_2Me)_2$ forms a crystalline ammonium salt, m.p. 166° (Franchimont and Klobbie, *l.c.*). *Ethyl bromonitromalonate*

$NO_2{\cdot}CBr(CO_2Et)_2$

is a neutral oil, b.p. 136°–137°/11 mm.; the *methyl ester* has b.p. 133°/16 mm. (Willstätter and Hottenroth, Ber. 1904, 37, 1775).

Nitromalonamide $NO_2{\cdot}CH(CO{\cdot}NH_2)_2$, forms six-sided colourless prisms, m.p. 172° (with decomposition). The *potassium* salt is colourless, but yields yellow solutions (Ruhemann and Orton, Chem. Soc. Trans. 1895, 67, 1002). *Bromonitromalonamide* $NO_2{\cdot}CBr(CONH_2)_2$, has m.p. 131°–132° and decomposes on boiling with water yielding bromonitromethane (Ratz, Monatsh. 1904, 25, 687).

Nitromalonanilide $NO_2{\cdot}CH(CO{\cdot}NHPh)_2$ (Michael, Ber. 1905, 38, 22; Whiteley, Chem. Soc. Proc. 1904, 93) forms pale yellow leaflets, m.p. 141°–142°.

Nitromalonic aldehyde $CHO{\cdot}CH(NO_2){\cdot}CHO$ has m.p. 50°–51°. For its condensation products with amines, hydrazines, and hydroxylamine, *v.* Hill and Torrey, Amer. Chem. J. 1899, 22, 89; Hill and Hale, Amer. Chem. J. 1903, 29, 253.

Ethyl ester of the seminitrile of nitromalonic acid or *ethyl nitrocyanacetate*, $CN{\cdot}CH(NO_2)CO_2Et$, yields a potassium salt, m.p. 240° (Conrad and Schulze, Ber. 1909, 42, 735). *Nitrocyanacetamide* (fulminuric acid, *q.v.*) $(CN)CH(NO_2)CONH_2$ has m.p. 145° (decomp.) (*ibid.* 739).

Nitrocyanacetyl carbamide

$CN{\cdot}CH(NO_2)CO{\cdot}NH{\cdot}CONH_2$

is obtained as its potassium salt by the oxidation of the corresponding nitroso compound.

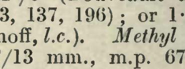
***iso*Nitrosomalonic acid and derivatives.** *iso*-*Nitrosomalonic acid* $(CO_2H)_2C{:}NOH$, m.p. 120°, first obtained by Baeyer by hydrolysis of violuric acid (Baeyer, Annalen, 1864, 131, 292; Conrad and Bischoff, Ber. 1880, 13, 595), is identical with the oxime of mesoxalic acid prepared from mesoxalic acid and hydroxylamine (Meyer and Müller, *ibid.* 1883, 16, 608). *Ethyl* iso*nitrosomalonate* $(CO_2Et)_2C{:}NOH$ (Conrad and Bischoff, Ber. 1880, 13, 595), is a colourless viscid liquid, b.p. 172°/12 mm., sp.gr. 1·206 at 4°/0° (Bouveault and Wahl, Compt. rend. 1903, 137, 196); or 1·149 at 15° (Conrad and Bischoff, *l.c.*). *Methyl* iso*nitrosomalonate*, b.p. 168°/13 mm., m.p. 67° (Bouveault and Wahl, *l.c.*).

The *iso*nitroso derivatives of malonamide and the substituted amides of malonic acid are obtained by the action of nitrosyl chloride at 0° on the amide dissolved or suspended in dry chloroform, and the yield is usually quantitative.

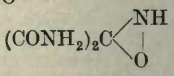
*iso*Nitrosomalonamide and the alkyl substituted derivatives are colourless, the aryl substituted derivatives are yellow, or exist in two forms one yellow and one colourless, exhibiting dynamic isomerism; all the *iso*nitroso derivatives form crystalline yellow alkali and silver salts, and deep violet or blue ferrous salts. It is probable that the yellow *iso*nitroso derivatives and the salts possess the true oximino structure

$$(CONHR)_2C{:}NOH;\ (CONHR)_2C{:}NOK,$$

whilst the colourless *iso*nitroso derivatives are

*iso*oximes 

$(CONHR)_2C\langle\begin{matrix}NH\\|\\O\end{matrix}$.

iso*Nitrosomalonamide* 

$(CONH_2)_2C\langle\begin{matrix}NH\\|\\O\end{matrix}$

colourless, m.p. 187° (decomp.); the *acetyl* derivative is colourless, m.p. 190°; *ethyl* derivative, pale yellow, m.p. 150°–151°; the silver salt $(CONH_2)_2C{:}N{\cdot}OAg,2NH_3$, deep yellow prismatic crystals; *potassium* salt

$(CO{\cdot}NH_2)_2C{:}N{\cdot}OK$

is yellow, and forms with ferrous sulphate the *ferrous potassium salt*

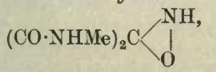
$$(CONH_2)_2{\cdot}C{:}N{\cdot}OK,[(CONH_2)_2C{:}N{\cdot}O]_2Fe$$

which crystallises in well-defined purple prisms with a bronze or green reflex. The *yellow* variety of *iso*nitrosomalonamide

$$(CONH_2)_2C{:}NOH$$

differs from the colourless form only in colour.

iso*Nitrosomalondimethylamide*



$$(CO{\cdot}NHMe)_2C\langle\begin{matrix}NH,\\ |\\ O\end{matrix}$$

m.p. 157°; the *potassium* salt

$$(CONHMe)_2C{:}N{\cdot}OK$$

is bright yellow; the *ferrous* salt

$$[(CONHMe)_2C{:}NO]_2Fe$$

is purple.

iso*Nitrosomalonanilide*. The *colourless* variety becomes yellow at 138°–140° and melts at 141°; the *yellow* variety becomes white at 120°–122° and melts at 141°; the equilibrium mixture of the two isomerides melts at 124°.

iso*Nitrosomalonmonophenylamide*

$$NHPh{\cdot}CO{\cdot}C(CO{\cdot}NH_2){:}NOH$$

has m.p. 180°–181° (decomp.).

iso*Nitrosomalondi*-p-*tolylamide*

$$(CONH{\cdot}C_7H_7)_2C{:}N{\cdot}OH$$

is pale yellow, m.p. 170°–171°; the *colourless* isomeride becomes yellow at 150° and melts at 170°–171°.

iso*Nitrosomalonmono*-p-*tolylamide*

$$C_7H_7{\cdot}HN{\cdot}CO{\cdot}C(CO{\cdot}NH_2){:}NOH$$

is lemon yellow, m.p. 183°.

iso*Nitrosomalondi*-o-*tolylamide*

$$(CONH{\cdot}C_7H_7)_2C{:}NOH$$

is yellow, m.p. 111°, the *colourless* isomeride changes to yellow at 75° and melts at 111°.

Ethyl iso*nitrosomalon*-o-*tolylamate*

$$C_7H_7{\cdot}HN{\cdot}CO{\cdot}C(CO_2Et){:}NOH$$

is pale yellow, m.p. 140°–141°.

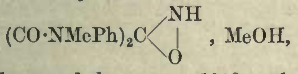
iso*Nitrosomalondi*-α-*naphthylamide*

$$(CONH{\cdot}C_{10}H_7)_2C{:}NOH$$

is orange coloured, m.p. 184°.

iso*Nitrosomalondi*-β-*naphthylamide* is pale yellow, m.p. 221°; the *acetyl* derivative is colourless, m.p. 179° (decomp.).

iso*Nitrosomalondimethylanilide* crystallises with 1 mol. methyl alcohol.



$$(CO{\cdot}NMePh)_2C\langle\begin{matrix}NH\\ |\\ O\end{matrix}\ ,\ MeOH,$$

is colourless and has m.p. 109°; the *acetyl* derivative has m.p. 130°, the *benzoyl* derivative m.p. 157°–158°, and the *ethyl ether* m.p. 138°.

iso*Nitrosomalontetraphenylamide*

$$(CONPh_2)_2C{:}NOH$$

forms pale yellow prisms, m.p. 237°–238° (decomp.); the *acetyl* derivative is pale yellow, m.p. 190°; the *benzoyl* derivative is colourless, m.p. 175°, the *ethyl ether* has m.p. 164°–165, (Whiteley, Chem. Soc. Trans. 1900, 77, 1040; 1903, 83, 18, 24; Chem. Soc. Proc. 1904, 93).

iso*Nitrosomalondiurethane*

$$(CONH{\cdot}CO_2Et)_2C{:}NOH,$$

m.p. 203°–204° (Conrad and Schulze, Ber. 1909, 42, 735). The *ammonium* salt forms bright orange prisms, m.p. 174°. The *potassium* salt $(CO{\cdot}NH{\cdot}CO_2Et)_2C{:}N{\cdot}OK$, is bright orange-red (Whiteley).

Derivatives of the seminitrile of isonitrosomalonic acid. *Ethyl isonitrosocyanacetate*

$$HON{:}C(CN)CO_2Et,$$

m.p. 133°, yields metallic derivatives (Conrad and Schulze, Ber. 1909, 42, 735).

The *methyl ester* has m.p. 123°. The *ethers*

$$EtON{:}C(CN)CO_2Et$$

b.p. 125°–127° 1/22–24 mm. and

$$EtON{:}C(CN)CO_2Me$$

b.p. 121°–124°/23–25 mm. and the corresponding benzoyl derivative, m.p. 131°–132° are described by Müller (Ann. Chim. Phys. [vii.] 1, 463).

Isonitrosocyanacetamide (Desoxyfulminuric acid) $CN{\cdot}C{:}NOH{\cdot}CONH_2$, m.p. 184°, (*ibid.* 738).

Isonitrosocyanacetyl carbamide

$$HON{:}C(CN)CO{\cdot}NH{\cdot}CONH_2$$

m.p. 220° (decomp.) (*ibid.* 741).

Isonitrosocyanacetyl urethane

$$HON{:}C(CN)CO{\cdot}NH{\cdot}CO_2Et$$

forms white crystals, m.p. 201° (decomp.) (*ibid.* 742).

Condensation of malonic acid with aldehydes. Malonic acid condenses with aldehydes according to the equation

$$(CO_2H)_2CH_2+OHC{\cdot}R=(CO_2H)_2C{:}CHR+H_2O.$$

The methylene malonic acids thus produced yield the corresponding alkyl or aryl malonic acids $CH_2R{\cdot}CH(CO_2H)_2$ on reduction; and lose carbon dioxide on heating to form the substituted acrylic acid $CHR{:}CH{\cdot}CO_2H$.

The *bis*malonic acid $CHR[CH{\cdot}CO_2H)_2]_2$ is sometimes obtained when the aldehyde and malonic acid are taken in the proportion of 1 mol. of the former to 2 mols. of the latter.

For the condensation products with formaldehyde, see Haworth and Perkin, Chem. Soc. Trans. 1898, 73, 339; Bottomley and Perkin, *ibid.* 1900, 77, 294. For the *ethylidene*, iso*butylidene*, iso*amylidene*, *œnanthylidene*, *valerylidene*, *citrylidene*, *furfurylidene*, *crotonylidene*, *benzylidene*, and *cinnamylidene*, *anisylidene*, *methylsalicylidene*, *piperonylidene* and *phenylpropionylidene* malonic acids and derivatives, see Kommenos, Annalen, 1883, 218, 145; Knoevenagel, Ber. 1898, 31, 2585; Braun, Monatsh, 1896, 17, 207; Riedel and Straube, Annalen. 1909, 367, 40; Knoevenagel, D.R.PP. 161171, 156560, 164296, 97735; Verley, Bull. Soc. chim. 1899, [iii.] 21, 414; Dakin, J. Biol. Chem. 1909, 7, 49; Röhmer, Ber. 1898, 31, 281; Riedel, Annalen, 1908, 361, 89; Stuart, Chem. Soc. Trans. 1883, 43, 403; 1885, 47, 155; 1886, 49, 360; Claisen and Crismer, Annalen, 218, 129; Einhorn and Gehrenbeck, Annalen, 1889, 253, 374; Claisen, Ber. 1903, 86, 3664). M. A. W.

MALONYLCARBAMIDE, *barbituric acid, v.* PYRIMIDINE.

MALT *v.* BREWING.

MALTASE is the enzyme which hydrolyses maltose to two molecules of dextrose. It is present in most, though not in all, species of yeasts: those yeasts (*e.g. Saccharomyces marxianus, S. exiguus* (Rees), *S. ludwigii, S. saturnus, S. anomalus*) which do not contain maltase are unable to ferment maltose. Maltase is found in *Aspergillus niger, Penicillium glaucum,* and other mould fungi; a maltose splitting enzyme is present in the intestine (Brown and Heron, Proc. Roy. Soc. 1880, 30, 393) and in numerous other animal tissues (Tebb, J. Physiol. 1894, 15, 421). Maltase is more difficult to extract than invertase; active extracts can only be obtained from yeast after the cells have been destroyed, or, better, after a preliminary drying in a thin layer at a low temperature. The enzyme is not liberated on shaking yeast with toluene water. Yeast juice made by Buchner's method of compression contains maltase. Brown and Heron found aqueous extract of pig's intestine to have no action on maltose, but after drying at 35° fine shreds of the intestine were active. Using similar methods Tebb found most maltase in the mucous membrane of the small intestine; it was also present in the spleen, lymphatic gland, liver, kidney, and in the pancreatic and salivary glands, and least of all in muscle. When the tissue is finely minced and sufficient time (several days) is allowed for adequate extraction, active maltase may be obtained from fresh tissues. Malt does not contain maltase.

Maltase is destroyed by precipitation of the aqueous extract with alcohol, so that it has not been possible to purify it.

Maltase also hydrolyses α-methylglucoside and other synthetical α-glucosides, although it is without action on the isomeric β-glucosides. Amygdalin is hydrolysed by an enzyme akin to maltase, present in some yeasts, to dextrose and amygdonitrileglucoside (Fischer, Ber. 1895, 28, 1508). This action is due, however, not to maltase, but to amygdalase (Caldwell and Courtauld, Proc. Roy. Soc. 1907, B, 79, 350). Maltase is able to cause synthetic as well as analytic changes (Croft Hill, Chem. Soc. Trans. 1898, 73, 634; 1903, 83, 578; *see* also Bayliss, The Nature of Enzyme Action, Longmans, 1911).

The optimum temperature of maltase is 35°–40° (*v.* Fermentation). E. F. A.

MALTHA. A variety of 'mineral tallow' or wax, sp.gr. 0·77, soluble in alcohol, naphtha, and oil of turpentine, said to be originally found on the coast of Finland. It is white, brittle, and stains paper like oil, melts at a moderate heat, and burns with a smoky flame. A similar hydrocarbon is met with in the oil-fields of California.

MALTODEXTRIN *v.* Dextrin.

MALTOSE *v.* Carbohydrates.

MAMMIN *v.* Synthetic drugs.

MANACCANITE. A variety of titaniferous magnetic oxide of iron found in grains and small angular fragments at Manaccan near Helstone, and other places in Cornwall, *v.* Ilmenite; Titanium.

MANCHESTER YELLOW. *Dinitronaphthol* *v.* Naphthalene. Dinitronaphthol-yellow has been used to artificially colour natural saffron. To detect the adulteration, an infusion of the matter is prepared, to which some tartaric acid is added. A hank of wool is then dipped in the boiling solution. The wool thus dyed is washed in very dilute sulphuric acid, and the acid afterwards neutralised with ammonia. If saffron contained any dinitronaphthol, the wool or the solution will be coloured yellow, whereas wool dyed with a decoction of genuine saffron and treated in the same manner becomes colourless (Cazeneuve and G. Ginnossier, J. Soc. Chem. Ind. 5, 437).

MANDELIC ACID (*Phenylglycollic acid; α-phenylhydroxyacetic acid*) $C_6H_5{\cdot}CH(OH)CO_2H$. Discovered by Winkler in 1852 in the emulsion of bitter almonds. It may be obtained by warming ω-dibromoacetophenone with dilute alkali (Engler and Wöhrle, Ber. 1887, 2202); by oxidising ω-hydroxyacetophenone with copper sulphate (Breuer and Zincke, *ibid.* 1880, 635); by boiling phenylchloracetic acid with alkali (Spiegel, *ibid.* 1881, 239); and by warming benzoylformaldehyde with alkali (Pechmann, *ibid.* 1887, 2905; Müller and Pechmann, *ibid.* 1889, 2558). It is best prepared by shaking commercial benzaldehyde with a concentrated solution of sodium disulphite, filtering off and drying the disulphite compound. This is then made into a paste with water, and the calculated quantity of potassium cyanide solution added with stirring. The oily mandelonitrile soon separates, and is hydrolysed by boiling with three times the theoretical quantity of hydrochloric acid (Pape, Chem. Zeit. 1896, 20, 90; Chem. Fab. vor. Hofmann and Schoetensack, Eng. Pat. 14886; J. Soc. Chem. Ind. 1896, 614; *cf.* Müller, Arch. Pharm. [iii.] 2, 385, 389; Ber. 1872, 980; Wallach, Annalen, 193, 38; Luginin, *ibid.*, 139, 299; Winckler, *ibid.* 18, 310).

Forms colourless rhombic prisms; m.p. 118° (Claisen, Ber. 1877, 847); sp.gr. 1·361 at 4°/4° (Schröder, *ibid.* 1889, 1612); readily soluble in alcohol and ether. On heating the acid at 200°, benzaldehyde and an amorphous mass is obtained; benzaldehyde, water and diphenylmaleic anhydride are formed when it is heated in a current of air under reduced pressure (Bischoff and Walden, Annalen, 279, 118; Liebig, *ibid.* 18, 312). Fuming nitric acid yields *o*- and *p*-nitrophenylglycollic acids (Pratesi, Gazz. chim. ital. 21, ii. 402). Electrolysis of an aqueous solution of the potassium salt results in the production of hydrobenzoin and a small quantity of *iso*hydrobenzoin (Walker, Chem. Soc. Trans. 1896, 1279); but according to Miller and Hofer (Ber. 1894, 469) benzaldehyde, carbon dioxide, and carbon monoxide are the products. By passing carbonyl chloride into an ice-cold solution of the acid in pyridine the bimolecular anhydride, m.p. 240°, is formed (Einhorn and Pfeiffer, Ber. 1901, 2951). Hydrogen iodide and phosphorus convert mandelic acid into phenylacetic acid, and fuming hydrochloric acid at 140° yields phenylchloracetic acid. Mandelic acid condenses with phenols in the presence of 73 p.c. sulphuric acid to *o*-hydroxydiarylacetic acid lactones and *p*-dihydroxydiarylacetic acids (Bistrzycki and Flatau, Ber. 1895, 989; 1897, 124); *v.* also Simonis (Ber. 1898, 2821) for condensation with β-naphthol, resorcinol, and orcinol. The nitrile prepared as above, is a yellow oil, solidifying at −10°. The amide has m.p. 190°, the anilide 151°–152°, and the phenylhydrazide 182° (Tiemann and Friedländer, Ber. 1881, 635; Reissert and Kayser, Ber. 1890, 3701; Biedermann, *ibid.* 1891, 4083; Bischoff and Walden, Annalen, 279, 118). The methyl ester has m.p. 52° (Zincke and Brewer, Ber. 1880, 636; Ruhe, *ibid.* 1895, 259), and the ethyl ester has m.p. 34°, b.p. 253°–255° (Michael and Jeanprêtre, Ber. 1892, 1684;

Beyer, J. pr. Chem. [ii.] 31, 389); m.p. 37° (McKenzie, Chem. Soc. Trans. 1899, 755).

Mandelic acid contains an asymmetric carbon atom, and hence can be split into two optically active isomerides. Lewkowitsch (Ber. 1882, 1505; 1883, 1565, 2722) obtained *l*-mandelic acid by treating the inactive acid with *Saccharomyces ellipsoideus* (Rees) and *d*-mandelic acid by using various microzoa, such as *Pencillium glaucum*, &c. Partial resolution of the inactive acid has also been effected by means of the fractional crystallisation of salts with alkaloids, such as quinine and morphine, and with active amines such as methylhydrindamine; and by esterification with active alcohols, such as menthol and borneol (McKenzie, Chem. Soc. Trans. 1899, 968; 1904, 378; McKenzie and Thompson, *ibid.* 1905, 1004; Marckwald and Paul, Ber. 1906, 3654; Kipping, Chem. Soc. Trans. 1909, 416; Findlay and Hickman, *ibid.* 1909, 1386). Racemisation is found to take place on boiling the active acid with alkali (Holleman, Rec. trav. chim. 1898, 17, 323; McKenzie and Müller, Chem. Soc. Trans. 1907, 1814). Asymmetric syntheses have been conducted by McKenzie and Humphries (*ibid.* 1909, 1106) from *l*-menthylbenzoylformate, and by Rosenthaler (Biochem. Zeitsch. 1908, 14, 238) from *d*-benzaldehydecyanhydrin. *d*- and *l*-Mandelic acids can also be prepared by the hydrolysis of amygdalinic acid (Dakin, Chem. Soc. Trans. 1904, 1512; *cf.* Wöhler, Annalen, 66, 238; Tutin, Chem. Soc. Trans. 1909, 663; Feist, Arch. Pharm. 248, 101; Rosenthaler, *ibid.* 105). Incomplete hydrolysis of the ethyl ester by *lipase* yields the *d*-acid, whilst the ester remaining is lævorotatory (Dakin, Chem. Soc. Proc. 1903, 161; J. Physiol. 1903, 30, 253).

l-Mandelic acid has m.p. 132·8°, and $[\alpha]_D$ −153·1° in water (Walden, Zeitsch. physikal. Chem. 1895, 17, 705; *cf.* Lewkowitsch, *l.c.*; Rimbach, Zeitsch. physikal. Chem. 1899, 28, 251; Ber. 1899, 2385). *d*-Mandelic acid has m.p. 132·8°, and $[\alpha]_D+156°$ (Kipping, Chem. Soc. Trans. 1909, 416). For experiments on the *Walden Inversion* with mandelic and phenylchloracetic acids, *v.* McKenzie and Clough, Chem. Soc. Trans. 1909, 777.

MANDRAGORA ROOT. In 1889 Ahrens (Annalen, 251, 312) extracted from *Mandragora* root an alkaloid possessing similar physiological properties to atropine, and which he named *mandragorin.* Thoms and Wentzel (Ber. 1898, 31, 2031) showed that the *mandragorin* of Ahrens was a mixture of bases, the chief of which was *hyoscyamine*, and subsequently isolated another base, which they named *scopolamine* (Ber. 1901, 31, 2031). Hesse (J. pr. Chem. 1901, 64, 274) further investigated the subject and found that *madragora* root contains 0·36 p.c. *hyoscyamine*, 0·04 p.c. *hyoscine* (*scopolamine* of Thoms and Wentzel), 0·01 p.c. *ψ-hyoscyamine*, and a still smaller quantity of a new base *mandragorine.* To obtain these alkaloids, the roots are powdered, moistened with a solution of caustic soda, and extracted with ether under a reflux apparatus. The ethereal solution is repeatedly extracted with dilute sulphuric acid, the acid solution being made alkaline with sodium bicarbonate and extracted with chloroform. This operation is then repeated, whereby the hyoscyamine remains in the aqueous solution. The bases from the chloroform extract are neutralised with hydrobromic acid, and the filtered solution allowed to crystallise. The hydrobromides of the bases are then extracted with acetone, which leaves the pure hydrobromide (m.p. 194°) of hyoscine, $C_{17}H_{21}NO_4$. The free base is decomposed by baryta into tropic acid and oscine, $C_8H_{13}NO_2$. The mother liquors of the hyoscinehydrobromide yield ψ-hyoscyamine on addition of sodium bicarbonate and extraction with chloroform. On adding sodium carbonate to the residual solution, a new alkaloid *mandragorine*, forming a gold double salt $C_{15}H_{19}NO_2HAuCl_4$ is obtained. The free base is decomposed by baryta into atropic acid, and a base resembling tropine.

MANGANATES *v.* MANGANESE.

MANGANESE. Sym. Mn. At.wt. 54·93. (Fr. *Manganèse*; Ger. *Mangan.*) Manganese is not found in the metallic state. In combination, especially as oxide, it is widely distributed. The most important ores are those corresponding with the dioxide MnO_2, *pyrolusite.* It is also found as the oxides *braunite* Mn_2O_3, *hausmannite* Mn_3O_4, as hydrated oxide Mn_2O_3,H_2O in *manganite*, and associated with barium oxide in *psilomelane.* As sulphide it occurs as *alabandite* MnS and *hauerite* MnS_2; as carbonate in *rhodocrosite* or *dialogite* $MnCO_3$; as silicate in *rhodonite* $MnSiO_3$. The latter is of a beautiful red colour, found largely in the Ural Mountains, and used as an ornamental stone. It is often present to a small extent in other silicates, and confers on them its colour. The chief sources of the manganese ores are Russia, the Caucasus, Brazil, and India. Manganese is present in soils, and frequently in mineral, particularly chalybeate, waters. It occurs in many plants, especially in tea and tobacco.

Preparation.—Metallic manganese is not used in the arts except when alloyed with other metals. It may be prepared by reduction of the oxide with carbon, but the temperature necessary for the reduction is so high (1105°C., Greenwood, Chem. Soc. Trans. 1908, 1491) that it is only obtained with difficulty in ordinary furnaces. The original method of preparation described by John (Gehlen's Jour. für. Chem. Phys. 3, 452) consisted in making an intimate mixture of finely divided manganous oxide and carbon by mixing with oil and heating, and exposing it to as high a temperature as possible in a crucible lined with charcoal. The impure manganese so obtained was purified by fusing under salt and nitre.

Brunner (Annalen, 102, 330) prepared the metal by heating a mixture of sodium and manganese chloride or fluoride in a blast furnace for 15 minutes. It may also be obtained by the reduction of the chloride by magnesium.

Deville obtained the metal by the reduction of the pure red oxide Mn_3O_4 by means of sugar charcoal present in insufficient quantity to reduce the whole (Ann. Chim. Phys. 1856, 46, 182).

Valenciennes (Compt. rend. 70, 907) produced it by reduction of the pure oxide with carbon in a magnesia-lined crucible as a hard and brittle mass, quickly oxidised by exposure to air.

Oxides of manganese are reduced to the protoxide but not to metal by ignition in hydrogen. Hugo Tamm (Chem. News. 26, 111) recommends the following process for the preparation on the large scale. Two fluxes are prepared. (1) A fusible 'white' flux of ground glass (free from lead) 63, quicklime 18½, and fluorspar 18½. (2) Flux No. 1 34 parts, lampblack 5½, native manganese dioxide of good quality 60½.

The crucibles used should be very refractory, lined with a mixture of 3 parts plumbago and 1 part fireclay, made into a paste with water. This casing resists the action of the flux for a considerable time. In such a crucible flux No. 2 is ignited at the highest temperature of a wind furnace with the production of 17½ parts of 'Cort manganese' and a green slag saturated with manganous oxide. Of this slag 635 parts are thoroughly mixed with 91 parts of lampblack (charcoal cannot be used), and then with 1000 parts of rich manganese ore. The whole is made into a paste with oil, pressed into the crucible, covered with a piece of wood to prevent oxidation, and luted down, leaving an aperture for the escape of gases.

The crucible is next heated in a blast furnace, at first gently, until fumes cease to escape, and finally to whiteness, for several hours. On cooling, the manganese is found as a coherent mass. The green slag may be used several times with the addition of a little white flux to increase the fluidity, provided too much gangue be not present in the ore.

Operating with an ore containing 79·5 p.c. manganese dioxide, 6·5 p.c. ferric oxide, and 10·5 p.c. gangue, the manganese obtained showed the following composition: Mn 96·9, Fe 1·05, Al 0·10, Ca 0·05, P 0·05, S 0·05, Si 0·85, C 0·95. This metal, when fused with one-eighth part of manganous carbonate, contained Mn 99·91, Fe 0·05, Si 0·015, C 0·025.

The metal is now almost entirely prepared either by reduction by aluminium by the Goldschmidt method or by means of the electric furnace. In the latter method pure manganous oxide is intimately mixed with carbon and heated in an electric furnace, a current of 300 amperes at 60 volts giving a yield of 100–120 grams of manganese in 5 or 6 minutes, or a current of 100 amperes at 60 volts giving the same amount in 10–15 minutes. Care has to be taken to avoid prolonged heating, as the metal readily volatilises in the electric furnace, and hence considerable loss may result. As carbon readily dissolves in manganese the metal so prepared usually contains from 5 to 14 p.c. carbon, which, if the manganese is volatilised, remains as graphite. By again fusing with oxide it may be obtained almost quite free from carbon and silicon (*v.* Moissan, The Electric Furnace).

Properties.—Pure manganese is soft and does not scratch glass; if it contains but little carbon it may be kept in open vessels. As the percentage of carbon increases it becomes more readily decomposed by the moisture in the air and small fragments exposed to the air become oxidised in 24 hours with the production of hydrogen and hydrocarbons. It appears to form a definite carbide Mn_3C, which is hard and brittle, and rapidly oxidises in air, and by moisture is decomposed according to the equation

$$Mn_3C+6H_2O=3Mn(OH)_2+CH_4+H_2$$

equal volumes of methane and hydrogen being evolved. This carbide is probably present in solid solution in the impure manganese, on which it confers its hardness.

The metal has been obtained crystalline by distillation in the electric furnace, and as a pyrophoric powder by gentle ignition of its amalgam in a current of hydrogen (Prelinger, Monatsh. 14, 353). If the temperature of ignition is too high it is no longer pyrophoric, and although paramagnetic at ordinary temperatures becomes ferromagnetic on heating.

The metal dissolves in dilute acids, and with hot sulphuric acid liberates sulphur dioxide; when used as an anode in electrolysis it behaves normally in acid and neutral electrolytes but becomes *passive* in alkaline sulphate or phosphate baths (Müller, Zeitsch. Elektrochem. 11, 755). Its sp.gr. is about 8.

The melting-point of a 99 p.c. manganese was found by Heraeus to be 1245° (Zeitsch. Elektrochem. 1902, 8, 185). When heated in nitrogen or ammonia a nitride is formed, possessing marked magnetic properties (Shukoff, J. Russ. Phys. Chem. Soc. 40, 457); the nitrides of composition Mn_3N_2, Mn_5N_2, and Mn_7N_2 are stated to exist (Wedekind and Weit, Ber. 41, 3769). From the lowering of the freezing-point by phosphorus the value 27·5 has been calculated for the latent heat of fusion (Schemtschuschny and Efremoff, J. Russ. Phys. Chem. Soc. 39, 777). At 1000° the metal is oxidised by carbon monoxide with formation of manganous oxide and carbon (Charpy, Compt. rend. 148, 560).

Detection.—All compounds of manganese, if strongly ignited, impart an amethyst-red colour to the borax bead in the oxidising flame; the bead can be rendered colourless by careful heating in the reducing flame. When heated with soda and a little nitre on platinum foil a very small quantity of manganese produces a green colour.

A very delicate test, in the absence of chlorides, consists in heating the substance or solution with dilute nitric acid and a little lead peroxide. The manganese is thus oxidised and imparts to the solution the pink colour of permanganic acid (Crum).

Minute quantities in soils, minerals, vegetables, &c., may be detected by incinerating, heating the ash with nitric acid, evaporating to dryness, taking up with water and adding to the filtrate some 40 p.c. ammonium persulphate and a drop of a 2 p.c. solution of cobalt nitrate when a pink colour is developed on boiling.

Tetraphenyldiaminodiphenyl methane is stated to be a very delicate test for manganese (in the absence of copper). The substance to be tested is warmed with sodium hydroxide, incinerated and the ashes moistened with acetic acid. On warming with the reagent a blue colour is developed. The same colour is also produced with lead.

Manganese may be detected in N/10000 solution of manganous salts by the red colour produced by the addition of a few drops of a N/10 solution of potassium periodate (Benedict, Amer. Chem. J. 34, 381).

It may also be detected and estimated by adding to 5 c.c. of the solution, 3 c.c. of glycerol, and 1 c.c. of a 50 p.c. solution of sodium hydroxide, and then drawing a current of air through the liquid. A fine ruby colour is developed, the intensity of which is proportional to the manganese present, so that the test may be used for colorimetric estimation (Tarugi, Gazz. chim. ital. 36, 332).

When manganese is present in its usual form, as a protosalt, sulphuretted hydrogen produces a flesh-coloured precipitate from alkaline, but not from acid or neutral solutions.

Potassium and sodium hydroxides precipitate white hydrated manganous oxide which rapidly becomes brown from absorption of oxygen. Ammonia produces the same precipitate, which is soluble in excess, especially in presence of ammonium chloride, but slowly forms a precipitate of the brown oxide.

Where the manganese exists as the acid oxide, as in manganates and permanganates, the reactions are different. Alkaline manganates produce green solutions which slowly become red on exposure to air, more rapidly on addition of an acid, from production of the permanganate. Both these compounds are rapidly reduced and rendered colourless by the addition of sulphurous acid, ferrous salts, or other reducing agent. The manganese then exists as a base and shows the usual reactions. All manganates and permanganates oxidise hydrochloric acid, especially when heated, with evolution of chlorine.

Estimation.—Manganese is usually precipitated as carbonate. To the nearly boiling solution, sodium carbonate is added drop by drop, until precipitation is complete, and the solution boiled for a few minutes and allowed to subside. The precipitate is washed by decantation three times and finally well washed on the filter. The dried precipitate is strongly ignited in a platinum crucible and weighed as Mn_3O_4, which contains 72·05 p.c. of manganese. The ignited mass should show no alkaline reaction with test paper. The precipitate of carbonate may also be converted into, and weighed as, sulphate.

A very delicate method of estimating small quantities of manganese, as in limestones, &c., has been devised by Chatard. The process, as modified by Thorpe and Hambly (Chem. Soc. Trans. 1888, 182), is as follows. The solution should be free from chlorides, should contain between 0·004 and 0·008 gram of manganese, and should occupy about 25 c.c. To it is added 5 c.c. concentrated nitric acid, 2 or 3 grams of lead peroxide, and 10–20 c.c. dilute sulphuric acid (1 acid to 2 water), and the solution gently boiled for 4 minutes. The sides of the flask are washed down to destroy any organic matter, and the liquid boiled for half a minute longer. The lead sulphate and excess of lead peroxide are allowed to subside and the solution is at once filtered (with the aid of a filter pump if possible) through a plug of asbestos recently ignited and washed with dilute sulphuric acid. The filtrate is heated to 60°C. and titrated with a weak solution of ammonium oxalate, freshly standardised by a standard solution of permanganate. It may also be titrated if desired with sodium arsenite, or hydrogen peroxide.

The separation from other metals is not difficult. From the alkaline earths it may be separated by addition of hydrated ammonium sulphide to the nearly neutral solution; the sulphide so precipitated is washed well, redissolved in hydrochloric acid, and precipitated as above with sodium carbonate.

From iron, chromium, uranium, and aluminium, it may be separated by digesting the dilute solution with freshly precipitated barium carbonate. These metals are thus deposited as hydroxides. The barium is removed from the solution by the addition of sulphuric acid, and the manganese precipitated as usual.

When manganese occurs together with a large proportion of iron, as in iron ores, iron, steel, &c., the following separation is useful. The nearly boiling solution of the substance in hydrochloric acid or *aqua regia,* which must be absolutely free from organic matter, is treated with ammonia, with constant stirring, until it becomes much darkened; weaker ammonia is then cautiously added until the liquid has become of a mahogany colour, but still without any permanent precipitate. A hot solution of ammonium acetate is then added. The precipitate of basic ferric acetate should be brick-red; if it be dark red, more ammonium acetate must be added. The solution is boiled for a few minutes only, and the granular precipitate filtered through a large filter paper. The filter with the precipitate is replaced in the beaker which still contains the remaining portions of the precipitate and is redissolved in hydrochloric acid, reprecipitated as before and filtered into the beaker containing the first filtrate. In this way the small portion of manganese contained in the first iron precipitate is separated. A portion of the second ferric acetate precipitate should, in important cases, be boiled with lead peroxide and nitric acid, when, if a trace of manganese be present, the liquid will acquire a pink colour.

The liquid containing the manganese may be concentrated by evaporation, filtered if necessary, and cooled. Sufficient bromine is added, with frequent shaking, to render it brown, and the whole rendered alkaline by ammonia. The manganese is thus precipitated as black hydrated peroxide.

The liquid is heated to boiling, filtered, and the precipitate washed and ignited as usual to Mn_3O_4. If a trace of organic matter be present in the solution, a portion of the iron will not be precipitated as acetate and will come down with the manganese. If this is the case the ignited oxide is redissolved and the iron precipitated as acetate, ignited, and weighed as Fe_2O_3 and its weight deducted from that of the manganese oxide obtained.

A convenient method for the volumetric determination of manganese in ores or alloys is due to Volhard, many modifications of which have been described. The method is based on the fact that manganese salts in the presence of zinc oxide are quantitatively oxidised to zinc manganite by means of potassium permanagnate ($3MnO+Mn_2O_7=5MnO_2$). The modification of Fischer (Zeitsch. anal. Chem. 1909, 48, 751; *cf.* Cahen & Little, Analyst, 1911, 36, 52) is as follows. One gram of the ore or alloy is dissolved in *aqua regia,* and the solution evaporated nearly to dryness with excess of hydrochloric acid. The residue is dissolved in 300 c.c. of water, mixed with a sufficiency of an emulsion of zinc oxide and made up to 1 litre. 100 c.c. of the clear solution are diluted to 500 c.c. and heated to boiling after adding 10 grms. of zinc sulphate. One gram of freshly ignited zinc oxide is added, and the liquid titrated with N/10 permanganate, boiling and shaking frequently until the supernatant liquid is red; 1 c.c. of pure glacial acetic acid is then added, when the red colour disappears, and the titration is slowly finished with permanganate in the hot but not boiling liquid.

Solutions of manganous sulphate are completely precipitated as manganese dioxide, which may be subsequently estimated, when boiled with excess of ammonium persulphate. Sodium bismuthate in cold nitric acid solution oxidises manganous salts to permanganate, which may then be titrated (*v.* ANALYSIS).

Iron alloys with manganese in all proportions (*see* IRON).

Copper and **manganese** yield a continuous freezing-point curve with a minimum of 866° at 65 p.c. copper. The form of the curve and the microscopic examination of the alloys indicate that a continuous series of mixed crystals exist, and that no compounds are formed. The alloys are only homogeneous if heated for some time below the melting-point. In appearance the alloys resemble bronzes, and are generally hard and malleable. A bronze—known as 'manganese bronze'—is made by adding a copper manganese alloy to the molten bronze and usually contains from 1 to 4 p.c. manganese, and from 80 to 90 p.c. copper. It forms a useful, workable alloy, possessing very great tenacity, and is used for stay bolts on some of the Continental railways. Alloys resembling German silver are also obtained from copper, zinc, and manganese.

Brunck describes an alloy with **aluminium** of composition Mn_2Al_7, which forms in white crystals soluble in hydrochloric acid (Ber. 25, 777). According to Hindricks (Zeitsch. anorg. Chem. 59, 414) two compounds exist, Mn_3Al and $MnAl_3$, both of which form mixed crystals. Alloys containing between 57 and 86 p.c. aluminium separate into two liquid layers.

Alloys with **Boron** may be produced in the electric furnace and exhibit magnetic properties due to the compound MnB. A second compound MnB_2 probably also exists, but is not magnetic (Jassoneix, Compt. rend. 142, 1336).

Antimonides may be produced by the 'thermit' method. By removal of excess of manganese by means of dilute acid and of antimony by chlorine, alloys regarded as MnSb and $MnSb_2$ have been obtained. Both are magnetic (Wedekind, Zeitsch. physikal. Chem. 66, 614).

With **Tungsten** alloys containing from 12 to 60 p.c. tungsten have been obtained by the 'thermit' method as hard, brittle, steel-grey ingots, from which dilute acids dissolve the manganese.

By the same method hard brittle homogeneous alloys containing from 12 to 29·6 p.c. **molybdenum** are obtained (Arrivant, Compt. rend. 143, 464, 94).

Nickel and manganese give a continuous freezing-point curve with a minimum of 1030° at 56 p.c. manganese.

With **silver** between 30 and 90 p.c. manganese, two liquids are formed, and no solid solutions (Hindricks).

With **tin** compounds $SnMn_3$ and SnMn are indicated by potential measurements. Alloys with below 40 atomic p.c. Mn are white and soft, above they become hard and brittle (Puschin, J. Russ. Phys. Chem. Soc. 38, 869).

Silicides are obtainable in the electric furnace, compounds Mn_2Si, MnSi, and $MnSi_2$ having been described. Of these the first forms lustrous prisms, which scratch glass, and the second can scratch topaz; the sp.grs. are 6·4, 5·9, and 5·2. The existence of these compounds is also indicated by the MnSi freezing-point curve (Doernickel, Zeitsch. anorg. Chem. 50, 117). Gin describes also a compound Mn_3Si_2 (Compt. rend. 143, 1229).

Phosphides are obtained by heating manganous chloride and phosphorus in a current of hydrogen. Compounds Mn_5P_2 and Mn_3P_2 are described, both of them magnetic. The latter is probably, however, an eutectic mixture (Schemschuschzy and Efremoff, *l.c.*, *supra*).

Manganese oxides. The compounds of manganese with oxygen are numerous. The lower or manganous oxide MnO is powerfully basic; the sequioxide Mn_2O_3 is less basic, the tetroxide Mn_3O_4 and the dioxide MnO_2 are practically neutral; the dioxide occasionally reacts as a basic oxide, but at other times as an acidic oxide forming *manganites* of the type M_2MnO_3, *i.e.* it belongs to the class of amphoteric oxides. The higher oxides, however, MnO_3 and Mn_2O_7, have decided acid-forming properties and produce well-marked series of salts.

Manganous oxide MnO is prepared by ignition of any other oxide, or of the carbonate, in a current of hydrogen. It is of an olive-green colour and absorbs oxygen from the air with formation of a brown oxide. In solution in acids it forms manganous salts.

Manganese sesquioxide Mn_2O_3 occurs in nature as *braunite* in brownish-black, anhydrous, acute octahedra frequently containing silica. In the hydrated form it occurs as *manganite* in brilliant, black or steel-grey, rhombic prisms.

It may be prepared hydrated, by passing chlorine, not to saturation, through water in which manganous carbonate is suspended, and removing the excess of carbonate by dilute nitric acid. It is slowly acted on by dilute acids yielding either manganic salts of tervalent manganese, isomorphous with the salts of aluminium and ferric iron, or a mixture of manganous salts and manganese dioxide. The colour of the amethyst is attributed to the presence of this oxide.

Manganese tetroxide. Red oxide of manganese M_3O_4 occurs as *hausmannite* in brownish-black octahedra, and in massive forms. It is produced by heating any oxide of manganese in the air. By the action of acids it yields a mixture of manganous and manganic salts or a manganous salt and manganese dioxide. It was formerly used as a pigment under the name of *manganese brown*.

Manganese dioxide. Peroxide or black oxide of manganese, frequently known as 'manganese,' MnO_2.

This important oxide occurs as *pyrolusite* in very pure iron-black or steel-grey, rectangular rhombic prisms of sp.gr. 4·8–5, and frequently massive or reniform, in radiating fibrous masses, usually brittle. Its hardness varies within wide limits, and it seldom occurs pure, but usually associated with other manganese ores.

A hydrated variety occurs largely as *psilomelane* in amorphous, massive, stalactitic, and frequently in botryoidal masses, but never in crystals. Its composition is very variable. It is usually found in the same localities as pyrolusite, frequently in alternate layers with that mineral. *Varvicite* and *newkirkite* are also hydrated varieties of pyrolusite.

Wad is an important earthy variety produced by the decomposition of other manganese minerals. It occurs, generally, in low-lying districts, in amorphous, earthy, dull black or brownish pieces of very variable composition and hardness. It frequently contains oxide of cobalt; one variety known as *asbolane* or *earthy cobalt* sometimes contains as much as 32 p.c. of cobalt. Another variety, *lampadite*, contains 18 p.c. of copper oxide. In addition to its employment as a chlorine producer, wad is used as an 'umber' paint.

Of these oxides pyrolusite is the purest and contains the highest percentage of oxygen; it has therefore the greatest commercial value. At a red heat it evolves one-third of its oxygen, leaving the red tetroxide.

When heated with concentrated sulphuric acid, it dissolves with formation of manganous sulphate and evolution of half its oxygen. If organic matter be present the oxygen decomposes it with evolution of carbon dioxide.

Its action on hydrochloric acid is of great importance. The hydrogen of this acid is oxidised, a portion of the chlorine thus liberated combines with the manganese, while the remainder is set free;

$$MnO_2+4HCl=MnCl_2+2H_2O+Cl_2.$$

On this account it is very largely used for the production of chlorine and of bleaching powder (*q.v.*).

Nitric acid has but slight action upon it. Pyrolusite is a good conductor of electricity and is strongly electronegative: it is used as the depolarisor in the Leclanché battery. In the electric furnace it melts and evolves oxygen forming the monoxide. It is used to destroy the injurious tint produced in glass by the presence of ferrous compounds. The oxygen converts the greenish salt into the nearly colourless ferric salt, whilst the slight pink tint imparted by the manganese still further counteracts the bluish colour. It seems probable that the effect is due principally to the latter cause, as red lead and other oxidising agents have not this decolorising power.

Pyrolusite is also used in the preparation of black enamel for pottery, and has been used as a pigment under the name of *manganese black*. It is used as a *drier* for oils, *i.e.* a substance added to confer drying properties to the oils. In this respect it is one of the most powerful driers known, and is added in the boiling in the proportion of about ½ lb. to 1 cwt. of oil.

(For further information regarding these oxides *v.* CHLORINE.) Manganese dioxide may be prepared artificially by moderately igniting the nitrate, boiling the residue with nitric acid, washing and gently heating (Berthier). The hydrated oxide has been used for the removal of iron from aluminium sulphate.

According to Fremy (Compt. rend. 82, 1231) it forms a definite sulphate on solution in sulphuric acid, and a solution containing this under the name of manganese peroxide sulphate, produced by the electrolysis of a sulphuric acid solution of manganous sulphate is used as a mild oxidiser in aniline dye manufacture. Double salts containing $MnCl_4$ also exist.

Manganese trioxide. Franke (J. pr. Chem. 1887, 14) has described a trioxide MnO_3; its existence has been confirmed by Thorpe and Hambly (Chem. Soc. Trans. 1888, 177). This oxide appears to form a sulphate $(MnO_3)_2SO_4$.

Manganese heptoxide Mn_2O_7 is a highly hygroscopic, non-volatile, reddish-brown liquid, which gradually decomposes on exposure to the air. Its composition was determined by Aschoff (Pogg. Ann. 3, 217). These two oxides are of interest, as they form the acid radicles of manganates and permanganates; thus, $MnO_3{\cdot}K_2O$, $Mn_2O_7{\cdot}K_2O$.

SALTS OF MANGANESE.

Of the salts corresponding to these various oxides, only two series are of practical importance, manganous salts, corresponding to the monoxide, and manganates and permanganates, in which manganese acts as an acid corresponding to the tri- and hept-oxides.

Manganous chloride $MnCl_2$ is produced by the action of chlorine gas on metallic manganese, or of hydrochloric acid gas on the heated carbonate. In solution, it is obtained by dissolving the oxide or carbonate in hydrochloric acid.

On the large scale it is usually produced from the residual solutions from the chlorine manufactures. This is first evaporated to remove excess of hydrochloric acid, and one-fourth of the solution is removed and precipitated by sodium carbonate. The precipitate, which contains manganous carbonate and ferric hydrate, is washed and boiled with the remainder of the solution. The iron in solution is thus precipitated as hydrate, being replaced by an equivalent quantity of manganese from the carbonate. Copper, if present, is precipitated by the addition of sulphuretted hydrogen, leaving in solution manganese, and usually calcium and other alkaline earthy metals. Cobalt and nickel may be removed by the addition of freshly precipitated manganous sulphide, as long as it becomes darkened; those metals are then precipitated as sulphides.

The manganese is precipitated by means of ammonium sulphide, washed, dissolved in hydrochloric acid, evaporated, and crystallised.

It may be obtained pure by evaporating the crude solution of the ore in acid to dryness, igniting gently in a crucible, exhausting the residue with water, concentrating and crystallising. It forms pink deliquescent crystals, containing 4 molecules of water, soluble in two-thirds their weight of water at 60°, soluble in alcohol.

In commerce it usually occurs as a rose-red, very deliquescent mass, obtained by evaporating the solution to dryness. It is used for dyeing cotton manganese-brown or -bronze. The fabric is soaked in a solution of the salt and then passed through a caustic alkali, whereby manganous hydroxide is precipitated in the fibre and by subsequent atmospheric oxidation becomes brown. The material thus treated may also be used for the subsequent dyeing by aniline black. The presence of over 1 p.c. calcium chloride in the salt renders it practically useless for calico-printing and dyeing.

Manganous sulphate $MnSO_4$ may be prepared by dissolving the carbonate or oxide in sulphuric acid. On the large scale it is usually obtained from the black oxide. This is ignited with about one-tenth part of powdered coal, and thus reduced to the monoxide. The mass is dissolved in sulphuric acid, evaporated, gently ignited to decompose the ferrous sulphate, and the manganous sulphate dissolved out by water. By another process the peroxide is first digested with dilute sulphuric acid to remove carbonates, and made into a paste with strong sulphuric acid, heated until the evolution of oxygen has ceased, and then to strong redness, cooled, digested in water, and the solution evaporated and crystallised. If iron be still present, it may be removed as in the case of the chloride by boiling with manganous carbonate. Manganous sulphate forms pink crystals very soluble in water, insoluble in absolute alcohol. It is used in calico-printing. It is also used as a drier for pale oils or for conversion into the oxalate or borate which are also used for the same purpose.

Manganese borate, used as a drier, is a salt of a faint pink colour, prepared by adding a solution of borax to one of a manganous salt, washing and drying the powder so obtained.

Manganese oxalate, also used as a drier, is prepared by precipitation of a manganese salt by a soluble oxalate, or by the action of oxalic acid on manganese hydroxide or carbonate. *Manganese linoleate* is also used for the same purpose, and prepared by addition of linseed oil-soap to manganous chloride.

Potassium manganate K_2MnO_4. This compound is produced when equal weights of finely powdered manganese dioxide and caustic potash are fused together, a sesquioxide of manganese being produced at the same time. By the addition of potassium nitrate or by performing the ignition in a flat vessel, a portion of this oxide is reoxidised, and increases the yield of manganate.

It dissolves in water, forming a fine green solution, which, on evaporation *in vacuô*, produces green crystals isomorphous with potassium sulphate and chromate. The solution, especially if dilute, when exposed to the air becomes converted into the permanganate with precipitation of hydrated manganese dioxide; the liquid passes through various shades from green to pink, whence its name of 'mineral chameleon.' In presence of excess of alkali this change does not take place. On the addition of free acid, especially sulphuric acid, the change is immediate, the alkali and manganese, instead of being liberated as hydrates, being at once converted into sulphates, and thus losing their tendency to reproduce the manganate. Potassium manganate is a powerful oxidising agent. Its general action in this respect resembles that of the permanganate.

Sodium manganate Na_2MnO_4 is largely manufactured for disinfecting purposes on account of its greater cheapness.

Condy's fluid consists chiefly of a mixture of sodium manganate and permanganate (*v. infra*). For its preparation 30 cwt. of soda ash are converted into caustic soda by lime; they are then mixed with 7 cwt. manganese dioxide, and ignited in a shallow vessel at a dull red heat for about 48 hours. The mass is treated with water, decanted, and the solution evaporated to the required concentration. When the product is required to consist only of permanganate the solution is treated with sulphuric acid, and evaporated until crystals of sodium sulphate separate. Sodium permanganate is, however, much more difficult to purify by crystallisation than the potassium salt (*v.* Hofmann, Reports on Chem. Processes at the Exhibition of 1862, 109).

According to Desclabissac (Dingl. poly. J. 201, 58), the following methods are used for the preparation of sodium manganate and permanganate on the large scale. (1) 500 parts of soda lye (45°B.) are evaporated with 100 parts potassium chlorate mixed with 180 parts of the finely powdered oxide, and ignited in iron pots until quietly fused, cooled, with constant stirring, again heated to redness, cooled, and extracted with water. (2) 12 parts of caustic soda, dissolved in 58 parts of water are heated with 12 parts potassium chlorate and 18 parts manganese dioxide, until it begins to crumble; the heat is then increased to redness, and the mass, after cooling, is extracted with 200–220 parts of water. (3) To a fused mixture of 10 parts caustic soda and 1 part nitre are added 6 parts strongly heated manganese dioxide; the cooled mass is ladled out and extracted as before.

Potassium permanganate $KMnO_4$ or $K_2Mn_2O_8$. This salt may be prepared directly by the addition of 10 parts of potash dissolved in the minimum of water to a mixture of 8 parts manganese dioxide and 7 parts potassium chlorate. The solution is evaporated to dryness, finely powdered, and ignited at a dull red heat for about 1 hour, until the chlorate has become decomposed. The mass is boiled with water, decanted, evaporated rapidly to a small bulk until crystals form on its surface, decanted from the precipitate which has fallen, and allowed to crystallise; 1 part of permanganate is produced from 3 parts of the oxide (Gregory, J. Pharm. Chim. 21, 312).

It is, however, usually prepared by the action of an acid on the manganate.

According to Städeler (J. pr. Chem. [i] 103, 107), 90 p.c. of the oxide may be converted into permanganate by first preparing the manganate and converting it into permanganate by the addition of chlorine instead of acid

$$2K_2MnO_4+Cl_2=2KCl+K_2Mn_2O_8.$$

The solution is evaporated and the permanganate crystallised, leaving the potassium chloride in solution.

Tessié du Mothay and Maréchal prepare it by addition of magnesium sulphate to the manganate, according to the equation

$$3K_2MnO_4+2MgSO_4+2H_2O$$
$$=K_2Mn_2O_8+2K_2SO_4+2Mg(HO)_2+MnO_2$$

It may also be prepared electrolytically by passing a current through a solution of the hydroxide using a ferromanganese anode (White, J. Physical. Chem. 10, 502).

Potassium permanganate forms fine dark

purple prismatic crystals of greenish metallic lustre, soluble in 16 parts of water at 15°C. When heated they decompose, evolving oxygen, and leaving a mixture of manganate and manganese dioxide. Heated in hydrogen they ignite and leave a green mass containing manganese monoxide and potash.

It is an extremely powerful oxidising agent; each molecule contains five atoms of 'available' oxygen, *i.e.* more than any other salt. It is largely used as a local disinfectant.

When triturated with sulphur or phosphorus it detonates; when mixed with carbonaceous matters and many other reducing agents, and heated, it burns. Mixtures containing permanganates and organic substances are very liable to spontaneous decomposition.

The crystals oxidise strong hydrochloric acid in the cold, with evolution of chlorine; in solution the same effect is produced on heating.

A solution of the salt is rapidly reduced by the addition of sulphurous acid, ferrous salts, and most other reducing agents; less rapidly by organic matter. The solution is therefore used as a test for such substances, and to estimate their amount.

Solutions of the salt can only be filtered through asbestos or glass wool, as they quickly destroy filter-paper.

Zinc, iron, lead, mercury, and many other metals are oxidised more or less rapidly by the solution. Pure potash has no action on permanganate, even when heated, but in presence of organic matter the permanganate is rapidly reduced to the green manganate.

On mixing concentrated solutions of this salt and of silver nitrate, a red crystalline precipitate of *silver permanganate* $Ag_2Mn_2O_8$ is produced. It may be used for the preparation of other permanganates. On mixing with a solution of barium chloride, silver chloride is precipitated, and *barium permanganate* remains in solution, from which *permanganic acid* may be produced by the addition of dilute sulphuric as long as a precipitate falls. On evaporation of the solution the acid is obtained as a brown, crystalline, very soluble mass, easily decomposed by heat.

Sodium permanganate $Na_2Mn_2O_8$ resembles in its properties the potassium salt (*v. Sodium Manganate*).

Aluminium permanganate. Condy (Eng. Pat. 1884, 10015) patented a method of preparing this salt for disinfecting purposes. It is said to give up five-sevenths of its total oxygen to reducing agents. The alumina present would also assist in the precipitation of impurities in water, &c. To 1000 parts of a solution of aluminium sulphate, containing one-third its weight of the sulphate, is added 53 parts of potassium permanganate, which is dissolved by the aid of heat. On cooling, potassium alum crystallises out, and the decanted solution, which contains the whole of the permanganate and a considerable amount of aluminium sulphate, is ready for use.

MANGANESE BRONZE *v.* Manganese; Tin.

MANGANESE-SPAR *v.* Rhodonite; Rhodochrosite; and Manganese.

MANGANITE. A manganese-ore consisting of hydrated sesquioxide $Mn_2O_3{\cdot}H_2O$ or $MnO(OH)$. It occurs as well-developed orthorhombic crystals of prismatic habit and as columnar masses. These possess three perfect cleavages in the direction of the length of the prism, namely, one parallel to the brachypinacoid and two parallel to the unit rhombic prism. The colour is dark steel-grey, with a sub-metallic lustre, and the streak is brownish; sp.gr. 4·3, hardness 4. Good crystals are found, often in association with barytes, at Ilmenau in Thuringia, Ilfeld in the Harz, Granam in Aberdeenshire, Pictou in Nova Scotia, &c. Manganite occurs together with the other black oxides of manganese (pyrolusite, psilomelane, &c.), but as an ore of manganese it is less abundant than these.

L. J. S.

MANGEL-WURZEL or **MANGOLDS.** *Beta vulgaris* (Linn.). A plant largely grown as a farm crop, the root being used as a winter food for cattle and sheep. It is a variety of the garden beet-root or of the sugar-beet. Many varieties are known, differing in size, shape, and colour. Average composition—

	Water	Protein	Fat	N-free extract	Crude fibre	Ash
Large roots .	89·5	1·3	0·1	6·7	1·0	1·4
Medium ,, .	88·0	1·2	0·1	8·7	0·9	1·1
Small ,, .	86·5	1·1	0·1	10·6	0·8	0·9

Large roots of any variety are more watery, richer in nitrogenous substances and crude fibre than small ones; they are not so valuable for feeding purposes nor do they keep so well. When first harvested, mangolds are not suitable for food, especially for sheep, but after keeping a few weeks they form a valuable addition to the dry, winter food of all farm animals. The beneficial effect of storage appears to be the conversion of nitric nitrogen into amides (Wood, J. R. Agric. Soc. 1898).

The nitrogenous constituents of mangolds include much non-proteid material, in which betaine, asparagine, glutamine, nitric acid, and ammonia are the most important. Of the total nitrogen in the root, about 48 p.c. exists as true proteid, from 1 to 6 p.c. as betaine, about 4 p.c. as ammonia, and from 10 to 15 p.c. as nitric acid; the proportions, however, are subject to great variations.

The nitrogen-free extract consists largely of sugar, but there are also present oxalic acid, citric acid, pectins, and pentosans.

As an example of a more detailed analysis of mangolds the results obtained by Pitsch (Landw. Versuchs-Stat. 1892, 21, 471) in an analysis of the dry matter of 'Golden Tankard' mangolds (the roots contained 86·82 p.c. water) may be quoted—

Protein	Pure proteid	Nitric acid	Fat	Sugar	Other N-free substances	Crude fibre	Ash
8·75	4·06	0·31	0·58	60·17	16·98	6·33	7·36

The ash of mangolds, according to König, contains—

Per cent. of ash in dry matter	K_2O	Na_2O	CaO	MgO	Fe_2O_3	P_2O_5	SO_3	SiO_2	Cl
6·44	53·0	15·4	4·1	4·5	0·8	8·4	3·1	2·3	8·4

The leaves are sometimes used as food for cattle, but are very watery and contain oxalic acid (3 or 4 p.c. of the dry matter). They sometimes produce poisonous symptoms if used in large quantities. The addition of about 1 part of finely divided calcium carbonate to 1000 parts of leaves is found to prevent the poisonous action of the oxalic acid. Kellner gives as the average composition of the leaves—

Water	Protein	Fat	N-free extract	Crude fibre	Ash
89·0	2·4	0·4	4·6	1·6	2·0

Mangold seeds have been examined by Devarda (Landw. Versuchs-Stat. 1897, 49, 239). They consisted of 11·55 p.c. of water and 88·45 p.c. of dry matter. The dry matter contained—

Protein	Fat	N-free extract	Crude fibre	Ash
12·84	6·08	38·41	34·01	8·38

The ash consisted of—

K_2O	Na_2O	CaO	MgO	Fe_2O_3	P_2O_5	SO_3	SiO_2	Cl
22·0	8·0	16·1	11·0	1·0	10·0	5·0	24·6	2·3

Mangolds require a deep, somewhat loamy soil, and, with abundant nitrogenous manuring, yield very heavy crops. They have a longer period of growth than turnips, and are less dependent upon phosphatic manuring. They are one of the few crops which are benefited by applications of common salt to the soil and, perhaps for this reason, grow well on land near the coasts. H. I.

MANGO. The fruit of *Mangifera indica* (Linn.), a tree of the East Indies, now grown in other tropical countries. It is eaten raw or used for the preparation of pickles and chutneys.

Prinsen-Geerligs (Chem. Zeit. 1897, 21, 719) gives the following data:—

	Mean weight in grammes	Flesh p.c.	Rind p.c.	Stone p.c.	The flesh contains Glu-cose	Lævu-lose	Suc-rose
Sweet variety	200	67	3	30	0·6	2·0	9·5
Sour variety	300	75	3	22	0·0	1·9	3·6

The gum of this tree was examined by Lemeland (J. Pharm. Chim. 1904, 19, 584), who found it to consist largely of galactose and pentoses. H. I.

MANGROVE BARK. The bark of the mangrove is exported from Mozambique, Parapat, Ibo, Pemba Bay, and other parts of East Africa, mainly to Germany, Russia, and the United States, and for use as a tanning material. It contains from 35 to 40 p.c. of tannin.

MANILA ELEMI *v.* Oleo-resins.

MANIOT or **MANIHOT** is the farina of *Manihot utilissima* (Pohl.), formerly known as *Jatropha Manihot* (Linn.), the plant which furnishes tapioca. Indigenous to America, but also cultivated in Africa and tropical climates generally. Maniot is occasionally imported under the name of 'Brazilian arrowroot.'

MANJAK. A form of asphaltum found in Barbadoes.

MANNA. The concrete juice of the manna-ash, *Fraxinus Ornus* (Linn.), although the name is also applied to the sweet exudations from other plants. Ordinary manna is procured by making incisions in the bark of the trees during the summer and allowing the sap to evaporate. Most of the manna of commerce comes from Sicily or Southern Italy. When freshly prepared, it is pleasant to the taste and is used, to some extent, as a food; but on keeping, it acquires mild laxative properties and is used medicinally.

Manna consists largely of mannitol (*q.v.*), of which it is usually stated to contain from 50 to 80 p.c., together with some invert sugar, gum, and ash. According to Tanret (Bull. Soc. chim. 1902, 27, 947), however, it contains notable quantities of two complex sugars, which he names *manneotetrose* and *manninotriose.* His analyses show ordinary manna to contain mannitol 40–55, lævulose 2·5–3·4, dextrose 2·2–3·0, manneotetrose 12–16, manninotriose, 6–16 p.c., together with small quantities of resin and ash.

Manneotetrose $C_{24}H_{42}O_{21}4H_2O$ forms monoclinic crystals, melts at 100°, and has $[\alpha]_D+150°$; it is very soluble in water, does not reduce Fehling's solution, and is hydrolysed by acetic acid or enzymes, yielding lævulose and manninotriose; by dilute mineral acids into 1 mol. dextrose, 1 mol. lævulose, and 2 mols. galactose.

Manninotriose $C_{18}H_{32}O_{16}$ separates from hot alcohol in spherical masses, melts at 150°, and has $[\alpha]_D+167°$. It reduces Fehling's solution, slowly ferments with yeast, and is hydrolysed by mineral acids, but not by enzymes.

Among many other vegetable exudations which go by the name of 'manna' the following may be mentioned:—

Australian manna: (*a*) from *Myoporum platycarpum* (R. Br.) contains mannitol 89·6, sugar 3·4, water 3·5, ash 1·1 p.c. (Malden, Chem. Zentr. 1894, ii. 341).

(*b*) From the leaves of *Eucalyptus dumosa* (A. Cunn.) containing sugar, inulin, starch, and gum (Anderson, quoted by König).

(*c*) From *Eucalyptus Gunnii*, var. *rubida*, contains water 9·7, ash 6·8, melitose 68·5, dextrose 20·9, sucrose 2·1, gum 3·2, insoluble 4·3 p.c. (Ebert, Chem. Zentr. 1908, ii. 1874).

Persian manna, from the leaves and thorns of the camel's thorn, *Alhagi maurorum* (Medic.) containing moisture 5·2, ash 9·4, chlorophyll and some gum 0·5, sucrose 42·0, gum 20·3, residue 32·0 p.c. (E.).

Sinai or *Tarfa manna*, exuding from punctures caused by an insect, *Coccus manniparus* (Ehrbg.), in the stems of *Tamarix gallica*, var. *mannifera*, containing chiefly sugar and dextrin. *Cedar* or *Lebanon manna*, from the branches of *Cedrus Libani* (Barrel. Ic.).

Trehala manna from the larval cocoons of a beetle, *Larinus maculatus*, living on the stems of *Echinops persicus* (Stev.), containing water 11·1, ash 2·6, trehalose 17·5, gum 27·1, tannin, starch, and residue 44·5 p.c. (Ebert, *loc. cit.*).

Manna of *olives*, a morbid secretion of bacterial origin initiated by the attacks of insects upon olive trees, contains 52 p.c. mannitol, 7·8 p.c. reducing sugars, and 21·5 p.c. of other organic matter (Trabut, Compt. rend. 132, 225).

The term 'manna' is also loosely used for the seeds of certain cereals, *e.g.* 'Boer manna,' and 'Kaffir manna' are often employed as names for certain millets. H. I.

MANNHEIM GOLD *v.* Gold, Mannheim.

MANNITOL, MANNOSE, MANNOTRIOSE *v.* Carbohydrates.

MANQUETA or **MAQUATA.** The African names of a fossil gum resin, resembling copal gum, found in Angola, below the surface of a ferruginous hard clay or soil, at a depth of a few inches to a couple of feet, often in pieces weighing several pounds.

MANTLES, GAS *v.* Gas mantles.

MANURE, ARTIFICIAL *v.* Fertilisers.

MAPÉ. A coarse starch obtained from

Tahiti, derived from the fruit of *Inocarpus edulis* (Forst.).

MAPLE. The name of trees of the genus *Acer*. Some species are valued as shade and timber trees, whilst one, *A. saccharinum* (Wangenh.), affords an important source of sugar in America and Canada. This tree, which attains a height of 100 feet with a trunk of 3 or 4 feet in diameter, affords a considerable quantity of saccharine sap if tapped in the early spring. The sap varies in composition, but, on the average, contains from 2 to 3 p.c. of sucrose, small quantities of proteids, ash constituents, and vegetable acids, mainly malic acid. The flow of sap is most rapid when frosty nights are followed by warm days. The sap is received in buckets and rapidly boiled down in an open pan, the proteid matter which coagulates being removed by skimming. A deposit, often containing calcium malate and silica, forms on the pan bottom. When the syrup has attained a sufficient density it is run off and either preserved as syrup, after filtration or sedimentation, or is boiled down still further, until it solidifies to a white or brown mass of sugar on cooling.

Maple sugar and syrup are highly prized for table use in America and Canada, and are chiefly used in the locality where they are produced. They vary considerably in composition according to the method adopted in their preparation, but generally retain a characteristic 'maple' flavour.

Genuine maple sugar is distinguishable from imitations made of cane sugar by the large precipitate it yields with basic lead acetate, mainly due to the malic acid present (*see* Winton and Kreider, J. Amer. Chem. Soc. 1906, 28, 1204). For the results of an investigation into the conditions affecting the flow of sap of the sugar maple, *see* Jones, Edson and Morse (Bull. 103, Vermont, Expt. Stat. 1903).

H. I.

MAQUI. The maqui is a small evergreen tiliaceous shrub (*Aristotelia Macqui*, L'Hérit.), common in Chile along the course of torrents, and in shady mountainous woods. It is not cultivated, but grows wild, and the berries, which in Chile are eaten either fresh or preserved, contain a red pigment, and are exported largely to Europe for the purpose of colouring wines.

MARBLE. Although this term should strictly be limited to those varieties of limestone which are sufficiently compact to receive a polish, it is loosely applied in trade to a great range of ornamental stones, including many which, like serpentine and alabaster, are not true limestones. Typical marble, such as that used for statuary, has a crystallo-granular texture, resembling that of loaf-sugar, whence it is termed 'saccharoidal.' Under the microscope it commonly shows an aggregation of grains of calcite, exhibiting twin-lamellæ. The development of such a structure appears to be due to that kind of metamorphic action which Sir A. Geikie has termed *marmorosis*. That an ordinary limestone may be converted by the operation of heat and pressure into a crystalline marble is known to every field geologist, while the fact has been confirmed experimentally by Sir J. Hall (in 1805) and others. Metamorphic limestones, such as statuary marbles, are often rich in various crystallised silicates, such as garnet, idocrase, tremolite, and mica, which are supposed to have resulted from the alteration of the foreign materials originally associated with the limestone.

Of ancient marbles, the most renowned for the purposes of sculpture was the *Parian*, obtained from the isle of Paros, one of the Cyclades, in the Ægean sea. The finest kind, known as *Lychnitis*, had a peculiar sparkling grain and a warm surface, which enabled the sculptor to render the texture of skin with great effect. The old quarries have been described by R. Swan (Brit. Ass. Rep. Newcastle, 1889). The famous *Pentelic* marble, largely used in Athenian architecture in the age of Pericles, was a coarser material, adapted for bold sculpture rather than for delicate statuary. *Carrara* marble, extensively employed in Rome under the name of *Luna* marble, and used by Michael Angelo and Raphael, is a very fine-grained saccharoidal limestone, still worked with other varieties at Carrara, Massa, and Serravezza, in the province of Emilia. According to the geological survey of Italy it is of Triassic age.

The ancient marbles used in Italy have been studied by Corsi and other antiquaries. *Giallo antico* was a fine yellow marble from Numidia, while *rosso antico* was a homogeneous red marble, probably from Greece, sometimes confounded with *porfido rosso antico*, a hard red porphyry with white felspar crystals, from Jebel Dokhan in Egypt, the quarries of which have been described by W. Brindley. *Verde antico*, or *verde antique*, is a mixture of serpentine and limestone from near Atrax, on the Peneus, in Sicily, quite distinct from the *porfido verde antico*, or Lacedæmonian stone, a felspathic porphyry from Mount Taygetus. Many marbles are known by fanciful names derived from colour, locality, or a superficial resemblance to natural objects: thus, *bardiglio* is a grey or bluish marble with white veins, whilst *cipollino* is a white marble with green veins of mica or talc. (For Italian marbles *v.* W. P. Jervis, I Tesori Sotterranei dell' Italia, vol. 4, 1889. For ancient marbles *v.* M. W. Porter, What Rome was Built with, 1907.)

The marbles of the British Isles are derived mainly from the Devonian and Carboniferous formations. *Plymouth* marble occurs in the Upper Devonian, while the Great Devon limestone, of Middle Devonian age, has been worked as a marble at Babbacombe and St. Mary Church. The *madrepore marbles* of Torquay are largely used for trivial ornaments. The Carboniferous limestone of Derbyshire has long been famous for the beauty and variety of its marbles, the best known being the *encrinital* marbles, which owe their characteristics to the embedded remains of crinoids or 'stone lilies.' Similar encrinitic marble occurs at Dent in Yorkshire and in King's Co., Ireland. *Rosewood* marble is a beautiful brown variety from Ashford in Derbyshire. *Black* marble, such as is worked in Derbyshire, Galway, and Kilkenny, usually emits a fetid odour when struck, and loses its colour on calcination. W. N. Hartley found 1·48 p.c. of carbon and 0·01 of sulphur in the black marble of Kilkenny (Proc. R. Dub. Soc. 5, 486). The black Carboniferous limestone of Belgium and France, with small white sections of encrinites, is termed locally *petit granit*.

Lumachella is an Italian name for any shelly marble, but is specially applied by mineralogists to a Liassic limestone from Bleiberg, in Carinthia, containing the remains of ammonites, which by their brilliant play of colour resemble precious opal. An argillaceous limestone, remarkably rich in dendritic markings, occurs in irregular masses in the Rhætic series, near Bristol, and has been polished under the name of *landscape marble.* The *ruin marble* of Tuscany is a soft argillaceous material, found near Pisa, and sometimes described as a kind of lithomarge. The *ammonite* marble, found near Yeovil, is a brown Liassic limestone, rich in the remains of ammonites. The oolitic formation known as *Forest marble* takes its name from Wychwood Forest in Oxfordshire, which yields a coarse shelly limestone, occasionally polished as an ornamental stone. The famous *Purbeck* marble, extensively used in Gothic architecture, especially for slender clustered shafts, is a grey fresh-water limestone of Upper Oolitic age, crowded with *paludinæ*; whilst the *Sussex* marble is a similar shelly limestone, of fresh-water origin, occurring in bands in the Weald clay. (For English marbles *v.* H. B. Woodward, Geology of England and Wales, 2nd ed. 1887. J. A. Howe, Geology of Building Stones, 1910.)

Among foreign marbles those of the Pyrenees and of Numidia deserve special mention. The so-called *Algerian onyx* is a beautiful stalagmitic form of calcium carbonate, formerly called alabaster, and now known as 'Oriental alabaster,' the adjective being used to distinguish it from true alabaster, which is a native form of calcium sulphate. The *Mexican onyx-marble* is a similar stalagmitic material, used as an ornamental stone. (For American marbles *v.* S. M. Burnham, Limestones and Marbles, Boston, 1883. G. P. Merrill, Stones for Building and Decoration, 3rd ed., New York, 1903.)

Ophicalcite is a name applied to serpentinous limestones, which generally display clouded patterns, due to the interblending of a white limestone or dolomite with a green serpentinous mineral. The 'Irish green' of architects is a rock of this character from Connemara in western Galway. Of a similar nature are the serpentinous marbles of Anglesey, the eozoonal marble of Canada, and the verde antique previously mentioned. As the two constituents of an ophicalcite are unequally attacked by atmospheric agents, such a rock is unsuited for use in exposed situations, since it soon weathers to a rough surface.

In fact, marble generally is hardly suitable for outdoor work in large towns. The atmosphere of a city becomes charged with the products of the combustion of coal, including acid compounds of sulphur, and must sooner or later attack all marble monuments. It has been shown by Sir A. Geikie that marble slabs exposed in the churchyards of Edinburgh suffer total destruction in less than a century (Proc. Roy. Soc. Edinb. 1880, 10, 518).

A minor use of marble is for the production of carbon dioxide in soda-water manufacture. In the United States about 25,000 tons of scrap marble are annually ground into dust for this purpose.

Reference.—W. G. Renwick, Marble and Marble Working, 1909. F. W. R.

MARCASITE. An orthorhombic form of iron disulphide FeS_2, dimorphous with the cubic iron-pyrites (*v.* PYRITES) and isomorphous with mispickel (FeAsS). Crystals are not infrequent, but their form is usually much obscured by twinning, producing more or less characteristic forms, which have given rise to the names 'spear-pyrites' and 'cockscomb-pyrites.' Stalactitic and nodular forms with an internal radiated structure are also common. The sp.gr., 4·8, is rather lower than that of iron-pyrites, but the hardness (H.=6) is about the same. The colour is pale brass-yellow, rather lighter than that of iron-pyrites (hence an old name 'white pyrites'), but the material frequently shows a surface tarnish. Marcasite is less stable than iron-pyrites, and in a moist atmosphere it decomposes more readily with the production of iron-vitriol. When the material shows no crystal-forms it is not always distinguishable from iron-pyrites.

Marcasite occurs in mineral-veins, as crystals and nodules in the chalk-marl of Kent, in lignite and clay at Littmitz in Bohemia, &c. It is much less abundant than iron-pyrites. When found in large amount it is used, like iron-pyrites, for the manufacture of sulphuric acid and iron-vitriol. L. J. S.

MARCASOL *v.* SYNTHETIC DRUGS.

MARCTINE. Trade name for an antithermic $CH_3{\cdot}C_6H_4{\cdot}NH{\cdot}NH{\cdot}CO{\cdot}NH_2(1:3)$, *i.e.* methyl-acetanilide, in which the acetyl radical is replaced by the group $NH{\cdot}CO{\cdot}NH_2$. For reactions and tests, *v.* Lemaire, Rep. Pharm. 1907, 19, 49; J. Soc. Chem. Ind. 1907, 342.

MARC BRANDY OIL *v.* FUSEL OIL.

MARETIN *v.* SYNTHETIC DRUGS.

MARGARIC ACID $C_{16}H_{33}COOH$ occurs in the wax of lichens, and is obtained by boiling margaronitrile with alcoholic potash (Becker, Annalen, 102, 209; Heintz, J. 1857, 355).

MARGARINE (American, *Oleomargarine*) is the generic term for butter substitutes, consisting either of a mixture of animal fats alone, or of animal and vegetable oils and fats churned with milk to a butter-like emulsion, and coloured yellow (unless forbidden by law) with annatto, methylorange, &c. During latter years, with the expansion of the margarine industry, two further kinds of 'margarine' have been brought into commerce, namely (1) margarine made exclusively of vegetable fats and oils churned to an emulsion with cow's milk, and (2) margarine made from vegetable oils and fats, wherein for cow's milk is substituted an emulsion made from kernels of almonds. Thus the last-named article consists exclusively of *vegetable* products. A variety of the last class of butter substitutes, no doubt suggested by the fact that their consistence was too soft, is made from a mixture of oleomargarine and milk of almonds (with an addition of sesamé oil, where prescribed by law).

The industry of butter substitutes owes its origin to experiments (induced by a prize offered by the French Government in 1869) made by Mège-Mouriès, which were worked out to a manufacturing process in Paris in the year 1870.

In the manufacture of the original margarine, as made by Mège-Mouriès's process, the animal fats used were oleomargarine—'oleo oil,'—and (or) neutral lard (the latter is almost exclusively used in the United States). Both ingredients must be prepared from the freshest beef fat and (or) hog-fat respectively.

For the production of oleomargarine, the rough fat is removed from the slaughtered animal as quickly as possible and brought into the works, where it is sorted. The kidney and bowel fats are selected, then carefully washed with warm water and thoroughly cleansed. The cleansed fat is brought immediaately into large, well-aired, artificially cooled rooms to dry and harden (being allowed to hang there suspended from tin hooks for several hours), or is immersed in iced water in order to secure more rapid hardening. The hardened fat is then cut up and shredded in a shredding machine, and finally ground between rollers. The disintegrated mass is introduced into tin-lined jacketed vessels ('melting kettles') and brought to a temperature not exceeding 42°C., this temperature being maintained by steam or hot water passing through the jacket.

At this temperature a portion only of the tallow contained in the tissue separates on the top of the comminuted rough fat. The settling and clearing is assisted by sprinkling salt over the surface of the melted fat. This melted portion, termed 'premier jus,' is run off into shallow tin-lined trays arranged in tiers in a cooled room, when the bulk of the 'stearine' separates in a crystalline condition. The crystallised mass in the tins is cut up into square pieces of about 3 lbs. weight each, wrapped in canvas cloths, and placed in hydraulic or mechanical presses.

For the best qualities of margarine, the 'premier jus' is remelted at a temperature not exceeding 45°C. and allowed once more to settle out, after salt has been added, whereby the last remnants of membrane and tissue are precipitated. In large works the clear fat is allowed to run into wooden vats, in which it stands for from 3 to 5 days at a temperature suitable for the crystallisation of the 'stearine.' The whole is then stirred up into a homogeneous pulpy mass; this is wheeled in wooden waggons to the presses and treated as described already.

The oleomargarine, 'oleo oil,' which runs out from the presses formerly constituted the exclusive raw material for the manufacture of margarine.

In some works the rough fat from which the 'premier jus' has been taken off (in the manner described above) is heated once more to about 50°C., when a second portion of fat is recovered. This is sold as 'secunda jus,' and is used in the manufacture of inferior kinds of margarine ('secunda' margarine).

Amongst the vegetable oils, cotton-seed oil and cotton-seed stearine, sesamé oil, arachis oil, and recently even soya-bean oil, are preferred. According to the intended quality of the margarine, the quality of the cotton oil varies. In any case the cotton-seed oil must be practically devoid of free fatty acids, and rendered as free as possible from the peculiar flavour characteristic of this oil. The best brand of cotton-seed oil used for margarine making is known under the name 'butter oil.' Arachis oil (also olive oil) and sesamé oil are used to a greater extent in Europe than in the United States. Refined cocoa-nut oil and palm-kernel oil are now incorporated to a very considerable extent with the fat stock of margarine.

The oleomargarine, 'oleo oil' (and neutral lard) is mixed in *churning machines* at as low a temperature as is consistent with a semi-fluid condition with the vegetable oils and fats, and with milk.

The quality of the resulting product depends, to a great extent, on the quality of the milk and on its treatment previous to its admixture with the fats. The milk may be either sweet milk or sour. Sweet milk is more difficult to amalgamate with the oils and fats, and is retained with greater difficulty than soured milk, but the advantage the employment of sweet milk offers is that the resulting product has a finer taste and keeps better. The soured milk is, however, more easily incorporated with the fats and gives a higher yield. The proper treatment of the milk in the margarine works constitutes one of the most important features, just as the corresponding part of the butter-making process does in large dairies. The milk should be worked up as soon as possible after arrival. In any case it should be pasteurised immediately after it is received, and no preservatives—not even salt—should be used to prevent the fermentation of the milk. If the cream has not been taken off before the milk reaches the margarine works, it is removed (for butter-making) by means of a centrifugal machine, &c. The regular determination of the fat in the milk is necessary, not only for the proper control of the works, but also for the further reason that it has not infrequently occurred (on the Continent) that too much cream is taken off by the seller and replaced by sesamé oil, cotton-seed oil, or even by margarine.

In place of cow's milk, kephir milk, or even kephir fungus, have been recommended (and patented). It is claimed that the margarine so obtained has a full butter flavour and 'browns' on being heated.

The churning machines consist of oval, jacketed vessels provided with one or two sets of stirring and mixing gear. During the process of churning a constant temperature must be maintained by means of steam sent through the jacket of the churn. The object of churning, besides thoroughly mixing the ingredients, is to destroy the tendency of the oleomargarine to crystallise, and to pulverise ('atomise') the mixture, as it were, into single globules, such as butter-fat forms in milk. The art of the margarine maker at this stage of the process consists, therefore, in carefully regulating the inflow of milk and fat stock, so that a thorough emulsion is finally obtained.

First, the milk is put lukewarm into the churn and is mixed up with a little cream, followed by the addition of butter (if any be added). When the mass is thoroughly emulsified, part of the oleomargarine is added carefully, and when this has been properly incorporated with the emulsion, the oils required for the margarine stock are entered gradually and only then the remaining oleomargarine is mixed in. At this stage some manufacturers add colouring matters. The steam is then turned off, and the warm material cooled to a definite temperature by cold water being sent through the jacket.

From the churn the cooled margarine is run into cooling tanks, which are built up of marble or white tiles or simply consist of large wooden tanks. While running out, the margarine is met by a current of ice-cold water, delivered under high pressure, in order to pulverise the mass thoroughly. The disintegrated globules, after solidifying, somewhat resemble butter granules.

The cooling of the still liquid margarine by running it off to a cooled table, has the serious drawback that the cooled mass is of uneven thickness, and hence an unevenly cooled product is obtained. This drawback is avoided by E. and H. H. Schou, who cool the margarine in a thin layer, of a thickness of about 1–1·5 mm., between two hollow cylinders which revolve in opposite directions and are cooled by a cold brine solution.

A large number of patents have been taken out for 'homogenising' or 'atomising' in special machines the mixture of milk and oils and fats. The merit claimed for these machines is that the product is more solid and has no 'oily' but 'rather a nut-like' taste. The important demerit of all these apparatus is, however, that the margarine retains more water, and hence the proportion of fat falls below 80 p.c. Therefore in those countries where the maximum percentage of 16 p.c. of water is prescribed by law, the sale of such margarine would meet with difficulties.

In order to obviate this drawback, and at the same time to dispense with the kneading machines, in which the excess of the milk is removed, Schroeder (D. R. PP. 204061; 204062) carries out the blending and emulsifying process in three churning machines arranged one above the other and working in conjunction with an 'atomiser.' The temperature in the three churns through which the mixture of fats and milk passes is regulated carefully so that the completely emulsified contents of the lowest churn can be discharged on to a cooled table, where the mass solidifies to a thin layer, which is scraped off by a tangentially acting 'doctor,' so that the thin solidified film is curled up and discharged into a waggon. The ingredients forming the margarine are mixed (*v. infra*) in the proportion of 80 parts of fats and oils, 16 parts of milk, and 4 parts of cream, consisting approximately of one-third of butter-fat.

The solidified margarine is taken out of the cooling tanks by means of long wooden spoons, placed in wooden waggons (where adhering water drains off), and is then carted to large kneading machines. These consist of huge circular wooden tables, which rotate slowly, while at the same time a set of conical, fluted, or specially shaped rollers move along the top of the revolving tables. The margarine is thus thoroughly worked through, and the excess of water squeezed out, so that a homogeneous mass results. This is then salted to taste, mixed with a little colouring matter (if permitted by law), and again submitted to thorough kneading in a second set of kneading machines of the same or of different type, in order to produce the required texture throughout the whole mass. At this stage also other additions (such as sugar, perfumes, &c.) are made. The margarine is finally moulded into lumps, pats, rolls, or any other desired shape.

A general working recipe for the manufacture of margarine is to mix 65 parts of oleomargarine, 20 parts of vegetable oils, and 30 parts of milk. The yield is 100 parts of finished product, 15 parts of water being eliminated in the course of manufacture. The more milk used, the better will be the margarine.

The object of the margarine maker being to render his product as closely similar to butter as possible, and to take away the 'tallowy' or too strongly 'oily' taste of the material, some manufacturers (provided the law permits) add cow's butter. Others add small quantities of volatile acids, volatile aldehydes, mixed glycerides containing butyric acid, such as dibutyromonostearin and dicaprylomonostearin, or 'butter perfumes,' which consist chiefly of volatile acids, such as propionic, butyric, caproic, and their ethyl esters. Also coumarin (sold as an emulsion with sesamé oil) would fall under the head of 'perfumes.'

It should, however, be stated that margarines prepared from the best material and in an unobjectionable manner do not require any of these additions. The latter are chiefly used in order to mask low-grade materials, or to afford analytical data which may create a fictitious impression as to the real nature of the product.

An important point in the manufacture is to produce margarine which will froth and 'brown' on heating, so that even in cooking the margarine may resemble butter. Since the property of butter to brown and froth is due to casein and milk sugar, it is evident that the more milk is used in the manufacture of margarine, the nearer will the product approximate to butter.

Milk is liberally used in this country and in America; but in some continental countries where the law forbids the addition of more than a strictly limited quantity of milk, a number of patents have been taken out for substances which are credited with imparting to margarine the desired properties. Prominent amongst these patented products are casein and other albuminoids. Some patentees claim cholesterol and cholesteryl esters, or lecithin. Lecithin is now incorporated with margarine in the form of egg yolk, which is, of course, cheaper than lecithin.

Vegetable waxes have also been proposed as admixtures, and the use of beeswax for this purpose has even been patented, although the addition of such substances must seriously interfere with the digestibility of the margarine.

Besides the taste, the consistence also plays an important part in the valuation of margarine. If the finished margarine has not been worked sufficiently on the tables, its consistence may be either too 'greasy' or too 'sandy,' *i.e.* the semi-crystalline mass has not been properly 'broken,' and its grain differs from that of a properly prepared dairy butter. Some margarines are also finally mixed with a little glycerin, or glucose, or sugar, in order to improve the texture or to give them a glossy appearance and also a sweeter taste. The addition of glucose or cane-sugar must, however, be considered a mistake, as this only leads to premature development of fungus on the margarine.

The manufacture of butter substitutes is differently affected by legislation in different countries. In this country the adding of butter to margarine in any proportion was at first allowed, for, according to the Margarine Act of 1887, any ‘ butter ’ containing even the smallest quantity of foreign fat was looked upon as margarine. By the Margarine Clause of the Food and Drugs Act, 1899, however, the maximum proportion of butter-fat in margarine has been restricted to 10 p.c.

This restriction has been confirmed by the Butter and Margarine Act of 1907, and it has been further enacted that margarine must not contain more than 16 p.c. of water. Margarine factories must be registered, and are open to Government inspection. Prohibited preservatives must not be used, nor is an excess of boric acid allowed. According to the same act ‘ margarine ’ means ‘ any article of food, whether mixed with butter or not, which resembles butter, and is not milk-blended butter.’ For the latest enactments in other countries the reader is referred to Lewkowitsch, Chemical Technology, vol. iii. 26–27.

In the *examination* of margarine the determination of the Reichert-Meissl value constituted the most important characteristic, as it indicated in the briefest and surest manner the amount of butter-fat contained in the margarine, either added as butter or originating from the milk which had been incorporated with the oils and fats in the process of manufacture. Since, however, considerable quantities of cocoa-nut oil and palm-kernel oil form ingredients of margarines, and since even margarines are made at present which consist exclusively of the last-named two oils, without even an addition of cow’s milk, the indications of the Reichert-Meissl value no longer have that importance which they formerly possessed. Accurate methods for the detection of butter-fat and cocoa-nut oil or palm-nut oil in the presence of other vegetable oils and fats have not yet been elaborated in such a satisfactory manner that complete confidence can be given to them. An important test is the detection and determination of unsaponifiable matter, as latterly unscrupulous manufacturers have again commenced to admix paraffin wax with margarine. J. L.

MARINE ACID. *Syn.* for hydrochloric acid (*q.v.*).

MARINE ANIMAL OILS *v.* OILS.

MARIPA FAT. The fat of the fruit of *Maximiliana* [*Attalea*] *Maripa* (Drude), used in the West Indies as a butter. It is employed in French Guiana as a medicinal liniment, and is practically identical with coco-nut fat in characters.

MARJORAM, *Origanum Majorana* (Linn.), a herb employed in flavouring. It is generally used in the air-dried state, when it has the following composition :—

Water	Protein	Fat	Ethereal oil	N-free extract	Crude fibre	Ash	Sand
7·6	14·3	5·6	1·7	35·6	22·1	9·7	3·4

Commercial dried marjoram often contains much sand; a good sample should not contain more than 14 p.c. of ash, of which not more than 3·5 or 4·0 p.c. should be insoluble in hydrochloric acid. The following analyses of the ash of marjoram were made by Rupp (Zeitsch. angew. Chem. 1892, 681) :—

	K_2O	Na_2O	MgO	CaO	Fe_2O_3	Mn_3O_4	P_2O_5	SO_3	Cl	CO_2	Sand
German	20·2	0·7	4·8	17·6	7·3	1·0	8·9	4·9	2·1	6·1	26·5
French .	18·3	0·7	6·7	24·8	6·1	trace	9·1	4·8	1·5	8·6	19·4

(*v.* OILS, ESSENTIAL). H. I.

MARKASOL. *Bismuth borophenate* (*v.* BISMUTH, ORGANIC COMPOUNDS OF).

MARKING-INK is used for stamping or marking fabrics, and should be permanent, and indestructible to the material. The basis of many marking-inks is a silver salt dissolved in aqueous ammonia containing a little gum. This is only coloured on decomposition, so a little dye is needful : dark-brown inks contain archil and chlorophyll, crimson contain carmine, whilst copper sulphate is an ingredient of blue ink.

Redmond’s ink is made thus : dissolve 3 oz. 2 drms. silver nitrate and 3 oz. sodium carbonate each in 2 pints boiling water, mix, and collect the precipitate so formed on a filter, wash with water, transfer to a mortar, add 10½ drms. tartaric acid, triturate the whole, and when effervescence has ceased, add 3½ oz. of ammonia (0·880), stir until dissolved, and add 1½ oz. powdered white sugar. Mix 1 oz. chlorophyll and 1 oz. archil with 4 oz. water, add 2½ oz. of acacia gum to this when dissolved, strain, add to the ammoniacal solution and make up to 20 oz. with water. This ink, if carefully prepared, contains only the tartrate of silver ; on heating metallic silver is left on the fabric.

An indelible ink is made by dissolving 1 oz. silver nitrate and 1½ oz. of sodium carbonate separately in 3 oz. distilled water; mix the solution, collect and wash the precipitate with distilled water. Add 160 grs. tartaric acid, dissolved in 1 oz. water, to the precipitate in a mortar, stir until effervescence ceases, and then add 2 oz. liquid ammonia to dissolve the precipitate. Mix in 80 grs. aniline black, dissolved in 1 oz. boiling water, and add 5 drms. glycerol and water to make up to 8 fl. oz. (Spon’s Workshop Receipts, 1909, 510).

Aniline marking-ink is prepared thus : in two bottles (1) add 1 fl. drm. aniline and 10 grs. toluidine to 2 fl. drms. mucilage of acacia and dilute hydrochloric acid, and mix ; (2) powder 40 grs. cupric sulphate, 20 grs. ammonium chloride, 20 grs. potassium chlorate, and dissolve in 6 fl. drms. water ; lastly, add 2 fl. drms. of thick mucilage and mix. Leave for 2 or 3 days before using. Equal parts of each solution are mixed immediately before using and applied with a quill pen (Scient. Amer. Ency. 1903, 276).

An ink suitable for rubber stamps, as it dries rapidly, is made by adding 15 oz. glycerol to a solution of ½ oz. aniline black and 15 oz. pure alcohol.

To use silver marking-ink for stamping, add to 1 oz. ink, 1 drm. glycerol and 1 drm. treacle.

To make an indelible red ink, dissolve 2 oz. shavings of dry white curd soap in 1 part balsam of copaiba by heating, add sufficient vermilion and stir occasionally until cold.

Indian-inks are used for marking.

An ink suitable for labels which cannot be bleached is made by mixing equal parts of pyrogallol and iron sulphate. The label is varnished when dry (Hiscox, Receipts, 1907, 407).

The juice of the banana and of the marking-nut have to some extent the properties of marking-ink, but no practical method of preparing them for sale has been developed.

MARL (Ger. *Mergel*), a name properly restricted to calcareous clays, but frequently extended so as to include any clay which, when dry, is readily friable. Thus the Keuper or New Red Marls, of Triassic age, often contain little or no calcareous matter. An analysis of a red Keuper marl, from Worcester, by Voelcker, yielded 4·85 p.c. of lime. Marls have been used for ages by agriculturists for the purpose of improving certain lands, the material for 'marling' being systematically dug from 'marl pits.' Since a marl is a calcareous clay, it may obviously pass into an argillaceous limestone; the *chalk marl* is a rock of this kind. When a marl becomes indurated it is often known as *marlstone* or *marl-rock*, and the hard beds of the Middle Lias, which in Yorkshire yield the Cleveland iron-ore, are recognised by geologists as the 'marlstone.' A laminated variety of hardened marl is termed *marl-slate*, which readily passes into a calcareous shale. The marl-slate occurring in the Permian series in the north of England is equivalent to the German *Kupferschiefer*, a bituminous marly shale, containing copper-ore. The *shell-marl* found at the bottom of certain lakes, especially in Scotland, is a calcareous ooze, consisting largely of organic remains. L. J. S.

MARRUBIIN *v.* Marrubium.

MARRUBIUM, *Horehound, Hoarhound.* (*Marrube blanc*, Fr.; *Andornkraut*, Ger.) Horehound has been employed for its mild tonic, stimulant, and laxative properties, especially in domestic medicine, for a long period. It consists of the leaves and tops of the *Marrubium vulgare* (Linn.), a perennial herb growing throughout most parts of Europe, Asia, and America (Bentl. a. Trim. 210). The only constituent which has been examined, except a trace of *volatile oil*, is the bitter neutral *marrubiin.*

Marrubiin was discovered by Mein (Gm. 18, 234), and further studied by Harms (Arch. Pharm. [ii.] 83, 144; 116, 141) and Kromayer (*ibid.* [ii.] 108, 257), and recently by Gordin (Amer. Chem. J. 30, 265). The dried plant is exhausted with hot water, the solution evaporated to a syrup, the syrup extracted with alcohol, and the extractive obtained, after distilling off the alcohol, is mixed with sodium chloride and treated with ether. On spontaneous evaporation of the ether the marrubiin remains (Harms). Kromayer takes advantage of the power of animal charcoal to absorb marrubiin from the juice of the plant or an infusion, and to yield it again on treatment with alcohol. An alcoholic extractive is thus obtained from which ether removes the marrubiin.

Marrubiin crystallises from ether in plates and from alcohol in needles. It has a bitter and somewhat acrid taste. It melts at 154·5°–155·5° (Gordin). It is insoluble in cold, very slightly soluble in hot water; but dissolves in alcohol or ether.

Marrubiin has the composition $C_{21}H_{28}O_4$; it does not contain any methoxyl groups, and does not decolourise bromine solution. When boiled with alcoholic potassium hydroxide it is converted into *potassium marrubate.*

Marrubic acid $C_{20}H_{29}O_3{\cdot}CO_2H$, m.p. 173°–174°, forms long white silky needles, and when heated at 190°–200° under 15 mm. pressure is reconverted into marrubiin. The acid reduces ammoniacal silver nitrate and Fehling's solution. It appears that marrubiin is a lactone, and can take up a molecule of water to form the hydroxy acid, marrubic acid. A. S.

MARSH GAS. *Methane* or *methyl hydride* (*v.* Methyl).

MARSH-MALLOW GUM *v.* Gums.

MARSH ROSEMARY. *Andromeda Polifolia* (Linn.); also an American name for *Statice caroliniana* (Walt.) [*S. Limonium* (Linn.)]. *Andromeda Polifolia*, belonging to the *Ericaceæ*, is the only British species of the genus; it is found also in peat-bogs throughout the north of Europe, Asia, and America. It is an acrid narcotic and is fatal to sheep pasturing off it.

Statice caroliniana is found in marshy situations from Maine to Florida. According to Parrish, it contains 12 p.c. of tannin and has been used in the manufacture of leather.

MARTENSITE. The principal constituent of all hardened steels containing over 0·16 p.c. of carbon. It is a solid solution of carbon in iron; when saturated, as in high-carbon steels, it is known as '*hardenite*' (Howe).

On a polished surface, etched with picric acid, it shows under the microscope three systems of cleavage planes inclined to each other at 60°. It is very hard and cannot be scratched by a needle.

Martensite is magnetic and forms one of the principal constituents of permanent magnets.

MARTIUS'S YELLOW. A synonym for Naphthalene yellow; known also as *Jaune d'or, naphthol yellow, Manchester yellow.* The sodium or lime salt of dinitro-α-naphthol (*v.* Naphthalene).

MASOPIN RESIN *v.* Resins.

MASS ACTION *v.* Chemical affinity.

MASSECUITE *v.* Sugar.

MASSICOT *v.* Lead.

MASTIC CEMENT *v.* Cements.

MASTIC RESIN *v.* Resins.

MASTIC VARNISH *v.* Varnish.

MATAZIETTE. A name given to an explosive made in Switzerland, formed of nitroglycerin, sand, and chalk, coloured with ochre.

MATCHES. (Ger. *Zündhölzer, Zündhölzchen*; Fr. *Allumette*; Sw. *Tändsticka*, pl. *Tändstickor*; Du. *Zwavelstokje, Fosforus-stokje*; It. *Zolfanello, Fiammifero*; Da. *Svovlstik*; Hung. *Gyufa.*)

Derivation and variants of the word 'match.'—Older Eng. forms, *mec(c)he, metch, matche, mache, macche*; O. Fr. *mesche, meiche*; Mod. Fr. *mèche*; Pr. *mecca, mecha*; Catal. *metxa*; Sp. and Port. *mecha*; It. *miccia*; perhaps from Gr. *μύξα*, L. *myxa, mixa, myxus*, lamp-nozzle, lamp-wick, mucus of the nose; connected with L. *muccus*, nasal mucus, whence It. *moccolo*, L. *mucculus*, snuff of a candle.

Definitions. I. (*Ordinary language*).—An instantaneous fire-producer, consisting of a short stem, rod, or tube, tipped at one or both ends with a composition or paste, inflammable by friction; or (as in the earlier forms) when brought into contact with a chemical reagent.

2. (*Military and mining*).—A cord or thread impregnated with combustible material, capable of burning along its entire length, so that fire can be conveyed from one point to another. This kind of match, which is better termed a fuse, is not ignitable by friction, and may be 'slow' or 'quick,' according to requirements.

I. Friction Matches.

History and development. Friction matches are among the most useful products of the period immediately preceding the Victorian age, and afford a signal instance of the ministration of science to human needs. Developed in less than three-quarters of a century from fire-producing appliances of the most primitive types, they have been so perfected that it is difficult to foresee in what direction further progress is possible.

Since the discovery of phosphorus in 1673 by Brand, of Hamburg, many attempts had been made to obtain light and heat expeditiously by its aid; one of the earliest consisting in rubbing a particle of phosphorus between folds of coarse brown paper, the flame produced igniting a sulphur-tipped splinter of wood. This plan was found to be inconvenient and dangerous, and phosphorus gradually fell into disuse. After the element had been, in a technological sense, left severely alone for more than a century, renewed attempts were made to utilise it. One contrivance was the somewhat impracticable '*phosphoric taper*' (1781). This was of wax, enclosed in a sealed glass tube, at one end of which was a fragment of phosphorus. After the tube had been dipped in warm water, the end remote from the phosphorus was cut off with a file, the taper was withdrawn, with some phosphorus adhering to it, and spontaneously inflamed. Another appliance was the '*phosphorus bottle*' of Cagniard de Latour (1810), containing partially oxidised phosphorus, some of which was withdrawn by a brimstone match, dipped into the phial, and then ignited by friction. A '*briquet phosphorique*,' brought out in Paris in 1786, consisted of a small tin box containing sulphur-tipped matches, together with a bottle coated internally with phosphorus. '*Pocket luminaries*,' soon afterwards sold in London, and '*portable fire boxes*' were similar. Various early devices for quickly producing fire were Homberg's '*pyrophorus*' (an oxidisable powder, free from phosphorus, prepared by roasting alum with flour, honey, or sugar, and inflamed by exposure to air), and Döbereiner's pyrophorus, of similar character; '*pneumatic tinder-boxes*,' containing amadou or ordinary tinder, ignited by the heat generated when air was compressed by a piston, such as Mollet's Pump, and Lorentz's '*light syringe*' (1807); '*electropneumatic fire-producers*' (invented by Brander, 1778, and by Fürstenberger, 1780), in which hydrogen was kindled by an electric spark—to which category belonged Mayer's apparatus (1811); Volta's '*inflammable air lamp*'; Fyfe's '*hydropneumatic lamp*'; and, lastly, Döbereiner's '*platinum lamp*' (in which contact with spongy platinum, or iridium, ignited hydrogen gas)—with Eisenlohr's, v. Babo's, v. Römer's, Palkl's, Hare's, Schiele's, and Böttger's modifications of the same.

The principal stages in the evolution of matches will now be referred to in chronological sequence. During the year 1804, phials, charged with a mixture of phosphorus, wax, and oil were sold in cases containing also some brimstone-tipped matches and a piece of cork. The matches were dipped into the mixture, withdrawn, and ignited by friction on the cork. In 1805, Chancel, of Paris, applying the principle discovered by Berthollet, of oxidation by chlorates in the presence of strong acid, invented '*oxymuriate matches*,' strips of wood tipped with a mixture of potassium chlorate, sugar, and gum, ignited by contact with sulphuric acid. In the same year, according to Niklès, *friction matches* containing the element phosphorus were made and used in Paris. In 1806 various improvements in the tinder-box were suggested by Phillips, who was followed by Lorentz (1807), with an apparatus for igniting hydrogen gas by the aid of an electrophorus, and with the 'light syringe' already mentioned (same patent). In 1809, to Derepas, of Paris, was granted a French patent 'for a peculiar composition of phosphorus match lights.' This was an attempt to render phosphorus more manageable and less inflammable, by intimately mixing 8 parts, 'half melted,' with 4 parts of magnesia. When cold, the substance was described as forming 'an opaque body fit for inflaming a common match' (Description des Brevets). During the year 1812, '*chemical matches*,' manufactured according to Chancel's invention, began to be sold extensively, a hundred for a florin, in Vienna. The sticks were tipped with potassium chlorate, sugar, and gum, or with the same ingredients and lycopodium: colophony, gum benzoin, &c., were also used. These matches, packed in suitable cases, together with bottles containing asbestos soaked in sulphuric acid (in accordance with a proposal made in 1812 by v. Römer, of Vienna), were sold more widely on the Continent than any others, up to the year 1844. Among the makers were v. Römer, Peters, Wagner, Siegel, Ehrlich, and Merckel. The cases were known as '*tunkfeuerzeugen*,' '*briquets phosphoriques*,' '*inflammable match-boxes*,' '*instantaneous light boxes*,' '*phosphorus boxes*,' &c.; and one form was prominently sold in this country as Heurtner's '*Eupyrion*.' Violence of combustion, and liability of the acid to be spirted about, were characteristics of these matches. In 1816, friction matches tipped with a composition containing phosphorus are stated to have been manufactured in Paris by François Dérosne, who by Gintl and others is regarded as the first maker of the phosphorus friction-match. The year 1823 is marked by the invention of the Döbereiner lamp, already referred to. About this time, too, were used, at Erfurt, in Prussia, small glass tubes containing equal quantities of phosphorus and sulphur carefully fused together, into which thin sticks or splints of wood were introduced, easily inflamed afterwards by friction. The early attempts to make friction matches in Paris and elsewhere appear to have failed completely; and the honour of having invented, in 1827 or earlier, the first practical and useful matches ignitable by friction, indisputably rests with an Englishman, John Walker, of Stockton-on-Tees, Durham (*d.* 1859). Walker was an apothecary, who had been apprenticed to a local surgeon before starting in business as a druggist. He was much interested in experimental chemistry, and for some years prior to 1827 had been preparing and selling, under the name of 'percussion powder,' dried mixtures of potassium chlorate and antimony sulphide, made up with gum-water. Eventually it occurred to him to dip splinters of wood into such a composition, and to supply these matches in tin boxes, together with a piece of folded glass-paper, under the name of 'friction-lights.' Samuel Jones, of 201, Strand, London, who from 1829–1830 onwards sold imitations of Walker's matches under the designation of '*lucifers*' (a name always repudiated by Walker), publicly announced in 1831 that about a year previously they had been 'lectured on at the London and Royal Institutions.' Matches resembling Walker's, but mostly sulphur-dipped, were made also by Jones's competitor, G. F. Watts, in 1831 ('*Watts's chlorate* or *lucifer matches*'), and by Richard Bell & Company in 1832 ('*improved lucifers*'). Watts and Bell both 'borrowed' the name 'lucifer' from Jones. '*Allumettes infernales*' were brimstone-dipped matches of the same type; and German matches of a similar kind, but not sulphured, were also manufactured. H. Link's '*allumettes chémiques*,' produced in Germany for the French market, and L. Achleitner's (Salzburg) '*snellzünder*,' were of like character. Among French makers of matches of an allied type were J. Joseph et Cie (1833), and A. Perpigna (1834).

Though non-phosphoric, Walker's matches inflamed when pressed between the folds of the glass paper and sharply withdrawn. Thus ignitable by friction, they were the lineal ancestors of twentieth-century matches.

Walker at first used strips of cardboard for the stems of his matches, but later he substituted splinters of wood, which he employed the poor people of the district to cut.

In the year 1828, Samuel Jones patented the '*prometheans*,' a return to the principle of the oxymuriate match. These consisted of slightly tapering, spirally-rolled paper tubes, containing in the broader or ignition end a minute fusiform glass tube (not a bulb, as usually stated), 10·5 mm. long by 1·0 mm. wide which enclosed a dark-blue liquid, shown by the writer's analysis to be composed of sulphuric acid coloured by indigo. The glass vessel was imbedded in a composition, variously stated to contain potassium chlorate and sugar, 'fulminate,' &c., but found by the writer to be composed of potassium chlorate, lycopodium, and sulphur. Neither sugar nor fulminate was present in the prometheans examined.

'*Lucifer matches*' or '*lucifers*,' *i.e.* non-phosphoric matches, of Walker's type, which inflamed when rapidly *drawn through* folded sand- or glass-paper, were followed in the early thirties by non-phosphoric friction matches, which could be ignited, though with difficulty, by being *struck upon rubbers affixed to the boxes*. Such were the friction matches made by Savaresse and Merckel (Paris), the igniting composition of which was a mixture of potassium chlorate, antimony sulphide, sulphur, and gum. The rubbing surface was composed of potassium chlorate, minium, pumice, and gum. Similar non-phosphoric friction matches were patented in 1832 by Siegel, an Austrian manufacturer; and Link's 'Chemische Streichfeuerzeuge' were of a like description. Matches, capable of being *struck upon the box*, soon became known as '*Congreves*,' both in this country and abroad; and the name was applied to the phosphoric friction matches which next came on to the market. 'Congreves' succeeded to 'lucifers'; 'lucifers' followed 'friction-lights;' 'friction lights' superseded 'chemical matches.'

It may be mentioned here that Samuel Jones seems to have been the first user of the word *fuzee*, or fusee, as applied to a match for lighting pipes or cigars. But Newton, a few months earlier, applied the term to a match for use by 'smelters.'

Hare's pyrophorus, described in 1831, was made by heating Prussian blue to redness in a glass tube, which immediately afterwards was hermetically sealed. On breaking the tube and throwing out the contents they took fire.

Efforts meanwhile were being made to produce *a practicable and satisfactory friction match*, in which *phosphorus* should take the place of antimony sulphide; and this important result appears to have been achieved simultaneously in several different places during the period 1831–1833. At all events, in 1833–1834, v. Römer, Preschel, and Siegel, in Vienna, and Moldenhauer, at Darmstadt, were manufacturing wooden friction matches, the igniting compositions of which contained phosphorus. The date of v. Römer's patent was January 4, 1834. Other pioneer makers, associates or otherwise of the above, were Pollak and Kreutz (Vienna); Anthon (Darmstadt); and Amüller (Waiblingen). Many of these early continental makers called their matches 'congreves.' In France, the invention of the phosphorus friction match is now generally attributed to Dr. Charles Sauria, of St. Lothair (*d.* 1895), who, in January, 1831, while a student at the College d'Arc, Dole (Jura), made very good friction matches containing phosphorus, but neglected to protect his invention. Sauria's claims have been well attested; and it is possible that a rumour of his experiments somehow was conveyed to other countries during the few months following the discovery. The French Government in 1884 recognised 'L'Invention des Allumettes Chimiques' by a grant to Sauria of a '*bureau de tabac*,' the Academic Nationale Agricole bestowed upon him a medal, and during the year 1896 there was a movement to set up a monument to him in Paris. The design was not carried into execution, however. J. F. Kammerer (*d.* 1857), of Ludwigsburg, Würtemburg, is in Germany usually credited with having invented phosphorus friction matches in 1833; and he is said to have worked out the idea during the previous year; but the invention was not protected, and was pirated in every direction. Claims have been advanced also for a young Hungarian student at the Vienna

Polytechnic School, named János Irinyi (who in 1895 was still living in south Hungary). He is alleged to have made the discovery in 1835, and to have sold his process to v. Römer. Possibly Irinyi's invention marked an advance upon the type of phosphoric friction match which had already begun to be manufactured. Lastly, a professor at the Technical High School in Stockholm, Dr. J. S. Bagge, between 1830–1840, worked out a method for procuring light by means of phosphorus friction matches, and drafted directions for their manufacture.

The oxidising agent used in the earliest matches was potassium chlorate only, but in 1835 Trévany partly replaced it, as being too violent in its action, by a mixture of minium and manganese dioxide.

In the United States of America the first patent for the invention of phosphorus friction matches was granted in 1836 to A. D. Phillips, whose igniting composition was a mixture of phosphorus, sulphur, chalk, and glue. In 1837, v. Römer substituted lead peroxide for potassium chlorate; in 1838, Preschel and Kreutz patented a composition consisting of phosphorus, manganese dioxide, nitre, and gum arabic; Beyer (Vienna, 1838) and Riess (Vienna, 1843) used as the oxidising agent a mixture of minium and nitric acid; and in 1842–3, Böttger, of Frankfort, recommended the substitution, for potassium chlorate, of mixtures of minium and saltpetre, or of lead peroxide and lead nitrate. Moldenhauer, about the year 1838, introduced the use of calcined magnesia in order to counteract the effects of the formation of hygroscopic oxidation-products of the phosphorus; and chalk also (introduced in 1836 by Ehrlich, of Prague) was used for the purpose. Preschel and Klug (1837) endeavoured to accomplish the same end by coating the match-heads with resinous spirit-varnishes. Between 1820 and 1840 various machines for cutting the wooden stems or 'splints' rapidly and in large quantities, were introduced; and the match industry has since developed in country after country until it is now of very great magnitude and world-wide importance. Although in the conditions and processes of manufacture, as well as in the character of the materials used (especially during the past 20 years), there have been improvements and modifications, so far-reaching and gigantic that the industry may be said to have been revolutionised, nevertheless the ordinary friction match of to-day is not *essentially* different from the 'lucifers' and 'congreves' made during the first third of the 19th century. But the use of machinery has been greatly extended. Continuous and automatic machines are at the present time widely and increasingly employed; and, following upon a gradual diminution in the proportion added, in only a very few countries now is white or yellow phosphorus used at all in the manufacture (*see post*, pp. 408 and 412). In 1855 J. R. Wagner recommended that less phosphorus should be used, and experimented with barium nitrate and potassium dichromate, as oxidising agents. The latter salt he considered too costly, and he remarked that lead dioxide, though more expensive and no better, had then largely replaced the mixture of minium and manganese dioxide. In view of the subsequent introduction and present widespread use of tetraphosphorus trisulphide, or phosphorus 'sesquisulphide,' P_4S_3, it is interesting to record that in 1860, Puscher, of Nuremberg, introduced the use of phosphorus sulphide instead of phosphorus, but found few followers. Bals (D. R. P. 89700, 1896) also tried a fused mixture of sulphur and red phosphorus. For making matches *waterproof*, Zimmermann (1864) used collodion, as an improvement on the resinous varnishes of Preschel, Klug, Winterfeld (1842), and Krutzler. Barker (1845), and, after him, Gaillard, applied a coating of sulphur over the friction composition, such matches being found by Abel (1863) to be waterproof, but somewhat difficult to ignite. Hannan and Mills (1882), for the same purpose, mixed paraffin, fatty bodies, or resins, with the compositions. The inventions of Thomas (1895), Fowler and Bower (1895), and Ramsden and Hirst (1900), had a similar end in view. *Scenting ingredients*, such as gum benzoin, frankincense, &c., were often added to the varnishes; and in 1854 Krakowitzer, of Pottenstein, Austria, introduced a process by which a metallic lustre was imparted to the heads of matches '*de luxe*,' or 'parlour' matches (containing lead compounds), by exposing them to sulphuretted hydrogen gas. This process was modified by J. Ginzky in 1860, and again by Schindler, in 1867. A later improvement (A. Kielmeyer, 1879) was to varnish over the silvered heads with an alcoholic solution of colophony, shellac, &c., to which an aniline or other dye was added. Thus, to obtain a greenish bronze, Kielmeyer used fuchsine or methyl violet; other colours employed were methyl green, aniline orange and the like.

Great as was the improvement effected by the substitution of phosphorus for the less easily oxidisable antimony sulphide, there were serious disadvantages attending its use. The poisonous nature of phosphorus, the somewhat too ready inflammability of the igniting compositions made with it, and especially the 'phosphorus disease' (a carious affection of the lower jawbone, leading to necrosis, from which a small proportion of the workers—especially the dippers—were liable to suffer), were much the most important of these. The phosphorus disease, first described in 1845 by Lorinser, of Vienna, has intermittently called for the anxious attention of match manufacturers and statesmen in most countries where white phosphorus has continued to be used in match-making, from 1870 to the present time. In Great Britain, and in other countries where the use of ordinary phosphorus in this industry is forbidden, phosphorus necrosis may be regarded as a thing of the past. But in countries such as America, where there is not yet prohibition, the prevention of the 'phosphorus disease' is still a 'burning question.' Good ventilation, impregnation of the air of the factories with the vapour of oil of turpentine, and scrupulous personal cleanliness on the part of the operatives, combined with particular attention to the condition of their teeth, have been found greatly to diminish the number of cases of necrosis. It was shown by Thorpe and Tutton that the disease is caused by the direct action of the vapour of phosphorous oxide P_4O_6 on the bone, and that the characteristic smell, noticeable in the dipping-room of a match-factory where white phosphorus is used is due, not to the vapour of the element phosphorus, but to the fumes of phosphorous oxide. Only those workers with carious teeth are liable to suffer from necrosis of the jaw. Recognising the bad state of the teeth of many of their workers, Messrs. Bryant and May, in London and Liverpool, some 16 years ago, before white phosphorus had ceased to be used, were the first match manufacturers to take the important preventive step of establishing dental departments, where all the workers could be treated free of charge. This great benefit to the workers is still available at the factories, although the use of white phosphorus in Great Britain has for a long period been discontinued. In the annual report of the German inspectors of factories for 1879 it was stated that, in that year, among 5724 workmen coming in contact with phosphorus vapours, only nine cases of necrosis were observed, six of illness, and three of death (Jettel, Chem. Zeit. 1883, 7, 89). In 1884, however, stringent regulations were put into force in Germany with regard to the arrangements in match-factories, especial stress being laid upon the efficient ventilation of the separate rooms in which the operations of mixing the igniting compositions, dipping, drying, and removal of the splints from the dipping frames, were to be conducted. Finally, in 1906, Germany adopted absolute prohibition of the use of white phosphorus (*see post*, p. 412).

In Denmark and Switzerland, the use of matches containing ordinary phosphorus was forbidden in 1875 and 1879 respectively; and only the so-called Swedish safety matches have been permitted to be used in Denmark since 1875.

Between 1879 and 1882 the use of matches free from phosphorus and inflammable on any surface was allowed in Switzerland; but a commitee appointed by the Department of Commerce found that these matches were unreliable and often dangerous: in 1882 the Swiss Government passed an Act, prohibiting the use of any but safety matches; and in 1906 Switzerland was one of the high contracting parties to the international treaty for enforcement of the total prohibition of poisonous phosphorus.

Efforts were early made to use red phosphorus, discovered by v. Schrötter in 1845; and G. E. Pasch, in 1844, took out a patent for a red phosphorus-product, which he believed to be an oxide of the element; and he is by some authorities regarded as the pioneer in the utilisation of red phosphorus. It is claimed for him that he discovered that a striking surface containing this substance could be used for matches free from phosphorus. Matches tipped with compositions prepared with red phosphorus were manufactured in Germany in 1850, in England (by Dixon & Co., and Bell & Black), Austria (Fürth, of Schüttenhofen, and Foster & Wawra, Vienna), and France (Coignet & Co., Paris), in 1851: but they were not successful; and, although improved matches of this description were patented by Albright, of Birmingham, in 1856, and were again to be seen at Paris in 1867, and Vienna in 1873, they did not come into general use. The higher cost of red phosphorus had much to do with this; but, in addition, the mixtures used were unstable and dangerous. Some of the earlier igniting compositions made with red phosphorus undoubtedly contained excessive proportions of the element. Of late years, matches of very fair quality have been produced, with far lower percentages; and there are upon the market at the present time various red phosphorus matches, some of which have been analysed by the writer. Many inventors of late years have proposed methods of diminishing the violence of the reaction between this variety of phosphorus and potassium chlorate, of lowering the ignition temperature of mixtures containing red phosphorus, or of rendering matches made with it less absorbent of moisture; such as previously mixing it with zinc (Simonet, 1893) or with sulphur (Bals and Gurowitz, 1896); substituting calcium plumbate for the potassium chlorate in red phosphorus compositions (Schwiening, 1896); adding chalk, &c. (Cordes, 1898); coating the red phosphorus with paraffin wax or some other suitable hydrocarbon (Akester, 1899, and Thompson, 1899); associating it with a borate or a phosphate (Säfström, 1901); boiling in aqueous solutions of various metallic salts (Purgotti, 1902); admixture with cork and flour (Bokmayer and Swoboda, 1905); or with zinc oxide and chalk (Chem. Fab. Griesheim Elektron, 1909). Schwiening's composition was adopted by the German Government, in consequence of the weighty objections to the use of ordinary phosphorus. The calcium plumbate apparently retards the explosion of the red phosphorus and chlorate mixture, thus moderating the violence of the combustion; but the matches have been subjected to somewhat severe and general criticism, on various grounds.

The Société Caussemille Jeune & Cie and Roche & Cie in 1909 proposed the treatment of red phosphorus by distillation and filtration, for the purpose of purifying it from acidity and alkalinity. The product they termed 'neutral amorphous phosphorus.'

In 1855 Lundström, of Jönköping, Sweden, acting on Böttger's suggestion, that friction matches might be so made as to be capable of igniting only on an especially prepared surface, manufactured the first true '*safety matches*,' by putting the oxidising mixture on the matchsticks and red phosphorus on the *box*. Such matches ignited only when rubbed on the specially prepared surface, or 'rubber,' on the side of the box. Lundström's process was patented in England in 1855 by F. May, of Bryant and May, and since that date 'patent safety matches' have been largely and increasingly manufactured in Great Britain (*cf.* p. 421). Matches on the same principle were made, soon after Lundström's invention, by Coignet & Co., by Fürth, of Schüttenhofen, and other continental manufacturers. In the 'allumettes androgynes' of Bombes Devilliers and Dalemagne (1859), the red phosphorus composition was at one end of the splint and the potassium chlorate at the other. The splints were broken, and the ends rubbed together. Field (1882) adopted a similar plan. The Swedish safety matches, so largely imported into this country, are on Lundström's principle. There have been comparatively few attempts to improve upon the safety match. Herz (1894) and Thimann (1894) worked in this direction. Viebig (1895) proposed to coat the heads of safety matches with a layer of the rubbing composition, or with a 'strike-anywhere' paste; and Craveri (1897), also Engl (1903), described safety compositions and rubbing surfaces therefor. It is common knowledge that some safety matches can be ignited, without the aid of an especial rubber, by friction—with a swift, sweeping movement—against a smooth, even surface, such as glass, polished oak or ebony, slate, &c.

A further step was taken in 1857 by Canouil, and by Hochstätter, of Darmstadt, in the production of '*non-poisonous safety matches*,' neither the igniting nor the friction compositions of which contained any variety of phosphorus. In Hochstätter's matches the oxygen compounds used were potassium chlorate, potassium dichromate, lead dioxide, &c., and the phosphorus was replaced by a mixture of antimony oxysulphide and flowers of sulphur. The oxidisable ingredients of Canouil's compositions, where stated, consisted of sulphur, iron pyrites, and various cyanogen compounds of lead. It is probable that some of the earlier so-called non-phosphoric matches were not altogether free from phosphorus. Vaudaux and Paignon improved upon Canouil's formulæ; and other compositions for non-phosphoric matches were those of Lutz (1858) and Kummer and Günther (Königswalde, Saxony, 1861). Schnell (London, 1861), Palmer (London, 1868), and others used lead thiosulphate, recommended by Wiederhold in 1861. Mayer (1865), C. Liebig, and Palmer (1869), also produced friction matches, containing, respectively, antimony sulphide and lead cyanide (Mayer), antimony sulphide and nitromannite (Liebig), and iron thiosulphate (Palmer), in place of lead thiosulphate. Jettel, in 1869, suggested the use of basic lead picrate. (Wiederhold had already tried potassium picrate.) Later, in 1879, L. Wagner, of Mühlheim, patented a match containing lead thiosulphate, antimony sulphide, sulphur, and finely powdered charcoal. Again, in 1881 and 1884, Schwarz, of Gratz, patented compositions containing lead thiocyanate, and lead sulphide in place—partly or entirely—of antimony sulphide. Among other substances proposed as ingredients of non-phosphoric safety match compositions are the thiosulphates of copper and sodium (R. Peltzer); copper thiocyanate, lead chlorate, finely divided metallic sodium (Fleck, 1868); and barium chromate (Garber, 1888).

Most of the compositions for non-phosphoric matches have been described by their inventors as 'ignitable by friction on *ordinary* surfaces'; in some instances, however, a special rubber was necessary. Many of the earlier non-phosphoric friction matches inflamed on ordinary surfaces with great difficulty; others ignited with almost explosive violence, and most were very hygroscopic. The vapours of lead, cyanogen, and thiocyanogen compounds, evolved during the manufacture and ignition of such matches, were probably in some cases injurious.

The more notable compositions for non-phosphoric 'strike-anywhere' matches, as now made, will next be described.

Among the various substitutes for white phosphorus, used of late years in strike-anywhere matches, phosphorus sesquisulphide undoubtedly holds the first place. Discovered by G. Lemoine in 1864, this compound was introduced in 1898 for match manufacturing purposes by H. Sévène and E. D. Cahen, of Paris. Having regard to present conditions, it is, in the opinion of practical match-makers whom the writer has questioned on the subject, unquestionably the best substitute for ordinary phosphorus so far discovered. It is non-poisonous, yields no injurious vapours during the operations in the factory, is reasonable in price, and the matches made with it are as sensitive as can be desired. Phosphorus sesquisulphide is a yellow powder, soluble in carbon disulphide, and inflames in air at 98°–99°C. This compound was at first adopted in 1898 by the French Government; it is used for 95 p.c. of the strike-anywhere matches manufactured in this country, and is becoming largely employed in the United States (*cf.* p. 412). On the Continent, also, phosphorus sesquisulphide is by most manufacturers preferred to other phosphorus substitutes.

Another ingredient, used in this country to a limited extent, is 'scarlet phosphorus,' or 'bright-red phosphorus,' patented in 1902 by W. Muir and C. R. E. Bell. This 'bright-red allotropic form of phosphorus,' which Schenk first prepared by boiling a solution of ordinary phosphorus in phosphorus tribromide, is chemically more active than dark-red amorphous phosphorus, inflames at *circa* 170°C., and, like phosphorus sesquisulphide, is claimed to be non-poisonous. About 5 p.c. of the strike-anywhere matches manufactured in the United Kingdom are made with scarlet phosphorus.

Several varieties of light-red amorphous phosphorus are in use abroad; and different compounds or derivatives of phosphorus have been patented or suggested—such as metallic hypophosphites (Bohy, Gallay & Co., 1898); hypophosphites in conjunction with chromium trioxide (Clayton, 1899); hydrides of phosphorus (Wheelwright, 1906 and 1909; Castiglioni, 1907); combinations of phosphorus with proportions of sulphur differing from that present in sesquisulphide (Wheelwright, 1902; Chem. Fab. Griesheim-Elektron, 1902; Huch, 1903; Gartenmeister, 1908); and the supposed suboxide P_4O (Chem. Fab. Greisheim-Elektron, 1903). The last-named company has introduced (D. R. P. 153188, 1902), under the designation 'sulfophosphit,' a product consisting of phosphorus, sulphur, and zinc, very intimately associated together, the basis of the invention being the production of metallic hypothiophosphites and thiophosphites by the union of red phosphorus, sulphur, and metallic sulphides, in theoretical proportions.

Besides the foregoing, inventors have proposed the use of lead thiosulphate, associated with calcium sulphide (Braly, 1897), and with potassium dichromate (Gurowitz and Bals, 1898; Trachsel, 1899); copper thiosulphate (Gans, 1898); tin thiosulphate (Jones and Bates, 1898); antimony thiosulphate (Truillet, 1899); copper thiosulphate and 'thiocyanite' (Rosenthal, 1899); cuprous thiocyanate (Purgotti, 1899); and the like. Craveri (1897) suggested the employment of persulphocyanic acid; and a later dipping-composition prepared by Gans

(1903) contained 'sulfocuprobariumpolythionate.'

Various materials for the stems have been suggested at different times, such as earthenware, pipeclay, bass, cotton or linen stiffened with chalk and gum (Bell, 1859); bone (Letchford, 1867); cardboard and stiffened calico (Cribb and Rackham, 1874); asbestos (Hynam, 1874); jute and glue in a double wire spiral (Byrt, 1882); wood pulp and paraffin (Molyneux, 1889); compressed peat, turf, or moss (Rosenkütter, 1891; Stiemer and Ziegler, 1892); paper (Farrel, 1890; Bowman, 1893); straw (Castner and Swoboda, 1897); straw, rushes, grasses of various kinds, and the like, dipped in solutions of inflammable substances (Carré, 1908); stems of dried leaves of alfa or esparto (Schaefer, 1906), &c., &c. Fredrikson in 1897 and Lärn (1907) used wooden cores for the stems of wax matches. Craveri (1899) proposed as a composition for the tapers a mixture of ceresin, resin, calcium sulphate, zinc oxide, and potassium nitrate. Steedman (1906) patented waxed stems made from single strips of veneer, with one or more threads applied longitudinally, the whole coated by wax; and the present writer has come across Finnish 'superior patent vestas' (of very poor quality), with stems made in a similar way: obviously the same patented method.

The treatment of the wooden stems has also varied greatly. In the early days of match-making the splints were usually dipped in melted sulphur (v. Römer and others), to ensure ready inflammability of the stems; and hot tallow, resin, and wax were sometimes used for the same purpose. Sulphur-dipping is in this country only of historic interest, but sulphur-coated splints are still to be seen occasionally in matches of the cheapest and worst qualities, mostly of continental manufacture. Of the above-named substitutes for sulphur, Böttger (1843) preferred wax, which was also used by Mennons (1857) and others. Later (1861), Letchford introduced the use of melted paraffin or petroleum, also a mixture of paraffin with stearin and Japan wax. Bruce (1863) saturated the stems with potassium nitrate by immersing them in a boiling solution of that salt. In 1891, Bell proposed the use of coloured paraffin. Match-stems have occasionally been impregnated with camphor. In 1867 resin was again applied by Letchford, and Grawitz (1873) used naphthalene instead of sulphur. Mapple (1881) preferred oil or tallow. Paraffin is now almost everywhere used.

Another method of treating the stems is widely adopted at the present time in Great Britain and abroad, especially for safety matches. It consists in impregnating the stems with solutions which have the effect of preventing the wood from burning or remaining red-hot. Stems so prepared become cool almost instantaneously, and do not readily break; there is thus less chance of the heads and fragments of the splints falling and giving rise to fires—a risk commonly present with the thin badly-cut splints (not so treated) of the cheaper sorts of foreign matches. To render the stems uninflammable, solutions of sodium phosphate, sodium tungstate, zinc sulphate, alum, ammonium sulphate, and magnesium sulphate have been used. Field (1879) employed solutions of phosphoric acid, ammonium phosphate, borax and ammonium phosphate together, or boracic acid and ammonium phosphate; Percival (1887) proposed the use of 'cyanite' for the end held in the hand, the body of the match being impregnated with a 'weak gummy varnish' to prevent the embers from falling about; and Louisa A. Thomas (1896) suggested the employment of sodium silicate.

F. Gerken and G. Goliasch (1883) affixed small friction-tablets to the stems, so that when a match was withdrawn from the case its head came in contact with the roughened surface on the stem of an adjacent match, and in this manner was inflamed. The proposals of Galy (1908) and Walsh (1908) were not altogether dissimilar. The last-named inserted the striking composition in a notch in the stem of the match.

Tubes, to hold a single match, have been so constructed that the match on withdrawal is inflamed by friction of the head against striking composition lining one end of the tube. The other end is closed. An allied device is a tube open at both ends, and on finger-pressure being applied to the match-stem projecting at one end, the head of the match is pushed past the striking composition lining the other end; on coming into the air directly afterwards it is inflamed.

To render match-stems waterproof, collodion, resinous varnishes, and caoutchouc solutions have been employed.

Headless matches have been suggested by Simonet (1893), Neuberg (1897), Fog and Kirschner (1898–9), Budde (1900), and Haffner (1907). Matches tipped at both ends were proposed by Scarlett (1891), Aldridge (1899), Potts (1901), and Nicolay (1904). 'Double-tip' matches, an important modern invention, are described further on.

The development of the machinery used in match-making has more than kept pace with the improvements in the compositions and in the treatment of the stems. Continuous and automatic machines will be described in the portion of this article devoted to details of the manufacturing operations.

Some remarks may now be made about vestas and fusees.

Vestas.—The earliest account of the *wax-taper* as a match stem is in the specification of an English patent taken out by W. Newton in 1832; and, according to Payen, matches of this description were first made in France in 1836 by Savaresse and Merckel, of Paris. Wax, however, in conjunction with colophony, was used in 1832 by Siegel, of Vienna, as an easily inflammable coating (in place of sulphur) for the previously carbonised splints of his oxymuriate matches. In 1862 J. Childs recommended a mixture, of high melting-point, of one part of Carnaüba wax with 9 parts of paraffin; in 1866 Letchford substituted jute for cotton in the tapers; and J. G. Gomez and P. Franco (1889) used strips of Bristol board, immersed in a mixture of resin, stearin, zinc-white, &c. Baron (1896) recommended wood-fibre. Hathaway (1897), Scott (1899), Glenister (1907), and others have employed paper in strips or coils. The use in the waxed stems of a wooden core has already been mentioned; and pine-wood sticks are very largely taking the place of wax tapers for this class of match. Wax vestas have been sold in metal cases containing sand-paper so folded that, on the withdrawal of a vesta, its head is inflamed by friction against the sand-paper, the act of withdrawal thus igniting the match.

Fusees, &c.—Cigar lighters—of brown paper, cardboard, German tinder and the like—impregnated with a solution of nitre, often scented, and tipped with various igniting compositions, mostly phosphoric, were made by Siegel (1832, 1835), v. Römer, and others. Of the newer kinds of cigar-lighters, variously known as 'flaming vesuvians,' 'etnas,' 'fixed stars,' 'braided lights,' &c., consisting generally of three parts—a stem of wood or glass, a head or ball of 'pastille' composition, and a tip of igniting composition—one of the first was described in 1849 by J. Palmer. Grimes (1859) introduced wires into the composition-ends of his splints, to prevent the heads from falling off when pressed against the cigar or pipe. Bell & Black (1859) made the stems of wire, coated with a non-conducting composition, such as gum and whiting, or glue and whiting or flour. Simlick (1862) put the composition on a tube fitted on to the end of the splint, and preferred glass. He also (1863) tried stems of slag and powdered oyster-shell, mixed into a paste and calcined; and wire covered with thread or cotton, dipped in coloured liquid gum. Battcock (1863) made stems of stone and slate; and Barker, in the same year, used pipeclay stems, tipped at each end. Ford (1878) softened the splints by treatment with caustic potash or soda, and then subjected them to the action of a solution containing 10 parts of nitre, 1 part of potassium chlorate, and 1 part of sugar in 12 parts of water: this process of course rendered the wood highly combustible. Methods of treating the wooden stems with alkaline and other solutions were patented by the Aktieselskabet 'Progress' (1902), and in the previous year by A. G. Haehre. Evans (1882) rendered the stems of his vesuvians incombustible, by the use either of asbestos paint or of sodium tungstate solution. The invention of A. Hill (1904) was similar. G. A. Sweetser (1884) formed his stems of plastic material moulded into the required shape and size round a core. In the 'braided' lights, still manufactured to a small extent by Bryant & May, and J. Palmer & Son, the composition is retained in position by pieces of thin wire, over which strands of cotton are twisted by the braiding machine. T. J. Clanchy, in 1868, obtained provisional protection for a combined match and fusee, consisting of a shaft or stem with a fusee-head at one end and a match-head at the other. In 1885 R. Bell, proceeding on closely similar lines, introduced the 'fusee vestas,' or wax-stemmed vesuvians, in which the essential parts of a vesuvian are present, but the stem was of jute, hemp, flax, cotton, or a mixture of some of these fibres, coated with paraffin, wax, or stearin. According to another patent of the same year, this inventor introduced a wire core into the stems; and in 1886, C. R. E. Bell devised a hollow cylinder or bead of combustible material, to be sold separately, for application to a match or vesta, for use in a light wind. J. J. Williams (1895) had a somewhat similar idea. Salts of strontium and barium have sometimes been introduced into the compositions of vesuvians, to cause them to burn with coloured flames.

Vesuvians have been almost entirely superseded in this country by vestas with pine-wood stems (such as the 'Swan' vestas, introduced by Bryant & May), and in America by the 'double-tip' match, invented in 1905 by the Saginaw Match Company. There is also a considerable production of matches with cardboard stems, somewhat upon the lines of the earlier 'fusees.' The 'book-matches,' made by Bryant & May, are of this type; two layers, stitched together, of flat, cardboard-stemmed matches, united by the base, are contained in a thin pasteboard case, with a red phosphorus striking surface on the exterior. These matches are of the safety class.

Repeating or continuous matches have been invented, but have never had much sale. The earliest English patent of this kind was that of Dove (1862), in which the igniting composition was attached at intervals to a continuous band or strip of material, inclosed in a box. Later devices of similar nature were those of Tylor (1865); Rogers (1869); Perkins (1869), who mixed the igniting composition with collodion, a strip so composed fitting into a case like a pencil case, from which it could be withdrawn at will; Samuel (1871); Jonas (agent, Pollet, 1878); and Klein, same year.

Cigar-lighting appliances of a special kind. Many instantaneous igniters, not matches, have been invented for the convenience of smokers. These contrivances, though numerous, have not interfered with the steady development and increase of the match industry; and a few types only of such inventions will be mentioned. Among the earliest were the 'D'Bleaml'n Cigarrenzünder,' cigar-lighters, made by Pollak, of Vienna. This appliance consisted of a small, nitre-steeped, variously coloured, artificial flower, the stalk of which was inserted in a cigar. A little boss of igniting composition in the centre of the flower was inflamed by friction. An alloy of the metals sodium and potassium has been used. A small quantity of the alloy is withdrawn from a case or tube by a wire, which is then rubbed across and ignites a charred wick (1887 and 1888). Another appliance is simply a pocket edition of the old flint, steel, and tinder-box. A fourth device (W. D. Borland, 1889) is an attachment to cigars or cigarettes, by which they are easily lighted, even in a high wind. A minute portion of nitrocellulose fabric, forming a ring round the cigarette, is inserted under the paper, and on applying a spark the material takes fire and slowly smoulders until the whole end is glowing.

Automatic igniters in which is used an alloy of cerium are now extensively sold in France, and to a smaller extent in this country.

Statistics and Legislation. According to the Census of Production, 1907, the total value of the output of matches of all kinds, including wax tapers, vesuvians, braided lights, &c., of British manufacture, was in 1907, £775,000. The value of the exports of matches of United Kingdom manufacture amounted in 1907 to £76,000, or about one-tenth of the output. The annual output of one British company alone, Bryant & May, is at present not less than about eight million gross of boxes.

The consumption in Great Britain and Ireland of *all* matches amounted in 1910 to about 17¼ million gross of boxes. In 1910 the matches consumed would appear to have been practically half British and half foreign. Safety matches have greatly increased in popularity. Whereas in 1899 about 18 p.c. of the matches consumed were safety, and 82 p.c. strike-anywhere, in 1910 the proportions were nearer 37 p.c. safety and 63 p.c. strike-anywhere. Vesuvians are almost obsolete, but *small* quantities of braided lights and flaming vesuvians are still made. Swan vestas, with pine-wood stems, introduced by Bryant & May, have virtually supplanted vesuvians, and have considerably reduced the consumption of wax vestas.

The value of *all* matches (British and foreign together) consumed in Great Britain and Ireland in 1910 may be computed at about £1,293,750. Assuming that 17¼ million gross of boxes, each containing, say, sixty matches, were so consumed, and taking the population of the United Kingdom at 45·2 millions (Census of 1911), this consumption would be equal to about nine matches per day per head of the population.

In the United States of America, there are said to be manufactured 250,000 million matches per annum. Assuming a census of 76·3 millions this is equivalent to nearly nine matches a day *per caput*.

At the present date (June, 1911) there are in Great Britain and Ireland eleven match factories. By far the largest and the most modern are those of Bryant & May, Limited, at Liverpool and Bow, London, E.

In Russia there are stated to be 49 factories, in Sweden 10, in Norway 2, in Belgium 14, in Germany 75, in Austria-Hungary (originally the chief centre of the European match industry) 10, and in France 7. The most important Swedish factories are those of the Jönköpings och Vulcans Tändsticksfabriks Aktiebolag, at Jönköping and Tidaholm, Uddevalla, Wenersborg and Anneberg, and these may be regarded as among the best-equipped of European match works. The total value of Swedish matches exported from that country was in 1902, £432,000, and in 1903 £466,000. Among the principal German factories are those of Stahl & Nölke, at Cassel and Kostheim a./M., the Deutsche Zundholzfabriks Aktien-Gesellschaft, at Lattenburg, Rheinaubaden and Vordamm, of the 'Union' Aktiengesellschaft, at Augsburg and Habelschwerdt, Ulm, Göppingen, and elsewhere, and of C. Grübel, at Habelschwerdt. The French factories, which are under the direct control and supervision of the Government, the manufacture of matches having been a State monopoly since 1890, are at Pantin and Aubervilliers (both near Paris), Marseilles, Bégles (Bordeaux), Aix-en-Provence, Saintines (Oise), and Trélazé (Angers). The total receipts of the monopoly in 1904 were £1,423,000, the profits being £1,048,000. Official estimates gave the receipts in 1905 as £1,427,000, with profits slightly exceeding those of 1904. In the United States there are 19 companies and firms and 16 factories, including the Diamond Match Company's five works in New York, Michigan, Ohio, California, and Wisconsin. The Diamond Match Company is by far the largest and most influential American company, and its output is probably about 75 p.c. of the entire production.

By the international treaty of Berne, 1906, most of the countries of Europe have bound themselves to enforce within their territories the prohibition of the use of white or yellow phosphorus. The importation and sale of matches containing ordinary phosphorus are entirely prohibited in Great Britain and her Crown colonies (since 1908); in Germany, France and her colonies, Austria, the Netherlands and the Dutch Indies, Luxemburg, Finland, Italy, Spain, and Switzerland (since 1906); and in Denmark (since 1875). In Australia the importation is forbidden. Similar prohibition may eventually be enforced in Canada, where a White Phosphorus Prohibition Bill has recently been introduced. In Norway and Sweden, the use of white or yellow phosphorus is forbidden in the manufacture of matches for home consumption, but not in making matches for export trade. As the outcome of the Conferences at Berne, in 1905 and 1906, of representatives of most European Governments, the British Legislature on Dec. 21, 1908, passed the 'White Phosphorus Matches Prohibition Act' (8 Edward VII., 1908, ch. 42), which has been in operation since January 1, 1910. With one exception, the countries which have not yet forbidden the use of white or yellow phosphorus in the manufacture of matches, namely Russia, Japan, Belgium, Hungary, and the United States of America, have passed very stringent laws regulating the operations and arrangements in the factories. Only in the United States is there no legislation relating to the manufacture or use of matches made with white or yellow phosphorus. The extremely sensitive and readily ignitable double-tip match of recent introduction, which in America is superseding the 'parlour' match (the ordinary paraffin-dipped strike-anywhere match), is stated to contain as much as 20 p.c. of white or yellow phosphorus, and in the course of manufacture this match is alleged to generate 40–50 p.c. more phosphorus oxide vapour than the ordinary match. The stringent regulations in European countries, previously to the entire prohibition of white phosphorus, kept down the quantity used to 6 or 7 p.c. (Denmark 10 p.c.); but American match manufacturers are now said to be using for their compositions from 14 to 20 p.c. The humidity and warmth of the American climate, increase the danger to the workers.

The President of the United States recommended the imposition of a heavy Federal tax in order to discourage the use of white phosphorus, and the Diamond Match Company have voluntarily surrendered their patent rights for the use of tetraphosphorus trisulphide, so that any match manufacturer in the United States is free to use this compound.

Great Britain's exports of matches to foreign countries are smaller than formerly, and even her Colonial trade has diminished. Notwithstanding excessive competition, the home trade is, nevertheless, very large.

As regards the quantities of phosphorus used in the match industry, there are not at the present time any figures available. Probably about 40–50 tons per annum were used in the British Isles over the 15 years prior to 1890. The relative quantities consumed of the two substances now used in this country in the manufacture of strike-anywhere matches, namely, phosphorus sesquisulphide and scarlet phosphorus, are about 95 and 5 p.c. respectively.

MANUFACTURE.

Probably the best way of conveying an idea of twentieth-century methods of manufacturing matches will be to begin by describing the operations as they are conducted in the most extensive and modern match works in this country—the factories in London and Liverpool of Bryant & May, Limited, who are, as already stated, the largest British makers, and among the largest in the world. The operations so described may be regarded as typical of the work as now carried on under the latest and most advantageous conditions. Some account will then be given of the manufacture as conducted upon a smaller scale, and of the more noteworthy differences and modifications in the machinery used, or processes followed, in other British, and—so far as space permits—in the more important foreign, match works.

The manufacture may be considered under the following heads: (1) *Ordinary matches*:—the nature of the wood used; making the match-sticks, or splints, and boxes; making and packing the matches; (2) *Wax matches*:—making the tapers; making and packing the matches; (3) *Safety matches*; (4) *Vesuvians*, (5) '*book-matches*,' and (6) '*double-tip*' matches.

1. Ordinary matches. *Nature of the wood used.*—There is considerable variety in this. Pine, aspen, spruce, fir, poplar, lime, willow, and beech-wood are used. Alder- and cedar-wood have also been employed. Aspen, and poplar-woods are imported into this country mostly from Russia (Riga, Libau, Windau, and St. Petersburg); pine, spruce, and fir from Canada and the United States of America. There is an increasing scarcity of timber, especially of pine-wood. For British matches, the splints formerly were chiefly, and still are largely, manufactured from pine-wood: aspen, poplar, and other woods have long been used for this purpose by continental makers. Aspen-wood for match manufacturers' requirements must be free from pith and knots; and stems from 10 to 20 inches in diameter are the most serviceable. Rafted aspen is less satisfactory than unrafted. Eventually in this country, aspen-wood, which is already used for match-boxes, may in a great degree supplant pine-wood. Already, aspen-wood sticks, imported in wooden cases holding about 1,000,000 ready-cut splints, are in use by some manufacturers. Spruce-wood is employed for the packing cases, planed and dovetailed boards for which are shipped to this country from Quebec. Canadian pine-wood splints for the larger square matches are now cut in the Dominion, and imported to this country; later on, they will be cut here.

Making the boxes and splints.—Although some of the smaller match-makers, here and in parts of the Continent, still use boxes made, or put together, by workpeople in their homes, a highly important and prominent department in the leading manufactories of Great Britain, America, and continental Europe, is that devoted to match-box making by machinery. The operations, both for box-making and splint-cutting, begin with 'cross-cutting,' by a circular saw, of the 7-feet long aspen-logs into 26-inch lengths. These are barked by hand, taken to the 'log-peeling-' or 'skillet-' (squelette) room, and placed in a species of lathe, the '*peeling-*' or *veneer-cutting* machine, made by A. Roller of Berlin (Fig. 1), in which they revolve against a horizontal planing knife acting upon the entire length of the log. A veneer is thus cut from the log, as wide as the rotating wood is long, and of a thickness which depends upon circumstances.

FIG. 1.

Log-peeling or veneer-cutting machine.

(*a*) *Splints.*—If the veneers be required for the production of splints, the machine is adjusted so that they are 2·3 mm. thick: if the thinner veneers, used for wooden match-boxes, are desired, the thickness is about $\frac{18}{1000}$ of an inch. Cutters, placed slightly above the planing knife, divide the veneers into narrow bands (=the length of a match), or wider bands (for box-work), as required. In the former case, the narrow bands, divided into convenient lengths and superimposed into piles of 70 or 80 veneers together, are passed under an alternately rising and falling knife, in a guillotine machine constructed by Roller, which cuts them into square or rectangular splints. These fall into a hopper, from which by a cyclone fan they are blown along a pipe into another building, where they are 'impregnated' with an acid ammonium phosphate solution and then dried in a revolving cylinder heated by a coke furnace, capable of drying 40,000,000 splints per day of 10 hours. Next, they are cycloned back to the peeling-room, where they are 'cleaned' in a Roller's '*splint-cleaning*' machine, 'straightened' in a '*straightening*' machine, and packed in trays ready to be fed to the *match-machine*. During both the cleaning and straightening operations, the splints are subjected to a 'jogging' or oscillating motion. This description of splint-making applies only to the smaller rectangular splints, of aspen-wood. The stouter and longer square match-sticks, used for the large ordinary and safety matches, are at present cut from Canadian pine-wood. The blocks are sawn from a deal, and fed into the hopper of a machine of the company's own construction, which cuts by means of lancets set horizontally, instead of vertically. These splints, after impregnation, are dried, not by the cylinder method, but by drying-chamber process. Eventually the larger match-sticks will be made at Bow, as already stated. There are two other kinds of wooden match-splints: round-sticks and grooved-sticks. But as these are cut actually in the match machines, an account of the process will be given when those machines are described.

(*b*) *Boxes.*—The thin veneers, intended for the boxes, are wider than those for splints, but they are produced by the peeling-machines in the manner already detailed, the wood being simultaneously scored in readiness to be folded by the box-making machine. They are then guillotined into sizes suitable for the insides and covers of boxes, and the edges of these 'skillets,' where the wood is not covered by the labels, are hand-dipped in pink dye by boys. The skillets for the 'cases,' 'covers,' 'outers,' or (as they are sometimes uneuphoniously called in America) '*shucks*,' are next folded up, pasted and labelled by '*outer*' box-machines, of which there is a row on each side of an endless band or conveyer, carrying the box-covers onwards to a drying chamber. The 'inners,' or drawers of the boxes, are made by Arehn's drawer-making or '*inner*' machines (Lundgren's patent), which fold up the skillets, paste, and paper-coat the drawers, and similarly feed them on to a carrier, by which they are transported to a drying chamber. Fig. 2 shows some of the box-making machines. The next step is the application of sand to the 'outers' by the 'sanding-machine' or '*sander*.' The 'inners' are put into the 'outers' by a machine called in the works a '*nester*.' In one room of one of the factories there are about 120 wooden-box machines. Thicker skillets are by some manufacturers used for penny vesta boxes, and these are cut from spruce-wood by an ordinary 'flaking' machine (Day's): but spruce is becoming scarce, and will probably be discarded for the purpose.

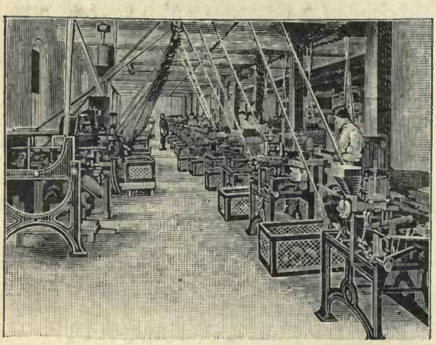


FIG. 2.
Wooden box-making machines.

Cardboard box-making.—The 'outers' of some strawboard boxes, are made by a machine which cuts and scores the cardboard for folding, pastes, and folds it into the form of a flattened tube, prints it above and beneath, glues and sands one side, cuts off the proper lengths, and ejects the finished cases at the rate of 1000 per minute. The insides are made by an equally ingenious machine which cuts out the pieces of cardboard, scores, folds up, glues the ends, and conveys the completed 'inners' in links of a travelling chain until they are dry and ready for filling. A cardboard box-room is shown in Fig. 3. In one room at Liverpool there are 150 cardboard box-machines. The cardboard 'outers' of some boxes for vestas (pine-wood and other) are made by hand, but the flaps and tabs are affixed by machinery of Bryant & May's construction. The 'inners,' of chip-wood, are machine-made, as above described.

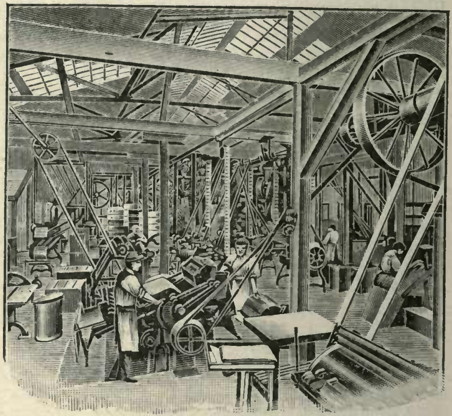


FIG. 3.
Cardboard box-room.

Metal box making.—The metal match-boxes used for 'knapsack' matches are made at Liverpool by a machine invented by Carbone.

THE MANUFACTURE OF WOODEN MATCHES.

A. By continuous and automatic machinery. In one form of match machine, used by Messrs. Bryant & May, the ready-cut square splints are fed into a hopper near the front of the machine, 'jogged,' and pushed by plungers into apertures in the iron match-plates, or carrier-plates, composing an endless chain about 700 feet long. The chain conveys the splints in enormous numbers, tips downwards, over a hot plate, then through a steam-heated bath of melted paraffin wax (m.p. 102°–105°F.), temperature *c.* 220°F., next over the dipping-roller, which revolves in a trough or vat charged with the match composition, and finally over a great series of drums or carrier-wheels. The period occupied by this is about an hour, and during the passage over the carrier-wheels the matches are dried by the currents of air to which they are freely exposed. There are 100 matches in each row on a match-plate. Having traversed the carrier-wheels, the dry and finished matches arrive near the starting-point, are ejected by plungers from the holes in the match-plates, and are filled into boxes by a '*box-filling* machine,' manufactured by the Diamond Match Company. This machine neatly and regularly deposits the matches in the drawers or insides of the boxes (to which a shaking motion is given, so that the drawers become filled, and there are no spaces left); sheaths the drawers in the covers; and passes the completed boxes along an endless band to an Arehn's *packing* or *wrapping* machine (Lundgren's patent), by which they are put up in the familiar 'dozen-packets.' Eight girls attend to a match machine; and the daily output of one machine is 1000 gross of boxes, averaging about 60 matches to a box=8,640,000 matches *per diem.* The machinery is continuous in its production, and automatic, from the feeding in of the match-sticks to the wrapping of the dozen-packets, which girls put up into gross parcels by hand. The gross parcels are packed in the Canadian spruce-wood cases, which are nailed together at the factories by an automatic nailing machine (W. S. Doig's patent).

The machines so far described yield square matches. But Messrs. Bryant & May use other match machines, also continuous and automatic, called *grooved-stick* machines. These yield matches with pine-wood stems, nearly circular, but scored longitudinally by two grooves, so that the stems are of the section shown in the figure (Fig. 4). A machine of this kind cuts its own match-sticks from pine blocks, $1\frac{7}{8}$ inches deep, fed in horizontally, but at an angle of 17° with the front of the machine. The match sticks are cut from the blocks by dies which act on the downward stroke, leaving the splints sticking up, to be grasped by their upper ends in the apertures of carrier-plates composing a conveyer-chain, just as in the machines last described. The match sticks, bristling from the under surface of the endless chain, pass successively over a hot plate, paraffin-bath, dipping-roller, and series of carrier-wheels, returning to the forepart of the machine, where the finished matches are discharged, and filled into the drawers or 'inners' of cardboard boxes fed to the filling apparatus by hand. Thence the filled drawers are passed along in a continuous stream to a revolving circular table, where sit six or eight girls to receive and sheath them in the cases, also to add a few matches to boxes not completely filled. Fifteen workers attend to a machine, and each machine produces 800 gross of boxes of matches (averaging 55 matches to a box) in a day of ten hours. The yield of matches per minute may be estimated at 12,000. One girl can feed the machine with 106 boxes a minute, or nearly two boxes a second. From the splint-cutting station of this match machine an exhaust fan draws out wood-dust and imperfect sticks, and conveys them by a pipe to the boiler-house.

FIG. 4.

Section of a 'grooved stick.'

The *round-stick* machines, which produce the circular-stemmed, pine-wood 'Swan' vestas, punch out round splints, but are constructed similarly to, and upon just the same principles as, the grooved-stick machines. Blocks of pine-wood are fed in; finished matches come out, and are automatically filled into the 'inners,' the final operations of 'boxing' being performed by eight girls stationed at a revolving circular table. Dust and imperfect splints are removed in the manner already described. One of these round-stick machines can turn out about 3,000,000 vestas *per diem.*

Larger-sized matches.—For the production of the larger-sized strike-anywhere matches and safety matches, with square sticks $2\frac{1}{4}$ inches long, the continuous and automatic machinery is of exactly the same kind as that used for the matches of 'minik' size, with sticks $1\frac{7}{8}$ inch long. The single-length splints (there is now no 'halving') are fed into the receptacle or hopper of the machine, and the finished matches are deposited in the drawers of the boxes by the filling apparatus previously mentioned. The drawers pass along a channel on to a circular table, where the cases or covers are put on by hand. The productive capacity of one of these machines may be estimated at 6,960,000 matches per day of ten hours. [*v.* Amer. Pat. 389435, 1888 (E. B. Beecher); and Eng. Pats. 20786, 1894 (E. B. Beecher and J. P. Wright); 17022, 1896 (J. P. Wright).]

Fig. 5 gives an idea of the general appearance of a match machine; Fig. 6 shows one of the machines at first installed, in greater detail and on a larger scale; and Fig. 7 shows a machine-room with its range of automatic machines.

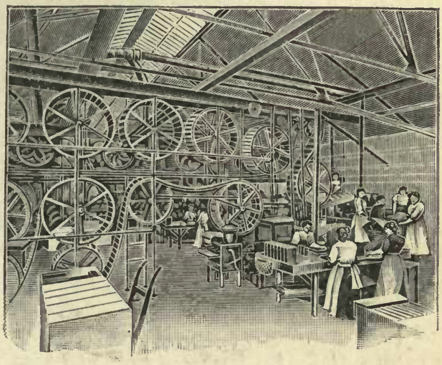


FIG. 5.

A match machine.

The adoption of automatic machinery has wrought so great a change in most of the operations of match making, in the conditions under which they are performed, and in the rate and amount of the output, that to describe the present mode of manufacture is virtually to relate the particulars of a new industry. The advantages of the automatic machinery, with the continuous system of manufacture, are enormous. Production is greater, with less labour, than in former days; and the operations are immeasurably more healthy for those engaged. It is scarcely an exaggeration to state that hand labour has been almost entirely eliminated from the actual manufacturing processes. Three or four workers now produce as much as 15 or 20 under the old conditions.

Examples of other forms of automatic match machines are Lagerman's machine, used at Jönköping (described on page 417, and Figs. 9 and 10), and Roller's. The last-named is constructed upon the same general principles as the match machines already described, but it is of smaller dimensions and capacity. This type of machine is used at Messrs. J. Palmer & Son's, Maguire Miller & Co's, W. J. Morgan & Co.'s, R. Bell & Co.'s, and Paterson & Co.'s, factories, for

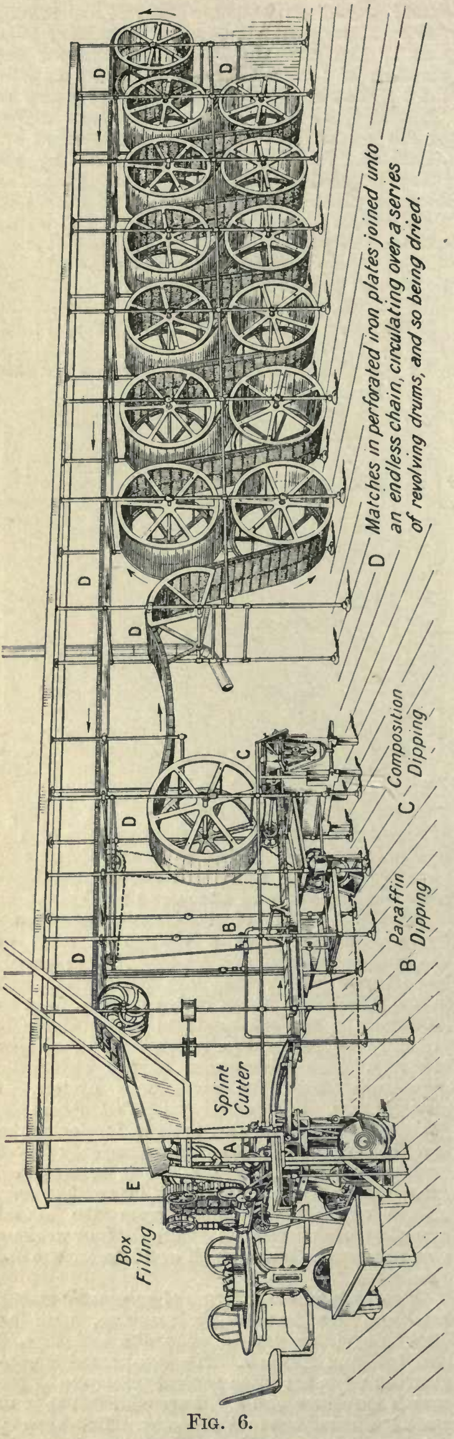


FIG. 6.
A match machine.

the manufacture of products such as the minik-sized 'Our Flag' matches, and the like. Ready-cut, single-length splints of aspen-wood are fed into the hopper of the machine; pushed into apertures—150 in a row—in an endless chain; paraffined; dipped; dried by passing over a series of drums; discharged or 'racked out,' and filled into the box 'inners.' These are sheathed in the covers by four workers. There are seven girls to a machine. Roller's and Arehn's wood box-making appliances are employed at Messrs. Palmer's factory for the ordinary boxes, one girl working each machine. Aspen-wood is planed into the thin box-veneers by a Roller's log-peeling machine, already described and figured; but the thicker veneers, used for penny vesta boxes, are at present cut from spruce-wood by a flaking machine (Day's).

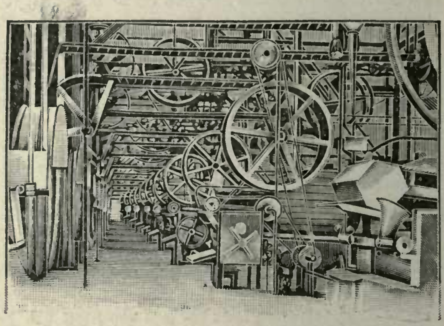


FIG. 7.
A match machine-room.

Besides the match machines described, there are other continuous and automatic machines, of which the 'Ideal,' made and supplied by Messrs. Sebold, of Durlach, Germany, is an example. An extensive trial, and with more or less success, has been made of this machine, recently, by S. J. Morland & Sons, of Gloucester.

Preparation of the Dipping Composition.

Almost every maker has his own especial composition and way of preparing it. But the mixtures in use for ordinary matches invariably contain—(1) an *oxidisable body* in a fine state of division, and intimately mixed with (2) *oxidising agents*; (3) *cementing* or *binding materials*; (4) certain chemically *inert bodies* added to increase friction; and (5) *colouring matters*. In strike-anywhere matches, the oxidisable or combustible body in general use is tetraphosphorus trisulphide. Other combustible ingredients are employed, mostly abroad. The more important have been mentioned (pp. 409–410). The oxidising agents principally employed are potassium chlorate, potassium nitrate, lead nitrate, minium, manganese dioxide, and lead peroxide: potassium dichromate, 'oxidised minium' (made by heating minium with nitric acid), ferric oxide, and litharge must also be mentioned. In English matches, potassium chlorate is the customary oxidising agent, used alone or with manganese dioxide, &c. Potassium nitrate is frequently present in continental matches. Glue, gum, gelatin, and dextrin are the binding media mostly used: in Great Britain, glue is almost exclusively employed. Very much depends on the quality of the glue, and its drying properties. Powdered glass, chalk, gypsum, and fine sand are among the indifferent bodies added. Prussian blue, ultramarine, smalt, vermilion, chrome yellow, and coal-tar dyes are used to colour the mixtures.

Excepting that phosphorus sesquisulphide is now in general use, and that coarsely crushed glue is preferred to glue in large pieces or cakes, there is not much that is new to relate about the operations in the composition mixing-room. There are, of course, numerous minor differences in the methods of mixing the ingredients of an igniting paste; but the guiding principles usually are that the oxidisable body is first mixed with a portion of the inert substances, and with part of the glue or other binding medium, previously dissolved in water, and that the oxidising substance or substances must be mixed separately in another vessel, with the remainder of the glue, &c. Each mixture is passed through a mill, after which the two sections are combined and the whole mass is milled. All quantities are weighed and checked, and proper precautions are taken to avoid 'firing.' Fig. 8 shows a composition mixing-room of the latest type. Some additional particulars, especially with regard to older methods of working, will be found on pp. 422–424. The other operations, paraffining, dipping, drying, discharging, box-filling, and packing, by automatic machinery, have already been described.

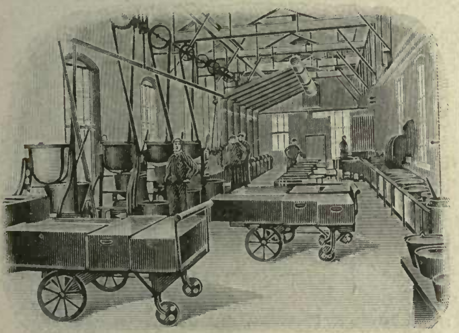


Fig. 8.

Composition mixing-room Liverpool.

The Manufacture of Matches abroad.

Sweden.—The most important Swedish match manufactories are those belonging to the Jönköpings och Vulcans Tändsticksfabriks Aktiebolag. The Jönköping works of this company are particularly well provided with labour-saving machinery, much of it the invention of the former chief engineer, the late Mr. Alexander Lagerman. These mechanical appliances for saving manual work have been in use for a considerable number of years, and include continuous machinery for paraffining, dipping, drying, and discharging the matches, machines for box-filling, 'sanding' or 'coating' machines, and wrapping machines. The writer is indebted to Chamberlain Berndt Hay, the general manager of the company, for the following particulars of the continuous machines at present in use at Jönköping.

The match sticks, cut and dried, are placed in magazines on the front top of the machine, whence the splints are pushed out into 'perforated wooden frames, moving upwards on endless chains.' The frames, holding the sticks at one-third of their length by means of springs, are brought along, one by one dipped in melted paraffin wax, and then in the strike-anywhere or safety-composition, as the case may be. After passing a 10-metre track, to dry the match heads, the frames return to the front bottom part of the machine, where the matches are discharged, apportioned off, and filled into the empty boxes brought to this part of the machine on a transporting chain, consisting of small iron plates. In Fig. 9 is shown some of the Jönköping machinery. A number of these machines are installed at the older of the two Jönköping factories. Fig. 10 shows one of the box-filling machines used at Jönköping. The striking-surfaces, whether of sand, emery, glass, or of a red phosphorus composition, are applied to the sides of the boxes by machinery ('sanding' or 'coating' machines); and the finished boxes are mechanically wrapped in parcels of ten or a dozen ('wrapping' machines). One of these machines will pack in a single day, under the management of two girls, a quarter of a million boxes of matches into finished, labelled 'dozen-packages,' thus doing the work of 16 or 17 hand-packers.

The Vulcan Factory, at Tidaholm, is a large, well-equipped match-works, where safety matches (chiefly) are now manufactured on a great scale. Continuous match machines are not in use at the Vulcan works, where no essential change has been made in the character of the plant during the past 12 or 13 years.

Holland. The industry in Holland is of comparatively small dimensions. At Loyens' factory at Breda, a box-filling machine, invented by Paulson, is in use, and is said to be very satisfactory.

Belgium. The principal Belgian factory is that of La Société Caussemille Jne & Cie. et Roche & Cie. (Ghent). Although there have been great improvements in the conditions of the industry during the past few years, Belgium must still be regarded as behind some other countries, in regard to her match-factory legislation, and in the quality of the matches produced.

Germany. The match manufacture is of considerable proportions in Germany, where, besides a great output of safety matches, there is a rapidly increasing use of the strike-anywhere match. The largest German company is the Deutsche Zundholzfabriks Aktien-Gesellschaft, previously mentioned (p. 412). The Aktien-Gesellschaft für Zündwarenfabrikation Stahl & Nölke, also mentioned above (*loc. cit.*), uses aspen-wood for the production of both splints and boxes, the veneers for which are cut in a 'peeling' machine of the usual type. 'Inner' and 'outer' machines, like those already described, are employed to make the boxes, into which the dipped matches are filled by a machine, similar in principle to those in use at Jönköping. The productive capacity of the box-filling or 'boxing' machine is such that, under the superintendence of one girl, it will yield 25,000 filled boxes in 10 hours. After filling, the boxes are coated on the two narrow sides with a striking composition, by conveyance on an endless band between two revolving brushes, supplied with the composition by rotating discs. The boxes are next carried through a drying channel 6 metres long; and, finally, a 'packing' or 'wrapping' machine automatically assembles the boxes in series of ten or twelve, wraps these in paper (cut by the machine from a roll, and properly folded), pastes the folded flaps, and labels the package. The writer is indebted to the Stahl and Nölke Company for some of the foregoing particulars, and for further information relating to the industry in Germany. Other German manufactories have been referred to on p. 412. One of the principal manufacturers of modern types of match-making machinery is A. Roller, of Berlin. A

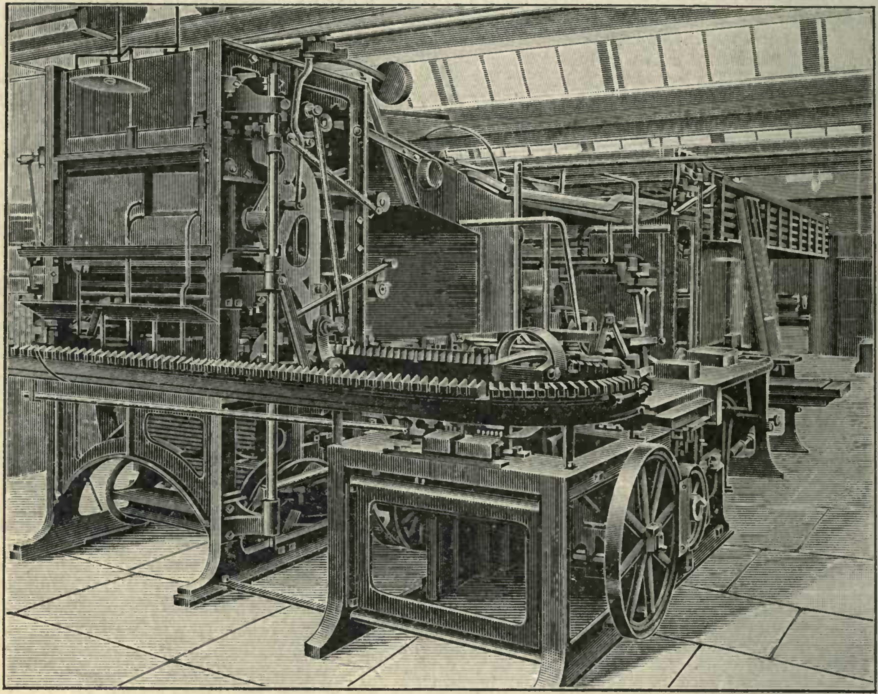


FIG. 9.

Automatic and continuous match machine used at Jönköping. (Inventor, the late A. Lagerman.)

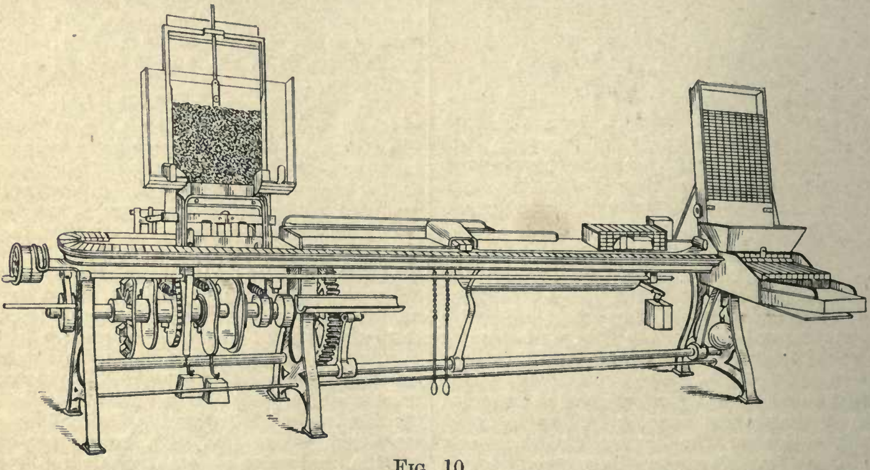


FIG. 10.

Box-filling machine used at Jönköping. (Lagerman's invention.)

large part of the aspen-wood used in Germany is imported from Russia; some, however, comes from native forests. But there is a growing scarcity.

Austria-Hungary. In Austria-Hungary, proably the most important firm, and certainly one of the oldest, is that of Bernard Fürth, at Schüttenhofen, in Bohemia, established in 1838. The founder is stated to have been the first to use red phosphorus as a substitute for white or yellow phosphorus, and in 1854–55 he sent into the market matches with red phosphorus in the rubbing surface on the box—thus adopting a suggestion made by Böttger. These first matches of the safety type were not commercially successful, however, and it was not until in 1855 Lundström improved the invention, that the 'safety match' of the present day became a practical match.

France. The processes and machinery in use at the two chief State factories in France are here briefly described. In the match factory at Aubervilliers, twenty automatic machines, invented by H. Sévène and E. D. Cahen, are employed. One of these machines, worked by only three operatives, can produce in 10 hours 50,000 boxes of 50 finished matches, or about 15 million boxes per annum. For the same output in the old days twenty workers would have been required. The French machinery is constructed upon the same general principles as that already described. Splints, fed into a receptacle by hand, fall from a vibrating hopper into 110 grooves of a horizontal iron plate, to be expelled by a plunger at every stroke of the machine into corresponding grooves of a charger, bridge, or transporting table, having a backward-and-forward motion between the horizontal plate and a vertical part of a long, endless band of carrier plates—the carrier or 'presse.' Each carrier plate is 2½ inches long (in the direction of its journey), 48 inches wide, and is perforated by five rows of equidistant circular holes, 110 in each row. The diameter of an aperture is equal to the side of the square section of a match-stick. When the charger approaches the 'presse,' a plate or 'follower' rises behind the grooves and prevents the sticks from receding. The splints, being longer than the width of the charger, project beyond its edge, and are pushed into the 110 holes of a row in the carrier plate. To prevent bending and breakages of the splints, a horizontal plate presses upon the grooves of the charger, which retreats empty to receive its fresh load. The endless band moves along, bristling with splints, which are carried, over a hot plate, and through a paraffining-bath, secondly, through a sulphur-bath, and thirdly over a rotating grooved cylinder partially immersed in the igniting composition or 'paste.' Thence the conveyer chain travels many yards, for the drying of the matches to be effected; and, finally, at the end of the cycle of operations, plungers expel from the holes the finished matches. These fall, in regulated series, into receptacles, whence pistons fill them into boxes, fed into the machine by an operative, but mechanically opened and shut.

In France, the splints are made of Russian aspen and French willow, the former being preferred. Birch and poplar are used as well. The timber is sawn and cut into splints at Saintines. 'Parlour' and safety matches are largely manufactured at Pantin; wax stems or tapers only at Marseilles.

Norway. The chief match works in Norway is the factory of the Nitedals Tandsticksfabriks, near Christiania. Fig. 11 shows Arehn's box-filling machine (Lundgren's patent) in use at most of the European factories and in many parts of the world.

America. An account has already been given of the present conditions of the industry in the United States of America, and of the Diamond Match Company's machinery, used in the States by that company, as well as in Great Britain by Bryant & May.

Japan. In Japan, a country enjoying at one period a virtual monopoly of the markets in the Far East, there are about 150 factories. Three-fourths of the workers, 25,000 in number, are women. Osaka and Kobé are the centres of the industry. As long ago as 1892 matches ranked fourth among the articles exported from Kobé, and in the following year many new factories were established in Japan, with the result that the output and export of matches enormously increased, and continued to expand until about six years ago. Depression of trade set in, and in 1910 seventeen factories in Kobé and thirteen at Osaka for a while suspended operations, with the result that the output fell off considerably. The most formidable competitors of the Japanese are the Chinese, Swedish, and German manufacturers, who have encroached upon the markets in the Far East. Phosphorus and sulphur matches are manufactured at Osaka; safeties at Kobé. The production of wax matches is almost entirely a household industry. In the year 1909, the total export of matches from Japan amounted to 41,407,083 gross, valued at £1,186,738. During the first half of 1910 there was a decrease of 40 per cent. in the export as compared with the corresponding period in 1909. The leading manufacturers in 1910 had in contemplation the incorporation of the industry into one company, and a monopoly of the export trade of matches from Japan.

China. In 1907 there were three factories in the Canton district: now there are works in Pekin, Hankow, Tientsin, Shanghai, and other towns. The largest works are at Hankow with 3600 operatives.

India. Hitherto the match industry has not prospered in the Indian Empire, but it has been pointed out that the natural advantages of the country, such as plentiful timber, cheap labour, and inexpensive water transport, justify a belief that the prospects of success are good, provided that the industry is developed on proper lines. India might ultimately secure some of the considerable trade of the Persian Gulf, at present enjoyed by Sweden.

2. **Wax matches.** The tapers for these are made as follows: from 60 to 100 strands of cotton, of about 20 threads each, are led from a bale, through a measuring machine and guides arranged at a convenient height, into a steam-jacketed tank, containing a mixture of stearin and gum copal or gum dammar, thence through perforations in a draw-plate, and afterwards over a '*drawing drum*' (Fig. 12), 6–10 feet in

diameter, revolving on an axis, by hand or steam power (Fig. 13).

From this drum the tapers are led back again through the bath to a similar drum on the opposite side of the tank, and by winding alternately from one drum to the other, they are made to pass 6–7 times through the bath, until the cotton has a coating of fat just sufficient to allow it to pass through holes in a suitable gauge plate. The tapers lastly pass through a perforated hot plate, which imparts a polish to the surface, and are again wound on to a drum, from which they are fed to a 'wax-match machine' of the above-described continuous type. In this machine, patented by the Diamond Match Company, the tapers are cut into stems of the usual length, and inserted in spaces (in which they are held in position by brass springs or clips) in the sections of an endless carrier chain. By this they are conveyed over the dipping roller. Of course, neither the steam-heated plate nor the paraffin-bath is in this case empoyled. The heads of the wax matches are dried by the journey over the carrier wheels, and the finished matches are automatically filled into the drawers of the boxes. These pass on to a circular table, where girls put them into the covers or outers—just as in the wood-match machines. Some wax matches, however, are filled into the boxes by hand. Each wax-match machine yields about 3 million matches *per diem.* Some manufacturers, Messrs. Palmer & Son, for instance, still use the frame-dipping method for wax matches. The taper is then either cut into lengths, which are bundled together and cut into vesta stems by a pivoted knife, the stems being afterwards filled into dipping frames by a small filling machine (Day's) worked by hand or steam, or 60–100 strands of it are wound upon a small drum, and passed from it through guides to a 'cutting and filling' machine of the kind indicated in Fig. 14. In this class of machine the tapers are caused to advance between two feed rollers covered with caoutchouc or other elastic material, and having an intermittent motion, their rotation at each revolution of the driving shaft, or movement of the treadles, being through such an angle as to

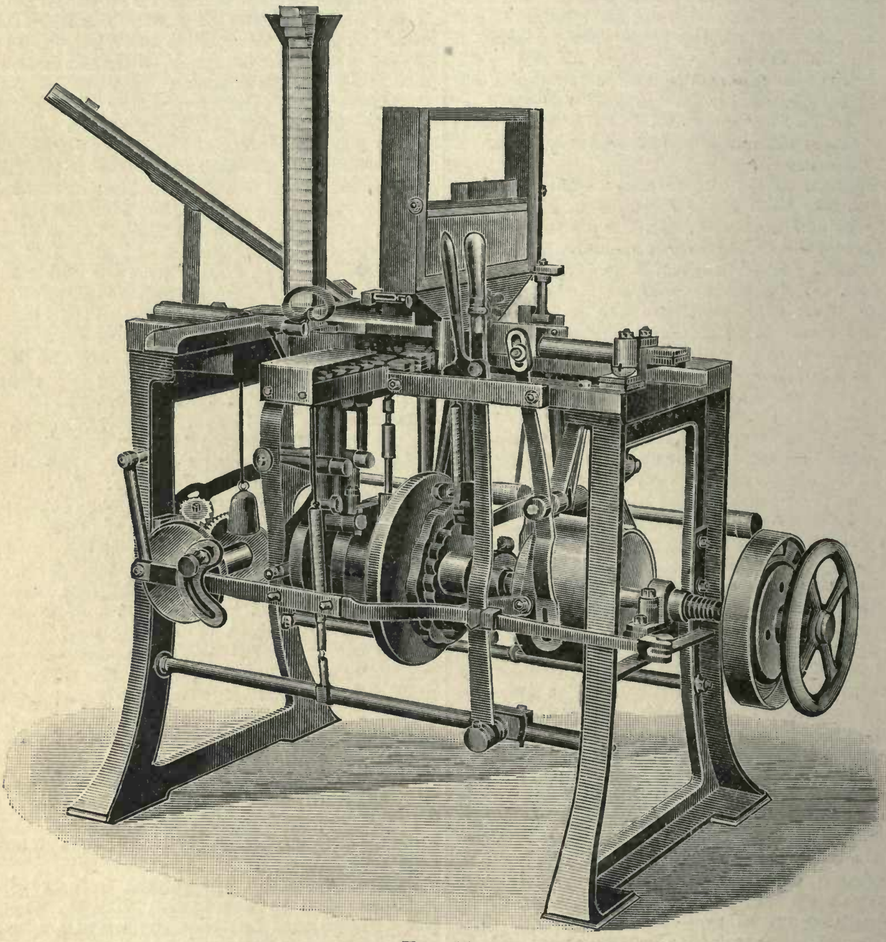


FIG. 11.

Arelın's (Lundgren's patent), box-filling machine, used at Grönvold, Norway.

advance the tapers the required distance under a cutter or cutters working in a vertical plane in front of the feed rollers. The dipping frame (which will fold 6400 stems (80×80) is held immediately in front of a perforated plate through which (when the machine is worked) the cut stems are pushed, so as to rest on a lath of the frame; the frame is now lowered, and the next lath is dropped into position, to receive a row of cut stems, immediately the treadles have been pressed down. When the frame is filled, the stems are dipped, on one side only, in the striking composition. At Messrs. Palmer's factory, the dipped frames of wax matches are dried on shelves in a square chamber, heated by steam pipes, and with a paddle fan in the centre. The 'racking out' is effected by hand, and the vestas are packed in the large penny boxes, or in the small 'Plaid' boxes for exportation, &c.

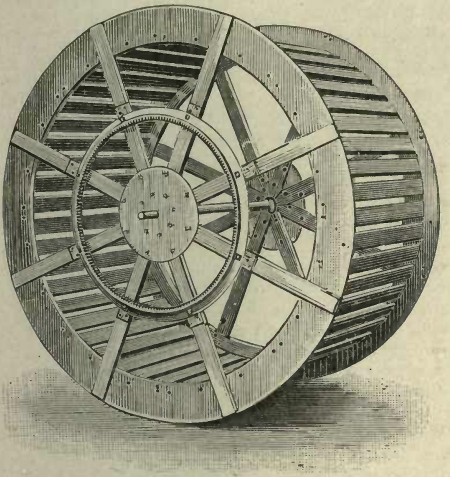


FIG. 12.
A drawing drum.

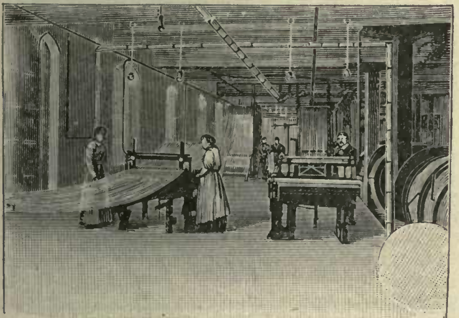


FIG. 13.
Taper-making room.

(For wax match machinery, *v.* patents of Beecher and Wright (1895), Hargreaves & Clegg (1896), Pickles (1899), Wiessner (1900), and Harvey (1901).)

3. **Safety matches.** All that has been stated, with regard to the processes of manufacture of ordinary matches, applies to safety matches, excepting the section on dipping compositions. Many more ingredients have been and are used for safety match compositions than are added to ordinary match pastes. So far, safety matches for the most part have been made with red phosphorus in the rubbers only: but attempts, mostly unsuccessful, have been made to manufacture matches, more or less of the safety type, but without phosphorus, either in the heads or rubbers. The best-known English, Swedish, and other safety matches belong to the first class. The igniting compositions of ordinary safety matches usually contain, as an oxidisable ingredient—apart, of course, from the red phosphorus in the rubbers—grey antimony sulphide, with or without sulphur; charcoal, too, is occasionally added.

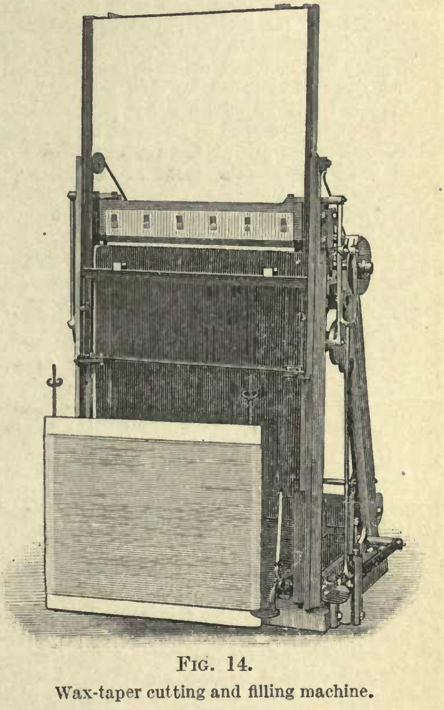


FIG. 14.
Wax-taper cutting and filling machine.

Potassium chlorate, potassium dichromate, and minium are the ordinary sources of oxygen, but manganese dioxide and nitre are also used: glue is the usual binding medium. Colouring matters are seldom added to safety match pastes, which are usually black.

Certain safety matches, made abroad and imported into this country, bearing on their boxes the legend 'Utan swafel och phosphor,' some years since were analysed in the writer's laboratory and found to contain much sulphur.

4. **Vesuvians.** The manufacturing processes for cigar lights, fixed stars, braided lights, and the like, differ little from the methods in use for ordinary matches. The stems, however, are generally of alder or other hard wood (when not of glass, &c.), circular in section, sometimes

braided and wired, and shorter than ordinary match sticks. Comparatively few braided lights are now made. Single workers are now employed occasionally in this branch of the industry, which used to engage the services of scores of hands. The dipping frames are smaller, usually filled by hand, and contain from 1600 (40×40) to 2000 short splints, which are dipped at one or both ends. Two distinct compositions are used: the pastille or burning composition, used for the head or ball; and the igniting or striking paste, with which the head is tipped. The pastille composition is a mixture of nitre with charcoal (or coal- or coke-dust), glass-powder, gum or glue, and some scenting ingredient, such as cascarilla bark, satinwood, gum benzoin, lignum vitæ, &c. The stems are dipped more than once in this composition, until the heads are of the required size, and a final dip in any ordinary striking composition is given to the heads after they have been dried. The early 'fusees' (of brown paper or cardboard, impregnated with nitre, tipped with sulphur, &c.) gave place to vesuvians, which in their turn have been largely superseded by wax matches, and these are being supplanted by pine-stemmed vestas. It will be seen in the next section that cardboard stems are at the present time once more used for certain sorts of matches (*cf.* 'book-matches').

5. '**Book**' **matches.** These, in one respect, are an interesting reversion to some of the very earliest types of matches, and to the original 'fusee'; the stems are of cardboard. Two layers of such matches connected together at the base are fastened in a little flat book, the pasteboard covers of which carry a special striking surface. These matches are of the safety type, striking only upon the prepared surface; they are manufactured by machines which automatically print the cardboard, cut it into combs, dip the teeth in the igniting composition, fold up, stitch into books, and affix to the outsides the special striking composition. [*v.* English Patent of Diamond Match Co. (C. H. Palmer, and J. W. Denmead), 21788, 1899.]

6. '**Double-tip**' **matches.** The genesis of the double-headed match is perhaps to be found in a proposal of R. and D. Maguire (1898), according to which a large flame-producing head, consisting of a composition containing no phosphorus, highly inflammable, but not ignitable by friction, is tipped with a cap composed of a white phosphorus bearing composition, readily ignited on any striking surface. The cap, which is applied by a second dipping, may contain 6 p.c. of white phosphorus (but this, of course, could not now be used in any country a party to the Berne treaty); and the inventors remark that they prefer red phosphorus, which answers satisfactorily. Somewhat similar suggestions are those of Lindner (1899) and the Saginaw Match Company (1905). The last-named company, which in America is credited with having originated the double-tip match, uses for the bulky part of the head a 'detonable composition,' consisting of an ordinary strike-anywhere 'parlour' match compound, containing about 6½ p.c. of white phosphorus, and for the cap or tip a noiseless and non-detonable composition, containing no less than 22 parts of white phosphorus. Matches of this character strike with delightful ease on any surface, and virtually without noise. But the large quantity of white phosphorus present is an obvious objection. It is said that double-tip matches in the States are very formidable rivals to the ordinary strike-anywhere, or 'parlour' matches. But if eventually the use of white phosphorus ceases in America, as appears probable, this competition must become less severe. At all events, the composition of the double-tip match will in such a case obviously have to be modified. In 1909, J. E. State patented a process for producing matches of an allied type, by dipping them successively in a material ignitable by friction, and in a material not so ignitable. The latter is then pushed back by mechanical means, such as a series of rollers, so as to leave exposed a portion of the striking composition at the extreme tip.

The striking surfaces or rubbers. For ordinary matches, mixtures of sand, glass, emery, and the like, with glue or gum, spread on the paper with which the sides of the match-boxes are coated, form convenient friction surfaces; metal gratings, tablets of unglazed porcelain, and porcelain or metal plates with parallel ridges very close together, are frequently employed; and practically any rough or uneven surface—even cloth—can be made to answer. The compositions used in the special rubbing surfaces for safety matches are very various; but the ingredients chiefly present are red phosphorus, antimony sulphide, and powdered glass, made into a paste with glue. The antimony sulphide is sometimes omitted, and manganese dioxide is not infrequently added to safety rubbers.

Among the patents for match striking or rubbing surfaces may be mentioned those of Neuberg (19418, 1897); Craveri (27520, 1897); and Prestwich (23048, 1904).

OLDER METHODS OF MANUFACTURE.

The complete process of manufacturing wooden matches formerly comprised the following separate and distinct operations, carried on for the most part, or at all events very largely, by hand labour: 1. 'Scurfing'; 2. Cross-cutting; 3. Steaming; 4. Splint Cutting; 5. Drying the Splints; 6. Filling the Dipping Frames or Coils; 7. Paraffining (originally Sulphuring); 8. Dipping; 9. Drying the dipped splints; 10. 'Laying out,' 'Racking out,' or 'Racking off'; 11. Halving (sometimes also called 'cross-cutting'); 12. 'Boxing'; 13. Packing. It has been shown that nearly all the work can be, and in the more extensive factories is, carried on automatically by continuous machinery; but in some smaller establishmntes the operations, or most of them, are still performed by the old ways. The three main operations are splint-cutting, dipping, and drying, but a summary of the entire older process will be given. [The smaller manufacturers buy their splints already cut and made up into bundles, or packed in cases.]

Splint-cutting. The planks of wood, usually 12–13 feet long, and 3 inches thick by 11 inches wide, are first of all freed from irregularities and roughnesses by the operation called *scurfing*, knives or cutters, rotatory or otherwise, cleaning and smoothing the surface. The planks are then *cross-cut* into blocks or lengths 4⅝ inches long × 3 inches thick × 11 inches wide. An ordinary English match-splint, to yield two match-stems, 2⅜ inches long, is 4⅝ inches long, so that the pieces cut off from the plank, measured in the direction of the grain of the wood, have just the length of a splint. Unless the wood is newly felled, and therefore sappy, these blocks must next be *steamed* (third operation) for about 20 minutes. They are then taken to the *splint-cutting* machine (fourth operation). Very many forms of such machines have been invented, but only three kinds have been at all generally used in the United Kingdom. The two earlier types of splint-cutting machines were the *toothing* machine and the *flaking* machine. The toothing machine answered well for 'clean' wood, such as pine-wood, but was not adapted for poplar, aspen, &c. The 'vertical flaking' machine is suitable for coarse-grained and even knotty wood, requires little skill in working, and is capable of cutting 650 bundles of splints in a day. The earliest machine belonging to the third class, or combined '*toothing and flaking*' machines, was invented by Tillett (1859). A machine, which for London work to a great extent superseded the foregoing kinds, was Pace and Howard's, and was an improvement upon Tillett's. Some years since, all English and nearly all foreign match-splints were square or rhombic in section. Round splints, such as were yielded by the early machines, were comparatively rarely seen, excepting in Vienna. But at the present time, as has been shown, round-stick matches, such as the pine vestas, and grooved-stick matches, are extensively used. Vesuvians, also, usually are round-stemmed.

Splints made from previously separated veneers are now very largely employed, and many of the later machines for splint-cutting have been upon this principle. Some account has been given (*cf*. p. 413) of Roller's log-peeling and splint-cutting machines; and this must serve; merely a reference can be made to the numerous patents for splint-cutting appliances taken out during the past 14 years. Some of these inventions relate not only to splint-cutting from veneers or otherwise, but to means of assembling the splints in coils, plates or other holders; also, in certain cases, the splint-cutting is described as the initial stage of a process of continuous manufacture.

The next operation is the *drying of the cut splints*. The splints were formerly always made into *bundles* and then dried. Now they are sometimes thrown loosely into large trays and dried by exposure to warm dry air. (Swedish splints are dried in wire-gauze cylinders revolving within a brick stove.) The dried splints are ready for the operation of *filling the dipping clamps or frames* (sixth operation). Prior to the use of dipping frames, there were the so-called 'bundle-dipped' and 'block-dipped' matches. In the earlier days of match-making, 'dipping-boards' were sometimes employed. 'Frame-' or 'clamp-dipping' was introduced in 1849, and its adoption, which by degrees became general, effected a great saving of time and labour. The dipping clamps are square frames with sides consisting of iron rods, on to which slip laths, each having grooves on its upper surface, and being lined with felt below. The match-splints are firmly held in the grooves by the pressure of the felt. Each frame holds 3900 splints, which, dipped at each end and halved, will yield 7800 matches. The dipping frames were at first filled by hand, but Hynam (1850) and Bell and Grimes (1854) invented machines for the purpose. Improvements followed, and in 1865 Simlick introduced self-acting machinery, driven by steam power, to produce the various movements of these frame-filling machines with greater rapidity and economy of labour.

In 1876, E. B. Beecher, of New Haven, Connecticut, invented machinery to replace frame-dipping, by 'coil'-dipping. This system of working having been introduced into the largest English match-works, effected great and, in many respects, beneficial changes in the method of manufacture; and coil-dipping, where it was adopted, for wooden matches entirely superseded frame-dipping. It is not adapted for the manufacture of vesuvians.

In Beecher's original machine (Eng. Pat. 4293, 1876) the splints were so delivered from a hopper as to be set at regular intervals between the coils of a long, flexible tape, band, or belt of cotton webbing, about the thickness of a splint, but considerably narrower than its length; this belt was continuously wound upon a short cylinder or drum adapted to a rotating mandril or axis, until a coil, or bundle, or frame, of the desired size was completed. The end of the binding tape was then secured to the preceding coil by a pin or otherwise, the drum and coil of match-splints thus bound upon it being now ready for removal from the mandril for dipping. Being separated from each other by the thickness of the webbing, and by an interval the width of a splint between every two splints, the splints individually received the proper proportion of composition when dipped, and could be conveniently dried in the coil. In an improved form of the machine (1887), Beecher employed an auxiliary or secondary band in connection with the first, for the purpose of holding the match-splints more securely.

The match-splints, having been arranged for dipping in one or other of the ways described, according to the older method now being described, are ready for *paraffining*, or 'the first dipping,' as it is sometimes called (seventh operation). The frames are put on a table, and the splint-ends are levelled, if necessary, by taps with a piece of wood: they are afterwards heated (to facilitate absorption of the paraffin) by application to a hot iron plate, and then immersed in melted paraffin contained in a shallow steam-heated iron tank. Both ends of the splints are thus treated. Sometimes the operation is effected in a brick stove, on the top of which are three shallow, flat-bottomed, square pans, one serving for the preliminary heating of the splint-ends, the second for the paraffining, and the third for the subsequent dipping in the igniting composition.

In all but the most inferior matches, paraffining has entirely superseded treatment with sulphur.

8. **Dipping.** The usual constituents of a match-igniting composition have already been enumerated (pp. 416, 417), and are mixed in the following manner. The glue and potassium chlorate or nitrate are dissolved in warm water, and the phosphorus (assuming that the worker is in a country where it is still legal to use it) is then added to and stirred in the liquid (which should be of a syrupy consistence and at a temperature of about 38°C.), until a perfect emulsion is obtained. The rest of the constituents, powdered glass or sand, colouring matters, and metallic oxides, if present, having been previously 'milled,' are now added, and thoroughly mixed with the emulsion. When, as is now generally the case, a substitute for white phosphorus is used, it is at first intimately mixed with part of the glue solution and inert materials only; the potassium chlorate, with the rest of the ingredients, being added later. The whole is finally put through a mill.

For the operation of dipping, which—in manufacturing upon the older lines—is performed by workmen in a separate apartment called the dipping-room, the emulsion is ladled from a steam-jacketed iron pan on to the dipping plate or table—generally a shallow, flat-topped, iron box, kept hot by steam admitted to its interior. The composition is spread over the plate, and levelled to the required depth by a gauge or 'strickle.' The ends of the splints in the filled frames (or coils) are then dipped in the thin layer of igniting composition. After the splint-ends on one side have been dipped, the frames or coils are placed in racks, the tipped ends downwards, for a few minutes. The opposite ends are then dipped.

Dipping by hand, as already described, is most usual in working upon a comparatively small scale; but the igniting composition is sometimes applied by the aid of cylinders or rollers, partly rotating in hot-water jacketed cases, receptacles, or boxes containing the mixture, endless chains conveying the frames or coils over the rollers. And it will have been seen (*ante*, pp. 414, 415) that this system is generally employed in the newer, automatic, and continuous methods of manufacture. Bevelled wheels and other devices (L. Urion, 1856) have also been used for the purpose.

9. **Drying.** The frames or coils of double-tipped splints are placed on supports or racks, either in the open air or in the drying-room—an apartment maintained during the summer at a suitable temperature by fans or otherwise, and in damp weather and winter kept warm and dry by pipes conveying steam or hot air.

10. **Laying out**; 11. **Halving**; and 12. **Boxing.** The 'headed' and dried splints are next taken out of the frames or coils, as the case may be. The operation is usually termed 'laying out,' 'racking out,' or 'racking off,' and in England is sometimes effected by hand, if the establishment be not very extensive. The nuts and crosspiece at the top of a clamp are removed, and then lath after lath is lifted and the row of double-tipped splints beneath deftly withdrawn. Laying out is also performed mechanically, the machines of Sebold, Schnetzer, and others being used, especially abroad. In the case of coil-dipped splints the process is called 'unwinding,' and differs, of course, materially from the methods applicable to frames. Beecher (1877) invented a machine which simultaneously performs this operation and the next, 'halving,' 'cutting-down,' or 'cross-cutting.'

According to the older method, for frame-dipped matches, handfuls of the laid-out, double-headed splints were divided, 'halved,' or 'cross-cut,' generally by a pivoted or 'lever' cutting knife, and the resulting matches were at once *boxed* (*i.e.* put into boxes) by women, who became exceedingly dexterous in taking up handfuls of splints of just the required size to fill two boxes. The operations of halving and boxing, where white phosphorus was used, caused more loss by 'firing' than any other part of the proceedings in a match factory. It has been mentioned that the loss during boxing or filling is quite trivial under modern working conditions. And, with the continuous manufacture, there is now no halving.

The writer is under obligations to Messrs. Bryant & May, and to Messrs. Bridwell, Hammond, Parrott, Marchant, and Crowther-Beynon for help in the preparation of this article.

E. G. C.

MATECERIC ACID. An acid obtained from the wax of the yerba maté (*Elaeodendron quadrangulatum* (Reiss.)). When the solution obtained by exhausting the leaves of this plant with ether, or better with ether-alcohol, is treated with lime, then filtered and evaporated, a waxy residue is left, which may be freed from chlorophyll by treating its ethereal solution with animal charcoal. This solution, agitated with water to remove caffeïne and other substances, and evaporated, leaves the pure waxy matter, which, when boiled with aqueous potash, partly dissolves, leaving a residue soluble in ether, much more butyraceous than the original substance and separable by treatment with alcohol into an insoluble yellow transparent substance, and a soluble portion which is white and melts at 55°. On neutralising with hydrochloric acid, the alkaline solution obtained by saponification of the wax, mateceric acid, is obtained as a white precipitate which has acid properties, and is soluble in ether and in boiling alcohol. It melts at 105°–110°, and has a density of 0·8151 at 26°. From the results of its analysis, it does not appear to belong to the acetic series, but its molecular weight is very high (Arata, Gazz. chim. ital. 1877, 366).

MATEZITE. A saccharine substance obtained by Girard from Madagascar caoutchouc; when treated with hydriodic acid, yields methyl iodide and *matezo-dambose*, an isomeride of glucose. Crystallises in radiating nodules. Rotatory power $[\alpha]_D + 65$; m.p. 187° (Girard, Compt. rend. 77, 995, and 100, 84; Combes, *ibid.* 110, 46).

MATICO CAMPHOR *v.* CAMPHOR.

MATLOCKITE. A lead oxychloride

$$PbCl_2 \cdot PbO$$

of a yellowish colour, found at Cromford, near Matlock, Derbyshire; sp.gr. 7·21.

MATRASS. An egg-shaped glass vessel with a narrow neck, used by the older chemists, mainly for sublimations.

MAURITIUS ELEMI *v.* OLEO-RESINS.

MAUVANILINE $C_{19}H_{17}N_3$. A base isolated by Girard, De Laire, and Chappolot, from the insoluble residues obtained in the manufacture of rosaniline (Zeitsch. Chem. 1867, 236).

MAUVE or **MAUVEÏNE** *v.* Azines.

MAYNAS RESIN or **CALABA** *v.* Resins.

MEAD or **HYDROMEL.** An alcoholic drink prepared by the fermentation of honey. Well-made hydromel has a colour between that of champagne and Madeira, is fine in flavour, and contains about 13 p.c. of alcohol.

MEADOW ORE *v.* Limonite; also Iron.

MEADOW SAFFRON *v.* Colchicum.

MEAT EXTRACTS. *Historical.* It is well known that extract of meat consists of beef tea evaporated to the consistency of a thick syrup. It therefore contains the whole of those constituents of meat which are soluble in hot water.

It was first correctly prepared in 1821 by Proust, by whom, in conjunction with Parmentier, it was very highly recommended as a stimulant quite as valuable for the strong and healthy as for invalids. In 1847 Liebig, in his celebrated treatise on 'Researches on the Chemistry of Food,' most warmly approved of Proust and Parmentier's extract, and subsequently made every effort to popularise the use of the preparation. The attention of many men of science, but more particularly of the medical profession in Germany, was attracted to Liebig's abstract scientific researches into the nature of meat, and it was ascertained that extract of meat was of great usefulness in medical cases.

In consequence, the *Extractum Carnis* was, without Liebig's assistance, introduced into the Bavarian Pharmacopœia of 1856, and from that time all Bavarian apothecaries were legally bound to keep the extract in stock, or to make it when required, just as any other drug. From Bavaria the knowledge and medical use of the extract spread over the whole of Germany, but its manufacture remained confined to pharmaceutical chemists, and its use to the sick chamber. Liebig, on the other hand, while fully appreciating the clinical importance of the extract, and further endeavouring to improve the alimentation of sick persons by various modifications of this invention, proposed to bring meat extract into commerce as an article of food, and to make its manufacture the object of industrial enterprise on a large scale. His endeavours were, however, without success until, early in 1862, George Christian Giebert, an engineer, well acquainted with the meat-producing districts of South America, went to Munich to receive instruction in the method of preparing the extract by Liebig himself, aided by von Pettenkofer, and then returned to Uruguay and established a manufactory on a considerable scale. In November, 1864, the first samples of Giebert's manufacture arrived at Munich and their quality far exceeded the expectation of Liebig. He consented to Giebert's proposition that the extract should bear the name of the inventor, on condition that it should always be free from fat and gelatin, and that each consignment should be subjected to a gratuitous analysis by him or his delegate. The establishment of Liebig's Extract of Meat Co., Ltd., was thus founded.

The industry has flourished and immense areas of land are farmed to produce cattle required for the manufacture of meat extracts. Take, for example, some facts connected with the enterprising company to which Liebig gave permission to bear his name. The Liebig's Extract of Meat Company farmed, in 1868, some 28,494 acres of land, and the total herd of horned cattle reared on this area was 12,000. In 1908, the acreage was 1,302,386 and the number of cattle 224,406, and in 1910 the acreage was 5,000,000, and the number of cattle 350,000. Striking as the figures may be as illustrating the enormous expansion of the cattle-rearing industry, they become still more impressive when regard is paid to the fact that the cattle are no longer, as in Liebig's day, and according to his own words, 'half-wild animals,' but are bred from the choicest pedigree stock taken from the farms of our best English breeders.

Each animal is allotted about 5 acres of pasturage. The average daily amount of grass consumed by one animal is 88 pounds; a herd of 250,000 would therefore consume *per diem* 22,000,000 pounds of grass, or approximately 10,000 tons. Thus the yearly consumption of grass would mean not far short of 4,000,000 tons. The composition of pasture grass, according to the average of a large number of analyses, is as follows:—

	Per cent.
Water	80·00
Proteins with a small quantity of nitrogenous extractives[1]	3·50
Fat	0·80
Carbohydrates	9·70
Fibre	4·00
Mineral salts	2·00
	100·00

This means for a herd of 250,000 head of cattle per year a food yield in the form of grass of the following quantities of its individual solid constituents:—

	Tons
Protein or flesh-forming substances	140,000
Fat	32,000
Carbohydrates	388,000
Fibre	160,000
Mineral salts	80,000
	800,000
Balance due to 80 p.c. of water in grass	3,200,000
Total	4,000,000

Similarly, the annual amount of water consumed, based on the fact of one animal requiring 30 litres per day, would amount to 700,000,000 gallons per annum for the herd. These figures refer only to the stock of one company. The Argentine, Uruguay, and Paraguay republics are immense fodder-yielding tracts, and the metamorphosis of grass proceeds steadily and uninterruptedly day by day on a colossal scale. There are occasions when the ordinary grass is supplemented by 'Alfalfa,' a rich clover corresponding to our lucerne and containing a good proportion of nitrogenous food.

Method of manufacture. In principle the lines laid down by Leibig, which he considered essential to success, are still followed by the Liebig Company. In the first place, the meat is hung in the cooling halls for 12 or more hours,

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[1] $N \times 6{\cdot}25$.

then the fat and sinews are carefully removed, and the meat is fed to chopping machines with revolving knives. From the chopping machines the meat emerges in chunks, which drop into mincing machines especially constructed for the purpose. The meat emerges from these machines as mincemeat, and is then transferred to the extracting pans, each capable of holding about 4 tons, in which it is left with its own weight of pure filtered water. After the addition of more water the mixture is heated to a temperature not exceeding 95° by means of steam jackets. During this time fat continuously rises and is skimmed off. The more or less clear liquor is then run off and the work of concentration is commenced. Fat is again skimmed off until at length the extract or soup is practically free. Concentration proceeds again *in vacuô*, and during evaporation is twice filtered before passing into the final concentrator, which is fitted with a revolving worm through which low pressure steam is passing. Constant stirring during the final stages of evaporation is essential to secure uniformity in regard to consistency and composition of the finished extract. The treacly mass is then run off while hot into 100 lb. tins, cooled, hermetically sealed and dispatched to the European blending factories.

The extract is finished within 3 days of the death of the animal.

One thousand pounds of lean meat, treated upon a manufacturing scale, furnishes 31 lbs. of extract. Commercial extract manufactured as described contains an average of 18·25 p.c. moisture, 61·5 p.c. of organic matter, 20·25 p.c. of mineral substances, and yields an alcoholic extract of 57 p.c.

It should be as free as possible from gelatin, fat, and coagulable or insoluble albumen. By far the greater proportion of the meat constituents, namely, the fibrin, gelatin-yielding tissue, and fat is therefore rejected in the preparation of extract.

Lemco, which is the standard extract manufactured by the Liebig's Extract of Meat Company, has the following composition :—

		Per cent.
Water		20·05
Organic matter		58·52
Mineral matter		21·43
		100·00
The mineral matter contains:		
Combined chlorine		1·88
Phosphates as P_2O_5		6·00
The organic matter contains:		
Total nitrogen		9·45
Distribution of the total nitrogen:		
Nitrogen in fibrin and albumen	0·14	
,, meat bases soluble in alcohol	5·64	
,, meat bases rendered soluble in alcohol	0·70	
,, gelatin	0·02	
,, albumoses	1·73	
,, peptones	1·17	
Ammoniacal nitrogen	0·05	
	9·45	
Creatine		1·85
Creatinine		4·95
Total		6·80
Fat (ether extract)		0·12

The meat bases constituting the essential part of the extract contain creatine, creatinine, xanthine bases, carnine, carnic acid, and other complex organic bodies.

Whilst all commercial extracts are essentially of the same character, the proportions of the various constituents differ. From Table I. it is observed that Nursing Oxo contains a proportion of proteins derived from the peptonisation of meat. Oxo and Bovril contain a higher proportion of water, and about 5 p.c. of meat fibrin derived from partially extracted lean meat.

TABLE I.

	Composition of Nursing Oxo p.c.	Oxo p.c.	Bovril p.c.
Water	23·53	41·00	41·90
Organic matter	59·26	39·74	40·58
Mineral matter	17·21	19·26	17·52
	100·00	100·00	100·00
The mineral matter contains:			
Combined chlorine	3·20	6·30	6·00
Phosphates as P_2O_5	4·40	3·40	3·10
The organic matter contains:			
Total nitrogen	9·68	5·89	6·10
Distribution of the total nitrogen:			
Nitrogen in fibrin and albumen	0·86	0·81	0·83
Nitrogen in meat bases soluble in alcohol	3·66	2·68	2·98
Nitrogen meat bases rendered insoluble in alcohol	0·32	0·35	0·40
Nitrogen in gelatin	1·50	1·34	0·85
,, albumoses	1·53	0·17	0·78
,, peptones	1·67	0·59	0·26
Ammoniacal nitrogen	0·14	—	—
	9·68	5·94	6·10
Creatine	3·64	1·58	1·99
Creatinine	0·83	1·97	1·56
Total	4·47	3·55	3·55

A practice has arisen of mixing meat extracts with extracts of yeast. The extract of yeast has valuable dietetic properties and contains the active principles of fermentation. It also resembles, in many respects, physically and chemically, the extract of meat, and can, therefore, be mixed with meat extract, and, being a cheaper article, forms a mixture which can be sold at a greater profit, and ought not to be classed as a meat extract.

According to Wiley the presence of yeast extract in meat extract can be determined by treating the mixture with a strong solution of zinc sulphate and filtering. In meat extract the filtrate obtained is always quite clear, but when a yeast extract is present the filtrate is turbid. Hehner applied the Folin reaction for the estimation of creatine and creatinine in meat extracts, and as yeast extract contains neither creatine or creatinine the test is of importance in determining the source and value of a meat extract.

The Folin method for the estimation of creatinine is a colorimetric one, based on the fact that creatinine gives with picric acid, in presence of alkalis, an orange to deep red solution, the intensity of the colouration depending upon the amount of creatinine present (Zeitsch. physiol. Chem. 1904, 41, 223). Folin recommends the use of Dubosq's colorimeter for making the colour comparisons.

The test is carried out as follows: With good quality extracts 5 grams are dissolved in water and the solution made up to 500 c.c.

Creatinine. 20 c.c. of this solution are taken for the determination of creatinine, viz. 0·200 gram of extract. To 20 c.c. of the solution in a 500 c.c. flask are added 20 c.c. of picric acid solution (saturated) and 5 c.c. of a 10 p.c. caustic soda solution.

The mixture is shaken and allowed to stand exactly 5 minutes, and is then made up to 500 c.c. with pure water at 18°, and its colour compared with that obtained from a standard solution of potassium dichromate (24·565 grams per litre).

All colorimetric readings are made with a Dubosq colorimeter, having the left-hand cylinder fixed at exactly 8 mm. depth of bichrome solution.

The following readings were obtained :—

8·2 mm.	8·1 mm.	
8·2 ,,	8·0 ,,	Jaffe's formula
8·1 ,,	8·0 ,,	8·11)81·00(9·99 mgms.
8·1 ,,	8·1 ,,	creatinine.
8·2 ,,	8·1 ,,	9·99 mgms. found in
——	——	0·2 grm.
8·16 ,,	8·06 ,,	

Average 8·11 m.m.

0·2 : 100 : : 0·0099 : x

x=4·99 p.c. creatinine.

Total creatinine and creatine. 15 c.c. of the extract solution (5 grams in 500 c.c. water) =0·15 gram extract, are placed in a porcelain basin 8 cm. diameter, and 10 c.c. of normal HCl (1 c.c.=0·0365 gram HCl) added, and slowly evaporated to dryness on a water-bath taking at least 2 hours for the evaporation. The residue is dissolved in 15 c.c. of water, then to the contents in the basin 20 c.c. picric acid are added, and 5 c.c. of the caustic soda solution. The mixture is stirred with a glass rod, and exactly after 5 minutes' standing transferred to a 500 c.c. flask, the basin being washed out several times into the flask, and the liquid made up to 500 c.c. at 18°. The following readings were obtained :—

8·4 mm.	8·5 mm.	
8·4 ,,	8·6 ,,	Jaffe's formula
8·5 ,,	8·6 ,,	8·49)81·00(9·54 mgms.
8·4 ,,	8·6 ,,	creatinine.
8·4 ,,	8·5 ,,	9·54 mgms. found in
——	——	0·15 grm. extract.
8·42 ,,	8·56 ,,	

Average 8·49 ,,

As 0·15 : 100 : : 0·00954 : x.

x=6·36 p.c.

6·36 p.c. acid treated.
4·99 p.c. creatinine.
——
1·37 creatinine due to creatine.
1·16 factor for converting creatinine to creatine.

1·37×1·16=1·5892 creatine.

Corrected results :

Creatinine	4·99 p.c.
Creatine	1·59 ,,
	——
	6·58 ,,

In carrying out this test care must be taken to observe all the details as regards :

(*a*) Strength of solutions employed ;
(*b*) Time of contact ;
(*c*) Dilution of original liquid ;
(*d*) Depth in mm. of the unknown solution should not vary more than between 7 mm. and 9 mm. ;
(*e*) Temperature to be as near 18°C. as possible.

With extracts that yield low creatine and creatinine figures it is necessary to treat the extract before applying the test. 10–50 grams of the substance are dissolved in the smallest bulk of water possible. Then 250 c.c. methylated spirits are added and allowed to stand for 12–16 hours, filtered, the alcohol distilled off, the residue dissolved in water, and made up to 100 c.c., an aliquot part not exceeding 20 c.c. being taken for the estimation.

It has been pointed out by Jaffé (Zeitsch. physiol. Chem. 1886, 10, 391), and more recently by A. C. Chapman (The Analyst, Nov. 1909), that other substances, such as acetone, dextrose, and lævulose reduce picric acid and produce the same colouration. When the presence of any reducing substance other than creatinine is suspected, preliminary treatment with methylated spirits is desirable.

Methods of analysis. For the sale of commercial high-grade extracts the following method is applied.

In some meat extracts during the cooling in pots, crystals and other solids settle to the bottom before the mass becomes semi-solid, consequently the material must be well mixed without warming before analysis.

Water. 2 grams are evenly spread by means of a glass rod round the inside of a porcelain crucible 37 mm. high and 55 mm. wide on top to within 10 mm. of top edge; dried for 36 hours in a water-oven at a temperature of 97°, cooled for 20 minutes in a desiccator over vitriol and quickly weighed. A Moslinger's cellular water-oven is best for this class of work.

Ash. 2 grams are weighed in a platinum basin and slowly burned without the basin becoming visibly red. The burner employed has a round cover 7 cm. in diameter with 28 holes, each 1 mm. in diameter. After carbonising, the mass is crushed twice and the ash obtained should be a greyish-white without showing fusion—too strong or too quick ignition will cause loss.

For absolutely correct ash estimation the basin is put on an asbestos sheet to protect the contents from sulphurous acid of the gas, or better still, burned in an electric furnace at 6–8 ampères until the ash is clear grey. This is weighed when cold and washed into a small beaker, acidified with nitric acid, and warmed until the light brown coloured matter coagulates. Filter and use the filtrate for the chlorine estimation, wash the carbonaceous matter from the filter into a small crucible, dry at 105° and weigh. Deduct this carbon from the former weight to get the true pure ash.

The chlorine is estimated in the acidified filtrate from the ash gravimetrically, as phosphates interfere with the volumetric estimation.

Alcoholic extract. By this is meant that portion of the extract soluble in ethyl alcohol, 80 p.c. by volume. 2 grams are weighed out into a small Soxhlet flask, 9 c.c. water added, and the extract dissolved without warming, 50 c.c. alcohol (93 p.c. by volume, sp.gr.=0·8234) slowly added with gentle shaking, allowed to stand over night at 17°–18°, and then carefully poured from the fast sticking mass into a weighed porcelain basin 76 mm. diameter and 34 mm. deep; the alcohol is evaporated slowly on a water-bath at 70°–75°. In order to prevent creeping the basin is placed on a layer of flannel over the hole in the bath, or in a copper basin soldered into the opening in the bath and having a layer of sand between the copper and porcelain basins. Meanwhile to the insoluble mass in the flask 50 c.c. alcohol of sp.gr. 0·8639 (80 p.c. by volume) are added with gentle shaking and allowed to stand at 17° until the first alcoholic solution is evaporated when the second portion is decanted into the basin, and this again evaporated until the contents have the consistency of honey. The basin is then dried at 98° in the water-oven for exactly 6 hours, cooled 20 minutes in the desiccator, and quickly weighed. The extraction temperature must be within 17°–18°, or variable results will be obtained.

General Analysis of Meat Extracts.

Modified Stutzer method. 30 grams are weighed, dissolved in water and made up to 250 c.c. A fair average sample is thus obtained, and all estimations necessary can be begun the same day.

Moisture. Cleaned ignited Calais sand is put into a flat nickel basin 9 cm. in diameter along with a small glass stirring rod until the whole weighs exactly 100 grams. Dried in steam oven until weight is constant, then 25 c.c. extract solution added (= 3 grams extract), stirred amongst the sand, evaporated until granular on a water-bath, transferred to a steam oven for 36 hours, cooled and weighed.

Ash. 25 c.c. (= 3 grams) evaporated and carbonised. Owing to the quantity of carbonaceous matter the estimation of ash cannot well be made direct, hence the charred mass has to be extracted three times with boiling water, and filtered through an ashless filter paper into a porcelain basin, the char and filter paper burned off in the platinum basin, and the filtrate put back in the platinum basin, evaporated, dried, ignited gently, and weighed. The ash is dissolved in cold water, acidified with nitric acid, made up to 250 c.c., and used for estimation of chlorides and phosphates.

Chlorides are estimated gravimetrically in 50 c.c.

Phosphates are estimated by the molybdate and magnesia mixture method in 50 c.c.

Fibrin and **already coagulated albumen.** 25 c.c.(=3 grams) are diluted and settled in a 100 c.c. cylinder over night. The top liquid decanted and the residue either transferred to a counterpoised filter, washed, dried at 100°, and weighed, or the residue transferred to a centrifuge tube, washed, and the nitrogen estimated by Kjeldahl's method.

Soluble albumen. The decantations from the above are acidified with acetic acid, boiled for 5 minutes, settled, filtered, and weighed or treated by Kjeldahl's process. If the total fibrin and albumen together be required, then it is only necessary to acidify 25 c.c. of extract solution diluted to 100 c.c., with acetic acid, boil for 5 minutes, settle, filter, and either weigh at 100° or treated by Kjeldahl's method.

Gelatin. 25 c.c. of extract solution (= 3 grams) are poured on to asbestos fibre in a small porcelain basin, evaporated to dryness, extracted with 93 p.c. alcohol three times, then with ice-cold water containing 10 p.c. alcohol, until the decantations are free from colour (the temperature must never rise above 5°). The gelatin is either dissolved and washed from the asbestos and treated by Kjeldahl's process, or the asbestos and gelatin may be put direct into the Kjeldahl flask. With some extracts it is better to take 25 c.c. extract solution, and, without evaporating, add 250 c.c. methylated spirit, stand 8 hours, decant off alcohol from the sticky mass and wash with 10 p.c. ice-cold alcohol until free from colour, then treat by the Kjeldahl method.

Total nitrogen. 10 c.c.(=1·2 gram extract) are treated by Kjeldahl's method direct.

Meat bases soluble in alcohol. 25 c.c. (=3 grams extract) taken in beaker, 250 c.c. absolute alcohol added with constant stirring and settled for 12–16 hours. The alcohol passed through filter into a 500 c.c. round-bottomed flask, the residue washed twice with 25 c.c. absolute alcohol, and the alcohol distilled off, standing the flask inside a water-bath. The meat bases are then treated by the Kjeldahl process in the flask without transference so as to avoid loss.

Residue insoluble in alcohol. The insoluble residue from the absolute alcohol is dissolved in water on the water-bath. A few drops of acetic acid added to coagulate the soluble albumenoids, then boiled and filtered into a 250 c.c. flask for the estimation of gelatin albumoses and peptones. The residue on the filter, consisting of fibrin, albumenoids, may be treated by Kjeldahl's method as a check on former estimation.

Total nitrogen in gelatin albumoses and peptone fraction. 50 c.c. of the 250 c.c. taken for the Kjeldahl process.

Albumoses and gelatin. 50 c.c. of the 250 c.c. are taken in a porcelain basin, and powdered zinc sulphate crystals added with frequent stirring until saturated. The precipitate is filtered, washed with saturated zinc sulphate solution, and subjected to Kjeldahl's process. The filtration of the precipitate is slow, but proceeds steadily, and works better if the liquid is rendered slightly acid with sulphuric acid (1 : 4).

Peptones, albumoses, and gelatin. 50 c.c. of the 250 c.c. are put into a beaker 50 c.c. sulphuric acid (1 : 3) added, and an excess of phosphotungstic acid, prepared by making a strong solution of sodium tungstate in boiling water, and adding phosphoric acid with continued boiling until the mixture gives a constant acid reaction.

An alumina-like precipitate is formed which, if left for a few hours, filters fairly well. The precipitate is washed several times with dilute sulphuric acid, and then treated by Kjeldahl's method. This operation has to be carefully conducted as the precipitate causes bumping.

The nitrogen from this estimation comes almost up to the total nitrogen of the section insoluble in alcohol, but a little of the meat bases are sometimes rendered insoluble by the alcohol, and the traces obtained by difference are to be added to the meat bases. Having obtained the gelatin figure by a separate estimation, then (gelatin and albumoses) − gelatin = albumoses, and (gelatin + albumoses + peptones) − (gelatin + albumoses) = peptones.

Ammoniacal nitrogen. Traces only of this are present, 50 c.c. of the standard extract solution (= 6 grams extract) are distilled with barium carbonate into standard acid.

All nitrogen determinations are made by the Kjeldahl-Gunning method, using about 15 c.c. nitrogen-free vitriol to start with. After frothing, and the thick carbonaceous mass has settled, 10 grams of potassium sulphate and a small crystal of copper sulphate are added. Heating must be continued until the yellow colour has changed to a clear blue, indicating complete oxidation. In distilling off the ammonia it is preferable to use steam with a small flame under the alkaline liquid to prevent dilution by condensation, instead of a naked flame under the distillation flask, when zinc-dust has to be added to prevent bumping.

In calculating the percentage of the various nitrogenous compounds in extracts it is usual to use the factor N × 6·25. This is not, however, strictly accurate, but is generally accepted as the best approximation to the truth. Analyses, therefore, should disclose the actual nitrogen figures obtained.

An auxiliary method for the estimation of gelatin is that of Beckmann (Forschungs Berichte, 1896, 3, 324) based upon the fact that gelatin and albumenoids are rendered insoluble by formaldehyde. 3 grams extract dissolved in 20 c.c. cold water are treated with 3 or 4 drops of formaldehyde solution (40 p.c. strength) and evaporated to dryness on a water-bath and for 2 hours in an air oven, then moistened with a 5 p.c. formaldehyde solution, and after standing 5 minutes, warm water, 60°–70°, is added and allowed to digest 15 minutes, the water is then decanted, and the washing repeated until free from colour. The insoluble mass is subjected to the Kjeldahl process. Care must be observed to use a formaldehyde solution which is neutral, since free acid affects the reaction.

A convenient method for the determination of the total soluble proteids in extract is based on the fact that halogens precipitate those bodies. Bromine water is for convenience employed. Allen and Searle take 1 gram of the substance dissolved in 100 c.c. water in a flask and acidify with dilute hydrochloric acid. A considerable excess of bromine water is added and the liquid shaken for some time. The precipitate is allowed to settle for several hours, the supernatant liquid decanted through an asbestos filter, the precipitate washed with cold water and treated by Kjeldahl's method. F. S.

MECCA BALSAM. *Opobalsam*; *Balm of Gilead* (*v.* OLEO-RESINS).

MECONIC ACID, MECONIDINE *v.* OPIUM.

MECONINE *v.* LACTONES.

MEDLAR. The fruit of *Mespilus germanica* (Linn.). When fresh, the fruit has a yellowish-white flesh, which is hard and of an unpleasant astringent taste; on keeping for some weeks, the flesh becomes brown, soft, and doughy, and possesses an agreeable flavour. In the latter condition, Bersch (Landw. Versuchs. Stat. 1896, 46, 471) examined the various parts of the fruit and obtained the following results:—

	Whole fruit	Rind	Flesh	Pips
Percentage of dry matter	30·9	36·9	24·8	61·6

The dry matter contained—

	Protein	Fat	Invert sugar	Other N-free extract	Crude fibre	Ash
Whole fruit	2·79	1·04	36·08	40·98	16·29	2·82
Rind .	4·12	2·66	—	72·62	17·51	3·09
Flesh .	2·62	0·57	48·56	37·63	7·35	3·27
Pips .	2·55	0·62	—	46·66	48·52	1·65

Malic acid, acetic acid (0·03 p.c.) and alcohol were present.

The ash of the medlar has been found to contain about 0·3 p.c. boron trioxide. In the N-free extract there is a considerable portion of pectin matter. H. I.

MEDULLADEN *v.* SYNTHETIC DRUGS.

MEDULLIC ACID $C_{20}H_{41}{\cdot}CO_2H$, m.p. 72·5°, an acid found as a glyceride in beef suet and in beef marrow, associated with oleic and palmitic acids.

MEERSCHAUM. A hydrated magnesium silicate $H_4Mg_2Si_3O_{10}$, occurring as nodules and compact masses, of white, grey, or creamy colour. From its appearance and its extreme lightness (sp.gr. 0·988–1·279) it has acquired the name of *meerschaum* or 'sea-froth' (*écume de mer*), although it is sometimes described by mineralogists under the name of *sepiolite*, a word introduced by Glocker to indicate its resemblance to the light white porous material known as the bone of the cuttle-fish or sepia. Meerschaum is a soft mineral (hardness 2–2·5), easily carved; has a greasy feel, and readily adheres to the tongue. In consequence of this porosity, a meerschaum pipe absorbs the oily matter of the tobacco; and, for a like reason it is difficult to determine the proportion of water in the mineral. The following analyses illustrate the composition of meerschaum:—

	I	II	III
Silica . .	60·87	61·30	53·8
Magnesia . .	27·80	28·39	23·8
Alumina . .	—	—	1·2
Water . .	11·29	9·74	20·0
	99·96	99·43	98·8

I. From Asia Minor, by Lychnell. II. From Greece, by Scheerer. III. From near Madrid, by Berthier.

Meerschaum is found as nodular masses in alluvial deposits in the plains of Eski-Shehr, in Asia Minor, where it is associated with magnesite ($MgCO_3$). It is here dug from a number (now some 1270) of shallow pits, from the bottom of which short galleries are occasionally run. The nodules are scraped free from earthy matter with a special knife, air dried, polished with wax, and sorted into a number of grades and sizes (J. Soc. Arts., 1909, 57, 411). It also occurs at Kiltschik, near Konieh, in Natolia; in Greece, Negroponte, and Samos; in Moravia; and in New Mexico. In New Mexico it occurs as nodules and seams in limestone, and has been exploited at two localities, namely Gila valley and Bear Creek (D. B. Sterrett, Bull. U.S. Geol. Survey, 1908, No. 340, 166). At Vallecas, near Madrid, it is said to be used as a light material for constructive purposes. Meerschaum has been employed as an ingredient in porcelain, while in Turkey it is used, when fresh, in the place of soap, and as a kind of fuller's earth. From the East large quantities are sent to Vienna to be carved as tobacco pipes. The pipes are prepared for use by being soaked in melted tallow and wax, and are polished with shave grass. Imitations are fabricated in plaster of Paris hardened with paraffin, and in a preparation of potatos treated with dilute sulphuric acid. L. J. S.

MEGASSE. Spent or crushed sugar-cane.

MEILER. The German name for the stack of timber piled up for burning into charcoal (*v.* Carbon).

MELACONITE. Native copper oxide CuO (*v.* Copper).

MELANTERITE. Native ferrous sulphate (*v.* Iron).

MELDOLA'S BLUE *v.* Oxazine colouring matters.

MELDOMETER. An instrument designed for the purpose of ascertaining the melting and boiling-points of small quantities of substances. It consists essentially of two pairs of forceps mounted on a stage and carrying between them a thin platinum ribbon. Through this ribbon an electric current may be passed, the strength of the current being regulated by a carbon-mercury rheostat. The apparatus is mounted on the stage of a compound microscope, provided with a 1-inch objective. The substance to be examined is placed in focus on the platinum ribbon, and then the current is gradually increased until the substance is melted or volatilised. Experiments made in this way show interesting phenomena, sufficiently characteristic in many cases to identify a substance at once. By arranging side by side different fragments it is easy to find their order of melting-points with greater exactness than can be the case when the blow-pipe is employed.

The meldometer is also of value in studying sublimates. A piece of glass is held over the heated strip and upon this the sublimate deposits. A long series of trials have led to the conclusion that the appearances so obtained are excellent as tests to the mineralogist and chemist (J. Joly, Industries, 1889, 20, and J. Soc. Chem. Ind. 8, 306).

MELEZITOSE *v.* Carbohydrates.

MELIBIOSE *v.* Carbohydrates.

MELICITOSE *v.* Carbohydrates.

MELINITE *v.* Explosives.

MELISSA. The leaves and tops of *Melissa officinalis* (Linn.) contain a small quantity of a volatile oil. They are used occasionally in the form of a warm infusion as a diaphoretic in slight febrile conditions.

MELISSIC ACID $C_{29}H_{59}COOH$ is obtained by heating myricyl alcohol with soda-lime at 220° until hydrogen ceases to be evolved (Stürcke, Annalen, 223, 295); m.p. 91° (Marie, Ann. Chim. Phys. [vii.] 7, 145). It is probably identical with an acid found in beeswax (Nafzger, Annalen, 224, 225; Marie, *l.c.*).

MELISSYL ALCOHOL, MYRICYL ALCOHOL *v.* Waxes.

MELITOSE, *Raffinose* (*v.* Carbohydrates).

MELLITIC ACID. *Benzenehexacarboxylic acid* (Ger. *Mellithsaüre*) $C_6(CO_2H)_6$. Obtained by oxidising charcoal with fuming nitric acid, fuming nitric acid and potassium perchlorate, or with sulphuric acid (Dickson and Easterfield, Chem. Soc. Proc. 1898, 163; Staudenheimer, Ber. 1899, 2824; Hübner, Chem. Zeit. 1890, 440; Verneuil, Compt. rend. 1907, 132, 1340; Bartoli and Papasogli, Gazz. chim. ital. 15, 546; Schulze, Ber. 1871, 802, 806; also *v. infra*). By the electrolysis of alkaline solutions, using graphite electrodes, mellitic acid $C_6(CO_2H)_6$, hydromellitic acid $C_6H_6(CO_2H)_6$, and pyromellitic acid

$$C_6H_2(CO_2H)_4$$

are formed (Bartoli and Papasogli, Gazz. chim. ital. 1882, 113; 1883, 37). Also formed together with pyromellitic acid as a decomposition product of sugar (Lippmann, Ber. 1894, 3408). Has been synthesised by passing a current of methyl chloride through a warm solution of toluene containing aluminium chloride and oxidising the hexamethylbenzene thus formed with potassium permanganate (Friedel and Crafts, Compt. rend. 91, 257; Ann. Chim. Phys. [vi.] 1, 470). Mellitic acid is best prepared in the following way: Carbon, fine enough to pass through an 80 or 90 sieve is boiled vigorously with nitric acid (sp.gr. 1·5) until the liquid becomes faintly amber in colour; this usually takes 3 days. The excess of nitric acid is distilled off at 130°–140° and the residue, containing 80–90 p.c. mellitic acid extracted with water (Holliday & Sons and Silberrad, J. Soc. Chem. Ind. 1908, 522; Eng. Pat. 24662; D. R. P. 214252). According to Michael (Ber. 1895, 1631), the raw material may be purified by boiling with acetic acid, filtering and concentrating the filtrate.

Mellitic acid decomposes when heated in an open tube at about 260° and has no definite melting-point under these conditions, but when heated in a closed tube melts at 286°–288° (Michael, Ber. 1895, 1631); crystallises in long needles, soluble in alcohol and ether: heat of formation, 546·8 cal.; heat of combustion, 788·2 cal. (Stohmann, Kleber, and Langbein, J. pr. Chem. [ii.] 40, 128); heat of solution +3·672 cal. at 20·4° (Berthelot, Compt. rend. 101, 685): dissociation of acid (Quartaroli, Gazz. chim. ital. 1905, 35, i. 470). It dissolves unchanged in boiling sulphuric acid, and is not acted on by chlorine, bromine, concentrated nitric or hydriodic acids. Dry distillation yields carbon dioxide and pyromellitic acid, and by strong heating with glycerol trimesic acid and carbon dioxide are produced. By fusion with caustic soda, benzene and carbon dioxide are formed (Baeyer, Annalen, Suppl. 7, 5); reduction with sodium amalgam yields hydromellitic acid. By the electrolysis of the aqueous solution, the chief gaseous products are oxygen, hydrogen, and carbon dioxide, very little carbon monoxide being produced (Boungué, Bull. Soc. chim. [ii.]

35, 561). Acetonitrile and mellitic acid give rise to the triimide, *paramid* $C_6(C_2O_2NH)_3$ and the diimide, *euchrons* $C_6(C_2O_2NH)_2(CO_2H)_2$, when heated at 265°–275° (Mathews, J. Amer. Chem. Soc. 20, 648). A warm aqueous solution of the acid acts on anhydrous or hydrated bismuth oxide producing bismuth mellitate $Bi_2C_{12}O_{12}$, which when heated under reduced pressure in closed tubes at 350° yields pyrophoric bismuth (Thibault, Bull. Soc. chim. 1904, [iii.] 31, 135). Mellitic acid condenses with resorcinol to form phthaleins (Silberrad, Chem. Soc. Trans. 1906, 1787; Green, Chem. Soc. Proc. 1907, 12) and with amino-phenols to form rhodamines (Silberrad and Roy, *ibid.* 1908, 204; J. Amer. Chem. Soc. 32, 189); these compounds are dyestuffs (Eng. Pat. 28638; J. Soc. Chem. Ind. 1903, 414). According to Van Loon (Ber. 1895, 1271), mellitic acid is not esterified by alcohol and acids; but Meyer (Monatsh. 1904, 25, 1201) states that by heating mellitic acid with methyl alcohol and sulphuric acid in a benzene bath, the *pentamethyl ester*, m.p. 141°–144°, is formed; at 100° a mixture of the pentamethyl and hexamethyl esters is produced and at higher temperatures the hexamethyl ester predominates. The *hexamethyl ester* melts at 187° and may be formed by the action of methyl iodide on the silver salt (Kraut, J. 1862, 281; Kraut and Busse, Annalen, 177, 273) or by the action of diazomethane on the acid (Pechmann, Ber. 1898, 501). The *hexaethyl ester* melts at 73°.

MELON. The fruit of various plants of the *Cucurbitaceæ* of tropical or sub-tropical countries. There are many varieties, among which may be mentioned musk-melon, *Cucumis melo* (Linn.), and water melon, *Citrullus vulgaris* (Schrad.). The characteristic of melons is the large quantity of water which they contain, while the solid matter consists mainly of dextrose.

Bersch (Landw. Versuchs. Stat. 1896, 46, 473) found the following:—

	Sugar melon		Persican melon		Water melon	
	Whole fruit	Flesh	Whole fruit	Flesh	Whole fruit	Flesh
Water .	92·85	95·15	93·87	95·90	93·44	93·69
Dry matter	7·15	4·85	6·13	4·10	6·56	6·31

The dry matter contained—

		Protein	Fat	Dextrose	Other N-free extract	Crude fibre	Ash
Sugar melon	Whole	22·25	6·73	36·32	12·97	14·90	6·84
	Flesh	13·39	1·69	70·63	0·29	6·90	7·09
Persican melon	Whole	20·71	13·14	30·18	4·49	21·50	9·94
	Flesh	11·80	1·85	65·85	3·44	8·44	8·62
Water melon	Whole	13·74	6·89	37·36	21·74	15·41	4·86
	Flesh	9·73	1·06	66·73	16·95	1·95	3·58

The seeds of melons contain much oil (30–40 p.c.).

For analyses of the pulp of several varieties of melon, *v.* Saco (Compt. rend. 94, 1126); also Jaffa (Rep. Agric. Expt. Stat. California, 1894–95, 155).

The ash of water melon is rich in potash and iron (Payne, J. Amer. Chem. Soc. 1896, 18, 1061). H. I.

MELTING-POINT. A knowledge of the melting-point of a substance, *i.e.* the temperature of its transition from the solid to the liquid state, is of importance for many reasons. Thus the melting-point of an *organic compound* affords a criterion of purity and constitutes a means of identification, and is of service in elucidating relations in chemical constitution.

Melting-points of *alloys* yield evidence of the existence of eutectics and compounds formed from the constituent metals.

Melting-points of *hydrates* may be used to determine their degree of hydration (Roozeboom, Zeitsch. physikal. Chem. 1893, 10, 477; Lidbury, *ibid.* 1902, 39, 453).

Melting-points of *silicates* serve to indicate the formation of double and complex silicates, and the dissociation of complex silicates into simpler molecules.

Melting-points of *pure substances* provide standards in calibrating thermometric apparatus.

Occasionally, on heating under ordinary conditions, sublimation occurs without melting, as in the cases of iodine and fumaric acid, when the usual methods are not applicable. But, generally speaking, every pure substance exhibits a definite melting-point, sharp and well-defined, and identical with its solidifying point. The slightest impurities, however, such as traces of moisture, frequently lower the melting-point considerably, although it may be still apparently sharp; whilst if foreign substances are present in larger quantity, it is no longer well-defined, nor coincident with the solidifying point. It has been observed (Rohland, Chem. Zentr. 1906, i. 1401) that in some instances addition of impurities may raise instead of lower the melting-point. Pure aluminium melts at a lower temperature than the impure metal, and alumina raises the melting-point of pure kaolin.

Within the ordinary limits, change of atmospheric pressure has no sensible effect upon the melting-point, but at high pressures the effects may be very considerable, *cf.* Demerliac (Compt. rend. 1897, 124, 75); Hulett (Zeitsch. physikal. Chem. 1899, 28, 629); Tammann (Ann. Chim. Phys. 1899, [ii.] 68, 553, 629). The melting-point of benzene, for example, varies from 5·4° to 36·5° with pressures ranging from 1 to 1200 kilos. per sq. cm.

For theoretical relationships, *see* Thomson (Phil. Mag. [iii.] 37, 123), Negreanu (Chem. Zentr. 1906, i. 116).

Pawloff (Zeitsch. physikal. Chem. 1908, 65, 1; 1909, 65, 545) finds that even with a pure substance, the melting-point is affected by the state of subdivision, that is, it is dependent on the surface energy, and he deduces an equation expressing the relation between the melting-point of a substance and the radius of its granules. Experiments with salol showed that particles of less than 2μ diameter melt 1·1° lower than those of 40μ.

He considers that the lowest attainable temperature in the region of fusion is determined by the melting-point of the crystalline germ of maximum surface, and that larger solid particles above this temperature are super-heated. Similarly the super-cooling of liquids is a general phenomenon, a liquid super-cooled to a definite extent being in equilibrium with solid particles of a definite size, larger particles causing crystallisation and smaller particles dissolving, and the limit of super-cooling is that temperature below which the crystalline germ can arise of itself in the interior of the liquid.

Apart from the foregoing considerations, the manipulative details concerned in the actual determination of a melting-point, particularly by the capillary tube method, *v. infra*, affect the result. This is due partly to unequal heating of the thermometer stem, which may be corrected by adding the value $n(\mathrm{T}-t)\times 0{\cdot}000143$ to the observed point of fusion (n=length of mercury column in degrees outside the bath, T=observed temperature, and t=temperature registered in the middle of the projecting portion of the column), or avoided by using a short-stemmed thermometer (see Fig. 1). Irregular and too rapid heating is also found to affect the value. Schuyten (Chem. Zentr. 1901, ii. 1326) adduces instances of the variations which may be obtained under different conditions of experiment.

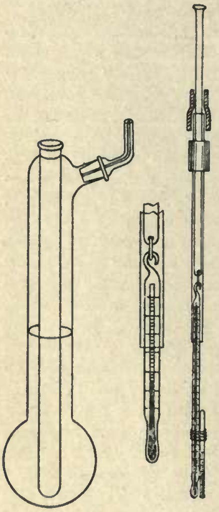


FIG. 1.

The fusion of a solid substance is accompanied by an absorption of heat ('latent heat of fusion'), the temperature remaining constant till all the solid has melted. This provides the most accurate means of determination (Landolt, Zeitsch. physikal. Chem. 1889, 4, 349), the thermometer, or thermo-element with galvanometer attachment, being immersed in the molten substance, and the temperature of the slowly cooling liquid noted at short intervals, the resulting curve indicating the stationary temperature. This method is suitable for all ranges of temperature and for all substances giving a definite melting-point, but requires the use of large quantities of material. In the case of organic compounds, a small quantity of the finely pulverised substance is introduced into a capillary tube closed at one end, and attached to a thermometer, close to the bulb, usually by a thin platinum wire or indiarubber ring, or by adhesion through a drop of sulphuric acid. Weyl (Chem. Zeit. 1910, 34, 488) uses a thermometer slightly expanded just above the bulb, supporting a glass ring carrying glass hooks upon which the tubes are hung in position close to the bulb. Other methods of attachment are described by Lenz (Chem. Zentr. 1906, i. 169); Landsiedl (Chem. Zeit. 1905, 29, 765).

The heating bath may be of glycerol, paraffin, or sulphuric acid, the last-named substance being most generally used. It is contained in a small beaker or long-necked flask, the thermometer and tube being either immersed in the liquid or enclosed in a tube dipping into the liquid.

A form of laboratory apparatus is shown in Fig. 2, unequal heating being avoided, as far as possible, by stirring with a glass stirrer passing through the cork holding the thermometer, or by heating very slowly with a small flame. For temperatures at which the escape of sulphuric acid fumes becomes unpleasant, the flask is provided with a side tubulure (Roth, Ber. 19, 1970), as shown in Fig. 1. Alternative apparatus for condensing the fumes are described by Houben (Chem. Zeit. 1900, 24, 538) and Matton (Zeitsch. angew. Chem. 1910, 23, 557).

A mixture of three parts potassium sulphate with seven of sulphuric acid, sp.gr. 1·84, boiled together for five minutes, may be used for temperatures up to 325°. From 360° to 600°, fused zinc chloride gives satisfactory results (Scudder, J. Amer. Chem. Soc. 1903, 25, 161).

Thiele (Ber. 1907, 40, 996) has devised a simple and effective apparatus, consisting of a glass tube 2 cm. diameter and 12 cm. long, with a bent tube of 1 cm. diameter sealed in as shown in Fig. 3. Sufficient sulphuric acid is poured in to cover the upper opening of the bend, and the lower bend is heated by a small flame which causes an even circulation of the acid.

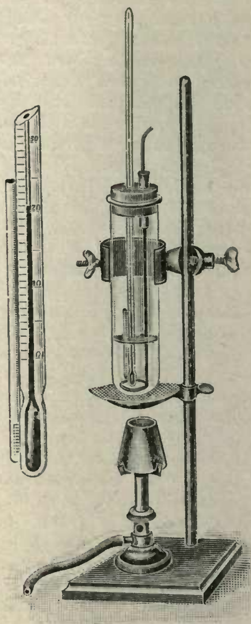


FIG. 2.

If the material is transparent, or becomes so before the melting-point is reached, observation of the exact point at which it liquefies is difficult, and Piccard (Ber. 8, 687) has proposed the apparatus shown in Fig. 4, in which the wide tube (*b*) is sealed after a small quantity of the substance has been melted and allowed to solidify in the capillary bend. On fusion the air pressure in *b* forces the liquid forward. The melting-points of coloured substances are conveniently obtained in this way (Baither, Ber. 1887, 20, 3290). The values are, however, slightly too high.

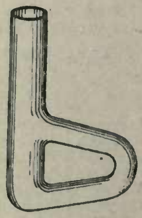


FIG. 3.

As modified by Potilitzin (Chem. Zentr. 1893, i. 379) for the melting-points of salts, the apparatus consists of a glass tube, 5 mm. wide and 50 cm. long, drawn out to a capillary at one end, the other being bent first at right angles, and then in the shape of a U to form an open manometer. The capillary is sealed with the molten salt and immersed in the bath. When the salt melts, the mercury sinks in the open end of the manometer. The method is employed to advantage where a non-transparent heating bath is used.

For organic compounds which decompose at or near the melting-point, Maquenne (Bull. Soc. chim. 1904, 31, 471) advocates the use of a metal block, rapidly heated, upon which the substance is thrown in small portions (0·1 m.g.)

at a time, till the point is reached at which the substance melts instantaneously. *See* also Michael (Ber. 1895, 28, 1629).

Fatty acids, waxes, and similar bodies are not easily introduced into capillary tubes, and in such cases Kuhara and Chikashigé (Chem. News, 1899, 80, 270) place a thin layer of the substance between microscope cover glasses suspended in a platinum foil support in a test-tube placed in the sulphuric acid bath. A modified method is described by Bunker (Pharm. J. 1909, [iv.] 28).

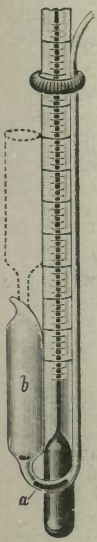


Fig. 4.

Air baths, which may be used at high temperatures instead of liquid baths, are described by Anschütz and Schultz (Ber. 1877, 10, 1800) and Kutscher and Otori (Zeitsch. physiol. Chem. 1904, 42, 193).

For a comparison of the different methods of procedure in the case of minute quantities of material, see Reinhardt (Zeitsch. anal. Chem. 25, 11).

The air thermometer has been adapted for use at extreme temperatures (Haase, Ber. 1893, 26, 1052; Meyer, Riddle, and Lamb, *ibid.* 1894, 27, 3129) but is less convenient than the thermo-element, for the application of which consult McCrae (Ann. Phys. Chem. 1895, [2] 55, 95); Carrara and Coppadoro (Gazz. chim. ital. 1903, 33, 1, 329); Guttmann (Chem. Soc. Trans. 1905, 87, 1037).

Stolzenberg (Ber. 1909, 42, 4322) has described two ingenious forms of apparatus for temperatures up to 350° and down to −60° respectively, which are similar in principle to that of Thiele, but the circulation is brought about not only by heating or cooling a spiral side tube, but also by bubbling dry carbon dioxide through it. For high temperatures, paraffin is used, and for low temperatures alcohol, the spiral being cooled in a Dewar flask with ether and solid carbon dioxide.

Slightly modified, it provides an accurate means of determining solubilities and (Chem. Zeit. 1910, 34, 66; Zeitsch. physikal. Chem. 1910, 71, 649) of measuring temperatures down to −140°, and is recommended as a low-temperature bath in physico-chemical laboratories. For further particulars and diagrams of apparatus, the original papers should be consulted.

A number of electrical methods have been devised, depending upon the completion of a circuit when the insulating coating of a substance on a platinum wire dipped in mercury melts (Löwe, Zeitsch. anal. Chem. 11, 211; Thierry, Arch. Sci. Phys. Nat. 1905, [iv.] 20, 59; or the breaking of a circuit when a wire connection in the case of metals (Loebe, Zeitsch. Elektrochem. 1907, 13, 592; Shukoff and Kurbatoff, J. Russ. Phys. Chem. Soc. 1907, 39, 1546; Jacquerod and Perrot, Arch. Sci. Phys. Nat. 1905, [iv.] 20, 28), or a bead connection in the case of borax and other glasses (Burgess and Holt, Proc. Roy. Soc. 1904, 74, 285) is broken on fusion, the temperature being ascertained by a thermo-element.

Burgess (Bureau Stand. Washington, 1907, 3, 345) describes an adaptation of the optical pyrometer to the determination of the melting-points of metals.

The melting-points of silicates are determined by Doelter by placing the finely powdered substance upon a small quartz plate heated in an electric resistance furnace, and observing with a microscope as the temperature is slowly raised (Zeitsch. Elektrochem. 1906, 12, 617).

A general account of melting-point methods at high temperatures is given by White (Amer. J. Sci. 1909, [iv.] 28, 453).

MENDIPITE. A lead oxychloride $PbCl_2{\cdot}2PbO$ found near Churchill on the Mendip Hills in Somersetshire. Crystallises in yellowish white rhombic prisms; perfect prismatic cleavage; adamantine lustre, sp.gr. 7·1.

MENHADEN OIL is obtained from the body oil of the 'Menhaden fish' *Alosa menhaden*, Cuv. (*Brevoortia tyrannus*), a fish somewhat larger than a herring. From about May until November this fish appears in enormous quantities off the Atlantic coast of America (especially of New Jersey), so that as much as 400,000 tons of fish are caught in one season.

The fish are delivered from the steamers by means of elevators, on to automatic conveyors, from which they are passed over automatic scales into large boiling pans. These are provided with false bottoms, below which open steam coils are fixed. On boiling the contents of the pan, the fish are disintegrated and the oil separates easily from the flesh. After turning off the steam and allowing the mass to rest, the oil rises to the top and can be easily skimmed off by means of swivel skimmers.

During the last few years, 'boiling' vessels have been introduced which permit of continuous working, the fish being passed on conveyors through the boilers continuously, whilst open steam acts on the fish. The time required for the fish to pass lasts from 15 to 20 minutes. The whole mass is then transported by screw conveyors into settling tanks, where the oil separates by gravitation. In either process, the 'fish scrap' falls to the bottom of the vessels, and is then pressed in hydraulic presses, similar to those used in the working up of 'tankage,' when a further quantity of oil, inferior in colour, is obtained. In some works, such pressed cake —termed 'chum'—is boiled out with hot water and pressed once more; but this process being unremunerative, except when the oil is very high in price, is not carried out in large works. The scrap is finally dried in continuous dryers, of which various types are in use (Anderson dryer, Cummer dryer, vacuum dryers), and is sold as a valuable manure. In fact, the 'scrap' was formerly considered as the main product, and it is owing to the demand for scrap that the fish oil industry has assumed such large dimensions. As the fish contain only from 1 to 16 p.c. of oil —rarely more—processes for its recovery from the scrap by means of solvents are most unlikely to prove remunerative, considering the enormous quantities of fish that must be dealt with.

With the extension of the industry, new uses have been found for the oil, which now not only ranks equal in value to the scrap, but has acquired a much higher price, especially at times when the price of linseed oil is very high.

The colour of menhaden oil varies in the first instance with the state of freshness in which the fish arrives, and in the second instance with the duration of the boiling process. The longer the oil has been allowed to remain in contact with the putrescible mass and the longer the fish has been boiled and hence the longer the oil has been in contact with the gluey water, the darker is its colour. Therefore, the separation of the oil from the gluey water is carried out as rapidly as possible. Fresh fish yield a light-coloured oil; the oil running from the 'scrap' in the presses is the darkest in colour.

In commerce the following three qualities are known: 'Prime crude,' 'Brown strained,' and 'Light strained oil.' Frequently the oils are differentiated into four grades—A, B, C, and D; A being extra pale, B pale, C brown, and D dark brown oil. Since the menhaden oil industry has extended along the Atlantic coast even down to Texas, the trade differentiates also between *northern menhaden oil* and *southern menhaden oil.* The process of refining consists mainly in brightening the oil by filtering, &c.

The light-coloured oils are allowed to rest some time in the cold, whereby 'stearine' separates; thus the 'winter oils' are obtained. They are then bleached by filtering over fuller's earth, &c.; in this manner two grades are obtained, viz. 'bleached winter white' and 'bleached winter' oils.

The sp.gr. of menhaden oil is 0·930 to 0·935. Freshly prepared menhaden oil has an iodine value reaching as high as 200 (Lewkowitsch). Most of the analytical data contained in textbooks must be corrected, especially as regards the iodine value, as those samples, the iodine values of which had been recorded, refer to oils which have undergone considerable oxidation on standing. Menhaden oil contains considerable amounts of clupanodonic acid. Thus the author obtained from specimens of pure menhaden oil as high a yield as 40 p.c. of clupanodonic octobromide.

The unsaponifiable matter consists chiefly of cholesterol, to the presence of which the slight optical activity of menhaden oil is due.

The principal use of menhaden oil is in the currying trade, and in the manufacture of sod oil. The oil is also employed in soap-making and for the tempering of steel. When linseed oil is high in price, menhaden oil is used to a considerable extent to adulterate linseed oil (to the detriment of the quality of the product) and further as a substitute thereof in the manufacture of varnishes, paint oils, and even linoleum. Menhaden oil is also used for adulterating Newfoundland cod-liver oil.

J. L.

MENTHANTHONES *v.* KETONES.

MENTHENE *v.* CAMPHORS, TERPENES.

MENTHOL *v.* CAMPHORS.

MENTHONE *v.* CAMPHORS.

MERCAPTANS (*sulphhydrates, thioalcohols*) are a group of substances derived from sulphuretted hydrogen in the same way as alcohol from water by the replacement of one hydrogen atom by an alkyl group. The mercaptans differ from alcohol in the same way that sulphuretted hydrogen differs from water; thus they have considerably lower boiling-points than the corresponding alcohols. They also possess one hydrogen atom replaceable by metal, but they are more acidic than the alcohols and form mercaptides of the heavy metals. The mercaptans were discovered by Zeise in 1833 (Annalen, 11, 2), and the name is derived from 'mercurio aptum,' owing to the formation of a characteristic mercury salt by the action of ethyl mercaptan on mercury oxide.

Formation.—General methods:

(1) By warming alkyl halides with potassium hydrogen sulphides in concentrated alcoholic solution.

$$R\boxed{X+K}SH=R{\cdot}SH+KX$$

(where R=alkyl, X=halogen).

(2) By heating alcohols or phenols with phosphorus pentasulphide

$$5ROH+P_2S_5=5R.SH+P_2O_5.$$

(3) By distilling a solution of potassium alkyl sulphate with potassium hydrogen sulphide.

$$R\boxed{OSO_3K+K}SH=R{\cdot}SH+K_2SO_4.$$

They are also formed in the reduction of thiocyanic esters, $CNS{\cdot}R+2H=HCN+HSR$.

Aromatic mercaptans can be obtained by acting on the diazo-aromatic compounds with potassium ethyl xanthate and decomposing the compound thus formed with caustic alkali (Lenhart, J. pr. Chem. [ii.] 41, 179; Bourgeois, Rec. trav. chim. 1899, 18, 426); by the reduction of the chloride of the sulphonic acid derivative, and by the electrolytic reduction of the thiochlorides or their nitro derivatives in sulphuric acid solution using lead electrodes and keeping the anode liquid at 20° (Fichter and Bernouilli, Ber. 1909, 42, 4308).

Mercaptans of the anthracene series are obtained by heating together the halogenated anthraquinones and the alkali sulphides or hydrosulphides (D. R. P. 204772, 208640; Frdl. 1908–10, 20).

Mercaptans of the anthraquinone series are obtained in the following manner: 10 kilos. of anthraquinone-α-thiocyanate are made into a paste with 20 litres of alcohol and boiled under a reflux condenser with 60 litres of a 10 p.c. sodium hydroxide solution until the product forms a clear cherry red solution in water. Hot water is now added until the whole product is dissolved and after filtration, the mercaptan is precipitated by addition of hydrochloric acid containing a little sulphurous acid (D. R. P. 208640, 1907; 212857, 1909; J. Soc. Chem. Ind. 1909, 469).

Mercaptans yielding dyes with diazo compounds can be obtained by heating sodium naphthalene-β-sulphonate and a 50 p.c. solution of potassium hydrosulphide for 3 hours at 200°–220° under a pressure of 10–12 atmospheres in an iron vessel. The product is then treated with dilute hydrochloric acid and extracted with ether. The disulphide which remains undissolved can also be converted into the mercaptan by heating with potassium hydrosulphide and alcohol. When benzene sulphonic acid and *m*-disulphonic acid are similarly treated, coloured products having the odour of mercaptans are formed (Schwalbe, Ber. 1906, 39, 3102).

Properties.—The mercaptans are mostly liquids insoluble in water, soluble in alkalis and, particularly the lower, more volatile ones, have a very characteristic disagreeable odour, their smell being indeed a far more delicate test than any of their chemical reactions. Like hydrogen sulphide they are readily oxidised by oxidising agents and even by air, forming disulphides $2R{\cdot}SH+O=RS{\cdot}SR+H_2O$. When oxidised with nitric acid they form sulphonic acids

$$R{\cdot}SH+O_3=RSO_3H.$$

Mercaptans condense with nitriles thus:

$$RSH+R'CN=NH:CR'{\cdot}SR$$

Thus by the action of ethylene cyanide on ethylene sulphhydrate, *succiniminodithioethylene ether* $(CH_2C(NH){\cdot}S{\cdot}CH_2)_2$ is formed, the hydrochloride of which is an amorphous dark green powder soluble in water; the solution dyes wool and silk a bright green, fast to light but turning yellow (owing to the liberation of the free base) when treated with alkalis (Autenrieth and Brüning, Ber. 1903, 36, 3464).

The alkyl mercaptans and their derivatives react in general with acid chlorides to form esters of the corresponding thio acids thus:

$$3RSH+PCl_3=P(SR)_3+3HCl$$

or $(COCl)_2+Pb(SC_6H_5)_2=(CO{\cdot}S{\cdot}C_6H_5)_2+PbCl_2$. The final products of the reaction, however, depend on the stability of the ester formed, or, if it is unstable, on the manner of its decomposition. When treated with hot potassium hydroxide solution, the stable esters are converted into the mercaptide, whilst with alcoholic potassium hydrosulphide they yield potassium thio salts (Jones and Tasker, Chem. Soc. Trans. 1909, 1904).

With sulphuryl chlorides, the mercaptans react thus:

$$8RSH+4SOCl_2=8HCl+2SO_2+3(R{\cdot}S)_2+R_2S_4$$

and $4RSH+SOCl_2=(R{\cdot}S)_2+R_2S_3+H_2O+2HCl$ which reaction preponderates depending on the conditions of the experiment (Jones and Tasker, *l.c.* 1910). The reaction of mercaptans with nitrosyl chloride and with thionylaniline is similar to that with sulphuryl chloride. When nitrosyl chloride is added to a mercaptan, the latter absorbs it, forming a rich cherry-red coloured solution which rapidly evolves nitric oxide and finally loses its colour. In a freezing mixture of solid carbon dioxide in ether, however, hydroxylamine hydrochloride is formed (Jones and Tasker, *l.c.*; Holmberg, Ber. 1910, 43, 226).

Mercaptans combine with aldehydes in the presence of hydrogen chloride, forming *mercaptals*, $R{\cdot}CH\boxed{O+2H}SR'=R{\cdot}CH(SR')_2$ (Baumann, Ber. 1885, 18, 883; Blanksma, Rec. trav. chim. 1901, 20, 399). They are insoluble in water, stable in the cold but readily decomposed on warming.

Mercaptans combine with certain sugars in cooled hydrochloric acid solution, forming mercaptals (Fischer, Ber. 1894, 27, 673).

Glucose ethyl mercaptal $C_6H_{12}O_5(SEt)_2$ forms slender colourless needles or thin plates, m.p. 127°–128°, α_D $-29{\cdot}8°$ at 50°. It has a bitter taste and decomposes on distillation, yielding a product with an odour of roasted onions. A number of other similar mercaptals are described by Fischer.

Similarly, the mercaptans condense with ketones, forming *mercaptoles*

$$R_2C\boxed{O+2H}SR'=R_2C{\cdot}(SR')_2+H_2O$$

(Baumann, *l.c.*; Posner and Fahrenhorst, Ber. 1899, 32, 2749; Blanksma, *l.c.*), and the latter, on oxidation, yield disulphones.

The nature and stability of the mercaptoles and disulphones formed by the interaction of ketonic esters and the mercaptans depend both on the nature of the ester and of the mercaptan (Posner, Ber. 1901, 34, 2643).

α-, β-, or γ-Diketones containing both carbonyl groups attached to methyl radicles, readily react with four molecules of a mercaptan yielding dimercaptoles which on oxidation yield tetrasulphones. If, however, one of the carbonyl groups of the diketones is attached to a substituted methyl group, the ketone reacts with only two molecules of a mercaptan forming a ketomercaptol which on oxidation gives a keto-disulphone. A number of these products are described by Posner (Ber. 1900, 33, 2983).

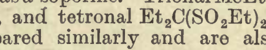
In the presence of hydrochloric acid, the mercaptans react with unsaturated ketones, forming both addition and condensation products (Posner, Ber. 1902, 35, 799; 1904, 37, 502; *see* also Fasbender, Ber. 20, 460); but if piperidine or sodium ethoxide is employed as catalytic agent instead of hydrogen chloride, only additive products are obtained (Ruhemann, Chem. Soc. Trans. 1905, 17, 461; Proc. Roy. Soc. 1904, 251). The number of mercaptan groups uniting with a diolefinic ketone also depends on the nature of the catalytic agent. The mercaptans also combine with many unsaturated hydrocarbons and acids (Posner, Ber. 1905, 38, 646; *ibid.* 1907, 40, 4788).

According to Stadler (Ber. 1884, 17, 2075), the mercaptans of the aliphatic series react with diazo compounds yielding explosive substances.

Ethyl mercaptan (mercaptan), produced technically by the interaction of ethyl chloride and potassium hydrogen sulphide, is a sparingly soluble liquid with a very disagreeable smell, b.p. 36·2°, sp.gr. 0·83907 at 20°/4° (*v. Ethyl sulphydrate*, art. ETHYL). It combines with acetone, forming dimethyl diethyl mercaptole, which when oxidised with potassium permanganate yields diethyl sulphomethyl methane (acetonediethyl sulphone) $Me_2C(SO_2Et)_2$. The latter crystallises in colourless prisms, m.p. 126°, is sparingly soluble in water and is employed in medicine, under the name 'sulphonal,' as a soporific. Trional $MeEtC(SO_2Et)_2$, m.p. 75°, and tetronal $Et_2C(SO_2Et)_2$, m.p. 85°, are prepared similarly and are also used in medicine (*v.* TETRONAL AND TRIONAL).

Ethyl mercaptan has no action on anthraquinone or phenanthraquinone, but it reacts with quinone forming quinol, quinhydrone, and thioaldehyde and under certain conditions it forms a red crystalline compound in which two hydrogens in the quinone nucleus are substituted by SEt groups (Tarbouriech, Bull. Soc. chim. 1901, [iii.] 25, 313; Sammis, J. Amer. Chem. Soc. 1905, 27, 1120).

Ethyl mercaptophthalimide



$$C_6H_4\left\langle\begin{matrix}CO\\CO\end{matrix}\right\rangle N(CH_2)_2SH$$

becomes plastic at 76° and melts at 79°–80°. When boiled with 20 p.c. hydrochloric acid it yields phthalic acid and aminomercaptan hydrochloride $NH_2C_2H_4SH,HCl$ (Gabriel, Ber. 1891, 24, 1110, 3098).

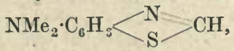
Phenyl mercaptan has b.p. 169·5°; *p-tolyl* *mercaptan*, b.p. 195°; *m-tolyl mercaptan*, b.p. 195·5°; and *β-naphthyl mercaptan*, b.p. 288° (Bourgeois, *l.c.*; Autenrieth and Geyer, Ber. 1908, 41, 4256).

p-Tolylaminoanthraquinone mercaptan

$$C_7H_7NHC_{14}H_6O_2SH$$

forms dark blue needles and yields on sulphonation a violet wool dye (D. R. P. 206536, 1909).

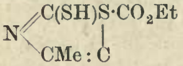
Anhydroformaldehyde dimethyl-p-phenylenediamine mercaptan (*5-dimethylamino-2-methyleneaminophenyl mercaptan*) $SHC_6H_3(NMe_2)N:CH_2$ is formed by treating *as*-dimethyl-*p*-phenylenediamine thiosulphonic acid dissolved in aqueous ammonia, with formaldehyde and hydrochloric acid. It rapidly polymerises and is isolated as the ferrocyanide $3C_9H_{12}N_2S,2H_4Fe(CN)_6,5H_2O$. When the freshly prepared mercaptan is treated with sodium nitrite and hydrochloric acid it yields 5-dimethylaminobenzthiazole



m.p. 73°-74° (Schmidt, Ber. 1906, 39, 2406).

Mercaptothiazoles are prepared by the condensation of α-halogenated ketones with ammonium dithiocarbamate (Miolati, Gazz. chim. ital. 23, i. 575).

Ethyl methyl mercaptothiazolecarboxylate

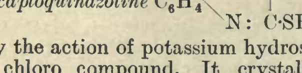


melts at 141°, and is soluble in alcohol and ether but not in water; the free acid has m.p. 211°-212°.

Methylmercaptothiazole melts at 89°-90° and is soluble in organic solvents. *Phenyl mercaptothiazole* melts at 168°.

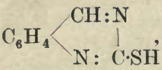
For a number of mercaptothiazoline derivatives, see Hirsch (Ber. 23, 964); Kahan (*ibid.* 1897, 30, 1318); Gabriel and Leupold (*ibid.* 1898, 31, 2837); Jänecke (*ibid.* 1899, 32, 1103); Straus (*ibid.* 1900, 33, 2830).

Mercaptogalactoxazoline



m.p. 185°-186°, is formed by heating galactamine with carbon disulphide. Like the corresponding dextrose derivative it gives a crystalline compound with silver nitrate (Roux, Compt. rend. 1902, 135, 691).

2-*Mecaptoquinazoline*



, is prepared by the action of potassium hydrosulphide on the chloro compound. It crystallises in hexagonal plates, sinters at 225° and melts at 229°-231° (Gabriel, Ber. 1903, 36, 800). Mercapto oxazoline derivatives are described by Maquenne and Roux (Compt. rend. 1902, 134, 1589).

Many other mercaptan derivatives have been prepared (Baumann, Ber. 1885, 18, 891; Jacobson, *ibid.* 1887, 20, 1895; *ibid.* 1888, 21 2624; Klason, *ibid.* 20, 3409; *ibid.* 28, ref. 942; Freund, *ibid.* 1896, 29, 2483; Brjuchonenko, J. pr. Chem. [ii.] 59, 46, 596; Eibner, Ber. 1901, 34, 657; Freund and Bamberg, *ibid.* 1902, 35, 1753; Posner, *ibid.* 799; de Jong, Rec. trav. chim. 1902, 21, 295; Autenrieth and Geyer, Ber. 1908, 41, 4249, 4256).

Mercaptides are formed by the action of the metal on the mercaptan (as in the case of the alkali salts) or by the interaction of an alcoholic solution of the mercaptan with the oxide or acetate of the metal.

Many such crystalline compounds are known. They are mostly decomposed by mineral acids, with liberation of the mercaptan, and react with alkyl halides forming thio ethers, thus:

$$RS|Na+I|R'=R\cdot S\cdot R'$$

(Otto, J. pr. Chem. 1895, [ii.] 51 285). With ethyl α-chloroacetoacetate they yield alkyl sulphide and ethyl diacetyl succinate:

$$2RSNa+2CMeO\cdot CHCl\cdot CO_2Et$$
$$=2NaCl+R_2S_2+(CHAc\cdot CO_2Et)_2$$

(Finger and Hemmeter, J. pr. Chem. 1909, 79, 449). The mercaptides react with mustard oils, forming dithiourethanes:

$$RNCS+R'SNa$$
$$=R\cdot N:CSNa\cdot SR' \xrightarrow{HCl} NaCl+RNH\cdot CS\cdot SR',$$

and this is suggested by Roschdestvensky as a good method of identifying the mercaptans (J. Russ. Phys. Chem. Soc. 1909, 41, 1438).

Mercury mercaptide $(EtS)_2Hg$ crystallises in white leaflets. With mercuric chloride, however, ethyl mercaptan forms a sparingly soluble double salt, EtS·HgCl. Similar iodide and bromide compounds are also known.

Mercapturic acids are hydroxycarboxylic acids in which the hydroxyl group is replaced by an SH group (Carius, Annalen 124, 43; Claesson, Ber. 1877, 1346; Friedmann, Beitr. Chem. Physiol. Path. 1903, 4, 486).

Mercaptal acids are obtained by the condensation of aldehydes with thiol acids (Holmberg and Mattisson, Annalen, 1907, 353, 123).

Selenium and tellurium form compounds corresponding with the mercaptans and having a similar offensive smell.

MERCERISING. Mercerising or 'lustreing' consists in impregnating cotton fibres with concentrated caustic soda lye, either with or without the application of tension, and in stretching the material before and during the removal of the soda by means of washing.

John Mercer noticed in 1844 that cotton fabrics, when immersed in concentrated soda lye, became transparent and that a considerable swelling and shrinkage of the fibres occurred. He also found that the soda could be readily removed by washing with water and that the fibres afterwards again became opaque and exhibited increased affinity for a number of dyestuffs. The fact that concentrated caustic soda lye causes the cotton fibre to contract seems, however, to have been known in France at the time when Mercer made his discovery (J. Hübner, J. Soc. Dyers and Col. 1911, 27). The treatment briefly described above was patented by Mercer in 1850. About the same time, he applied his discovery to the 'crimping' of cotton fabrics, by printing stripes upon the fabric with thickened concentrated caustic soda lye, with the result that the portions printed upon became contracted, whilst the parts which had not been acted upon by the soda became drawn together or 'crimped.'

It has been suggested that 'hydrated cellulose' is the result of mercerisation, but although mercerised cellulose contains more water in the air-dry condition than ordinary cellulose, C. G.

Schwalbe (Zeitsch. angew. Chem. 20, 2172, 1907) and H. Ost and F. Westhoff (Chem. Zeit. 33, 197, 1907) state that they have not been able to prove that mercerised cellulose contains chemically combined water. It should also be pointed out that the excess of water contained in mercerised cotton can be readily removed by drying (J. F. Copley, J. Soc. Dyers and Col. 24 72); by the application of heavy pressure after mercerising, whilst the material is still in the wet state (J. Hübner, Eng. Pat. 12455); by extraction with absolute alcohol (J. Hübner and F. Teltscher, J. Soc. Chem. Ind. 1909, 28, 641) and by drying at ordinary temperature over calcium chloride or phosphorus pentoxide.

In 1889, H. A. Lowe observed that if a cotton fabric is prevented from contracting during treatment with concentrated caustic soda lye and subsequent washing it acquires a silk-like lustre (Eng. Pat. 20314). Lowe allowed his patent rights to lapse and in 1895 Thomas and Prevost patented the same process in Germany (Ger. Pat. 85564). This patent was, however, ultimately annulled. Mercer had already noticed that effects, similar to those obtained by caustic soda, could be produced by the application of sulphuric acid, phosphoric acid, and zinc chloride.

Soon after the publication of Thomas and Prevost's patent, a large number of patents of doubtful value were taken out in order to protect the application of various mercerising agents. The fact that a superior lustre could be obtained on the long-stapled Sea Island and Egyptian cottons was also made the subject of a patent (*see* Gardner, Die Mercerisation der Baumwolle).

Knecht (J. Soc. Dyers and Col. 1896, 12, 89) found that cotton could be mercerised by treating it with nitric acid of 83° to 84°Tw., and J. Hübner and W. J. Pope (J. Soc. Chem. Ind. 1903, 22, 70) discovered that saturated solutions of iodides produce a similar effect. A saturated solution of barium-mercuric iodide produces practically the same degree of shrinkage and increased affinity for dyestuffs as concentrated caustic soda lye.

Mercer pointed out that soda lye of as low a strength as 20°Tw., produces a distinct effect on the cotton fibre, and it had been commonly accepted that lyes below this strength exerted practically no action on the fibres. Hübner and Pope (J. Soc. Chem. Ind. 1904, 23, 404), however, found that a lye of only 1°Tw. concentration appreciably increases the affinity of the cotton fibre for the substantive dyestuffs and produces a certain degree of shrinkage. They also showed that the degree of shrinkage is not directly proportionate to the concentration of the lye used, and that maximum shrinkage is produced by a soda lye of about 45°Tw., whilst the shrinkage again decreases if the strength of the lye is increased above 45°Tw.

This supplied an explanation of the fact that cotton yarn and cloth, after treatment under tension with soda lye of 60° to 70°Tw., are frequently torn on the mercerising machine during the first stages of washing.

It had been generally assumed that a mercerising agent, in order to produce lustre on the fibre, must exert a shrinkage and swelling action. Hübner and Pope (*l.c.*) observed that the agent must also be capable of untwisting the naturally twisted cotton fibre.

This, coupled with the fact that single cotton fibres (Fig. 1) are twisted in parts to the right and in parts to the left, several changes in the direction of the twist being noticeable in a single fibre, affords a rational explanation of the production of lustre in mercerising. As a result of the untwisting of these different twists during mercerisation under tension, during which operation the fibres are firmly held by the twist of the yarn, the original ribbon-like twisted fibre becomes converted into a straight rod, of nearly circular cross-section, which carries on its surface smooth elevations in the shape of rounded ridges, which reflect the light falling on them from any direction (Fig. 2). Maximum lustre can, therefore, only be obtained if the mercerising agent is capable of producing shrinking, swelling, and untwisting of the fibres in a high degree. Waterglass, glycerol, common salt, if added to the caustic soda lye used in mercerising, diminish the extent of the swelling and the shrinking of the fibres, the lustre obtained is, therefore, inferior to that produced by caustic soda alone. Sodium sulphide, nitric acid, and hydrochloric acid, which cause untwisting of the fibre, accompanied, however, with but little shrinking and swelling, give still less lustre, whilst barium-mercuric iodide, which produces maximum swelling and shrinking but no untwisting, produces practically no lustre.

Fig. 1.

Gladstone (Quart. J. Chem. Soc. 1853, 5, 17) suggested that in mercerising a definite chemical compound, ‘soda cellulose’ $(C_6H_{10}O_5)_2NaOH$, is formed, which decomposes readily on treatment with water. J. Hübner and F. Teltscher (J. Soc. Chem. Ind. 1909, 28, 614) have shown that the existence of such a definite compound is very doubtful and that the amount of soda retained by the cellulose after extraction with absolute alcohol is much smaller than that given by Gladstone.

The dyeing properties of mercerised cellulose have been studied by a number of investigators. R. Haller (Zeitsch. Farb. und Textilchemie, 1907, 8, 125) assumes that the soda lye removes the cutinised layer from the fibres, thus exposing pure cellulose, which is capable of absorbing dyestuffs more readily.

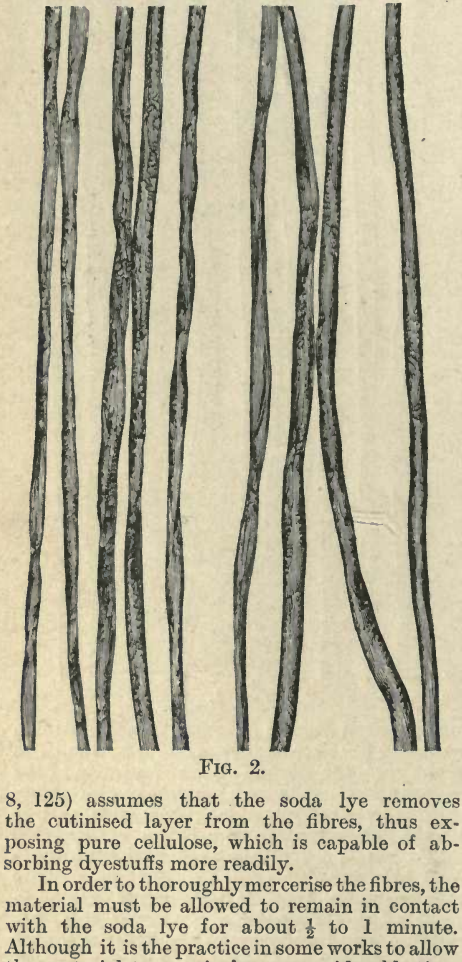


Fig. 2.

In order to thoroughly mercerise the fibres, the material must be allowed to remain in contact with the soda lye for about ½ to 1 minute. Although it is the practice in some works to allow the material to remain for a considerable time after impregnation in contact with the soda lye, and before stretching and washing, the results obtained are in no way superior to those obtained when working continuously.

Uniform results in mercerising can only be obtained if the soda lye used is kept at uniform strength and temperature. Special refrigerating machines are frequently employed for cooling the soda lye.

Doubled yarns, made of long-stapled Sea Island or Egyptian cotton, give the most brilliant results in mercerising, but good results can also be obtained on yarns spun from combed American cottons. Single yarns cannot be successfully mercerised on account of the twist being too weak to resist the shrinking of the fibres. The best results in mercerising cotton fabrics are obtained on face cloths, such as sateens, Italian linings, &c. A considerable change in the structure of the fabric takes place during mercerisation (J. Hübner, J. Soc. Dyers and Col. 1911, 27, 128).

The removal of all loose fibres from the surface of the material by careful singeing leads to an increase of the lustre of the mercerised fabric.

Cotton yarn is usually mercerised after it has been boiled in the kier whilst cotton fabrics are sometimes only scoured before mercerising. More frequently the fabrics are mercerised after the first ‘boil’ in the kier, or in some cases after they have been bleached (‘chemicked’). Cotton in the loose state, as it comes from the bale, cannot be successfully mercerised.

A number of methods have been suggested for mercerising cotton in the state of ‘sliver,’ but none of these methods has, so far, found any extensive practical application.

No satisfactory lustre can be produced by treating cops or ‘cheeses’ (cross-wound spools) with caustic soda lye; but cotton yarn in the hank is very largely and successfully mercerised. Automatically working machines are used for this purpose, in which the yarn is stretched, by subjection to tension, over heavy iron rollers, both during impregnation with the lye and during washing.

Cotton warps can be mercerised in a machine resembling the ordinary warp-dyeing machine. The warp is usually impregnated with the soda lye in the first two compartments, while it is washed free from soda in the other compartments. Provision should be made in order to allow each successive set of squeezing rollers to be run at a slightly higher speed. In some cases, warps are mercerised in a machine resembling the ‘warp slasher.’

Although a great variety of machines have been invented and used for mercerising cotton piece goods, machines in which the fabric after impregnation is stretched on a ‘clip stenter,’ are now chiefly employed. A complete mercerising range consists of a padding mangle, the stenter with washing arrangement and the necessary washing, souring, and washing cisterns. In the padding mangle, the cloth is usually twice impregnated with the caustic soda lye and squeezed after each impregnation between cast iron and indiarubber bowls. The trough containing the lye is often provided with an outer cavity to which ice may be supplied or through which refrigerated brine may be circulated in order to keep the lye at a low and uniform temperature. After impregnation, the cloth passes usually directly on to the stenter in which the edges are seized and held by two endless chains of clips, which travel along each side of the stenter. The end of the stenter at which the cloth enters is tapered and thus the fabric is gradually stretched out to its ‘grey width,’ after which the chains run parallel to the delivery end. While on the stenter the caustic soda is removed by showering hot water on the cloth. The economy of recovery of the caustic being of importance, it is customary, in order to obtain a wash-water containing a high percentage of caustic soda, to conduct the washing on the counter-current principle.

For this purpose three or more sets of spirt pipes are provided, clean hot water being introduced into the first set of pipes, which are placed nearest the delivery end of the machine, whilst the same water is then used successively in the other sets. The cloth is ultimately released from the clips and passed through a number of tanks containing hot water and weak acid and passes finally through a washing machine.

With a view to ensure complete penetration of cotton fabrics when mercerising at a high speed, Mather and Platt have introduced a mercerising plant in which the fabric, after having been impregnated in the mangle, is conducted over a number of iron drums, from which it passes into a second impregnating mangle, before being conducted on to the stentering frame.

Krais has patented an arrangement by means of which the soda lye is forced out of the cloth by blowing steam against it.

In order to enable the soda lye to be used over again, the washwaters are concentrated in multiple-effect evaporators and ultimately treated with caustic lime.

Reactions for the characterisation of mercerised cotton.—Although thoroughly mercerised cotton fibres exhibit very specific microscopic characteristics (see Fig. 2), it is exceedingly difficult in many instances to decide with certainty whether goods have been mercerised or not, because the fibres have frequently only been incompletely penetrated by the soda lye. The following chemical reactions (J. Hübner, J. Soc. Chem. Ind. 1908, 27, 105) may be used in order to ascertain whether cotton has been treated with caustic soda lye.

1. If dark coloured samples have to be tested, it will be necessary to first discharge the colour and to completely remove any starch which may be present. The sample should then be squeezed between filter-paper and immersed for a few seconds in the following solution: 20 grams iodine dissolved in 100 c.c. of a saturated solution of potassium iodide. If a non-mercerised sample is immersed along with a mercerised one and if, after removal from the iodine solution, both samples are washed repeatedly in water, it will be noticed that the non-mercerised cotton becomes white, whilst the mercerised sample remains of a bluish-black colour, which only fades very slowly on prolonged washing.

2. Two solutions are prepared, (*a*) containing 280 grams of zinc chloride in 300 c.c. of water and (*b*) 1 gram of iodine, 20 grams of potassium iodide, 100 c.c. of water. The reagent is prepared by adding about 10 drops of (*b*) to 100 c.c. of (*a*). A mercerised pattern, immersed in this solution for about 20 minutes, turns a dark reddish-blue, whilst non-mercerised cotton remains practically white.

By immersing samples which have been mercerised with known strengths of caustic soda along with the one under examination, it is possible, by comparing the depth of colouration of the samples, to ascertain, with a certain degree of accuracy, the strength of caustic soda which has been employed in the mercerisation.

J. Hü.

MERCURIC FULMINATE *v.* Fulminic acid; also Explosives.

MERCUROL, MERCURIOL, MERCOCHINOL, MERGOL, MERIODIN *v.* Synthetic drugs.

MERCURY. Quicksilver. (*Mercure*, Fr.; *Quecksilber*, Ger.) Sym. Hg. At.w. 200.

Ores. *Native mercury* occurs as a decomposition product of cinnabar in the upper portions of the deposits of that mineral. The mercury is usually disseminated through the ore in the form of minute globules which sometimes collect in cavities in the rock. In California, native mercury disseminated through serpentine or in detritus has been found near the outcrops at the Sonoma mine, Rattlesnake mine, &c., associated with mere traces of cinnabar. At greater depths the ore is always cinnabar alone (Egleston's Metallurgy of Silver, Gold, and Mercury in the United States, ii. 801).

Native amalgam containing about 70 p.c. of silver is found in crystals belonging to the cubic system at Arqueros, near Coquimbo, at Moschellandsberg in the Rhine provinces and elsewhere. Native calomel (*horn mercury*) HgCl occurs at Idria and Almaden, and selenide, sulphoselenide (*onofrite*), and other compounds of mercury have also been found in small quantities in various localities.

Cinnabar HgS is the only ore which is regularly worked for mercury. It occurs in rhombohedral crystals, but is usually found massive or earthy, intermixed with quartz, sandstone, schists, bituminous substances, iron pyrites, &c. It is distinguished by its red colour and scarlet streak. When intermixed with bituminous substances which give it a dark colour, it is known as hepatic cinnabar. Cinnabar occurs in eruptive rocks and in sedimentary rocks of all ages.

The chief deposits are at Almaden in Spain, at Idria in Carniola, at Monte Amiata in Tuscany, at Nikitowka in South Russia, and at New Almaden, New Idria, and other localities in California. There are also deposits in Mexico, Hungary, and many other countries.

The famous Almaden mines in Spain were known to Theophrastus, 315 B.C., as furnishing cinnabar to the Greeks, and they were afterwards worked by the Romans. The cinnabar permeates or occurs as pockets in thick veins of quartz inclined at a high angle and contained in Silurian slates (Phillips' Ore Deposits, 374). The ore contains bituminous matter and iron pyrites. Native mercury accumulates in the numerous clefts and cavities in the deposit. The richest ore contains about 25 p.c. of mercury, and the mean yield of the ores, worked in 1908, is stated to be 2·5 p.c. (Mineral Industry for 1909, 18, 843).

At Idria the sulphide occurs as a dark-red slaty deposit contained in veins or disseminated in triassic shales and limestones. Some hepatic cinnabar occurs and also *korallenerz* or coral ore, which contains calcium phosphate (Phillips, *l.c.* 329; Lipold, Oesterr. Zeitsch. 1882, 30, 84). The mines were discovered in 1490 and have been in the hands of the Government since 1580. The ore varies in grade from *stahlerz*, containing 75 p.c. mercury, down to ores containing 0·2 p.c., the average being 0·6 p.c. in 1908.

At Monte Amiata, cinnabar occurs as

segregations in Eocene formations. These deposits were exploited by the ancient Etruscans and again in the Middle Ages. The present operations were begun at Siele in 1846. The average amount of quicksilver contained in the ores was 0·8 p.c. in 1908. The output has risen from 173 tons in 1898 to 684 tons in 1908 (Spirek, Zeitsch. prakt. Geol. 1897, 369; Schnabel and Louis' Metallurgy, 2nd ed. ii. 335).

At Nikitowka, the ore consists of sandstone of carboniferous age impregnated with cinnabar. In 1906, the yield of mercury was only 0·28 p.c. and the production fell from 616 tons of mercury in 1897 to 47 tons in 1908. The deposits were worked by the ancient Greeks, and after a lapse of 2000 years operations were begun again in 1886 (Schnabel and Louis, *l.c.*).

In California cinnabar occurs disseminated through a zone of slates, serpentine, sandstones, and limestones of Cretaceous and Tertiary age. Some rich ore occurs, especially where serpentine and sandstone are in contact, but the average yield is now under 0·75 p.c., although it was 36 p.c. in 1850 with a similar output. The deposits were known to the Indians, who used the cinnabar as paint, but the mines were first worked systematically in 1845. The most important mine, that at New Almaden, is now almost exhausted.

Mercury also occurs as a sulphide in ores of other metals. The *mercurial fahlore* (*see* FAHLORE) of Hungary contains up to 17 p.c. of mercury. At Kotterbach this fahlore occurs in spathic iron ores (Schnabel and Louis, *l.c.* ii. 438). According to Bellingrodt (Chem. Zeit. 1886, 10, 1039), zinc blende roasted at Oberhausen contains 0·2 p.c. of mercury which is extracted as a by-product. Zinc ore is also treated for mercury at the Taghit mine, Algeria (Min. Ind. for 1902, 11, 548).

Extraction from ores. There are two methods of extracting mercury from cinnabar suitable for use on a large scale:—

1. By heating cinnabar in air, the action being represented by the equation

$$HgS+O_2=Hg+SO_2.$$

2. By heating cinnabar with lime or iron, air being excluded. The chemical action may be represented by the equations

$$4HgS+4CaO=4Hg+3CaS+CaSO_4$$
$$HgS+Fe=Hg+FeS.$$

In each of these cases, the temperature necessary for the reaction is higher than the boiling-point of mercury, so that the latter is volatilised and has to be condensed. In the air roasting process, the mercurial vapours are mixed with a large volume of sulphur dioxide, nitrogen, carbon dioxide, and other gases, and condensation is difficult. Nevertheless, the roasting process is now generally used, partly owing to the high cost of retorting with lime or iron, which prohibits the use of that method for poor ores, but mainly on account of the injury to the health of the workmen by the concentrated mercury vapour which they inhale when the retorts are emptied.

Some of the difficulties of treating cinnabar by the roasting process are as follows:—

1. The amount of mercury in the ores is small, sometimes only 0·2 or 0·3 p.c., and part of this is obstinately retained by the residues, necessitating long-continued treatment at a red heat.

2. The mercurial vapours readily penetrate the brickwork of the furnace and condensers. This is checked by keeping the pressure of the gases inside the furnace and condensers slightly below the outside atmospheric pressure by means of a fan placed at the outlet. By this device also the workmen are protected from the mercury vapours. The exhaust must not be excessive or the retention of the mercury in the condensers would not be complete. The furnaces are now always covered with iron plates, so that penetration of the masonry by mercury occasions only a temporary loss.

3. Liquid mercury penetrates the furnace bottoms. According to Spirek, over 1000 centners of mercury have been recovered from the foundations of furnaces at Idria. To prevent ultimate loss, furnaces stand on iron plates with upturned edges, draining to a little sump where the mercury may collect.

4. The gases from the furnace are acid, owing to the presence in them of SO_2 and SO_3. The condensed water accordingly attacks iron condensers, whilst most other metals, such as copper, would form amalgams with the condensed mercury. Stoneware, glass, and wood, as well as iron are used in the construction of condensers.

5. *Stupp* or mercurial soot is formed, consisting of finely divided mercury together with mercury sulphate, and chloride, and sooty products of the fuel and the bituminous and other constituents of the ore. The soot accumulates in the condensers and is treated subsequently by special processes. At Monte Amiata, it contains 70 or 80 p.c. of all the mercury recovered. Although inconvenient if formed in very large quantities, however, soot is useful when amounting to about 1 p.c. of the ore treated, as it assists the condensed mercury (*quicksilver-mist* or *quicksilver-foam*) to settle in the condensers and dust chambers and reduces the vapour loss by forming a dry crust over the liquid quicksilver.

According to Christy (Trans. Amer. Inst. Ming. Eng. 1884, 13, 547; 1885, 14, 206), the issuing gases are saturated with mercury vapour at New Almaden, and the loss as vapour can be calculated from the vapour pressure of mercury at the temperature of the gases. According to Spirek, however (Min. Ind. for 1897, 6, 571), the gases at Monte Amiata had a saturation of only 30 to 45 p.c., owing to the action of the stupp. In any case, it is clear that the temperature and volume of the issuing gases should be kept as low as possible.

The mist loss, due to fine particles of mercury being carried away mechanically in the effluent gases, depends on the method of condensation and the velocity of the gaseous current. It is usually from 2 to 2½ times the vapour loss.

The total losses of mercury, which, according to Schnabel, formerly amounted to 50 p.c. or more, have now been reduced to 5 p.c. or even less of the mercury present in the ores, in spite of the great fall in the richness of the ores treated. This reduction of loss is largely due to the labours of the metallurgists at Idria since 1870, the names of Exeli, Langer, Czermak, Spirek, Novak, and others being associated with improvements in the methods of treatment.

Ores are not usually finely crushed for the roasting process, and they are not now prepared for reduction by means of concentration in water at any works, as the additional cost and the heavy losses in the tailing outweigh any advantage to be gained. For ten years the ore at the Cornacchino mine, Monte Amiata, was dressed. with the production of a concentrate containing 25 or 30 p.c. of mercury, and tailing assaying from 0·6 to 1 p.c. of mercury which was thrown on the dump. The tailing was subsequently treated at a profit in the continuous fine ore roasters and concentration has been discarded (Mineral Industry for 1897, 6, 569).

Types of furnaces. A number of different furnaces have been used for the treatment of mercury ore in the course of the last 100 years. In the discontinuous shaft furnace (Aludel and Idria furnaces) the ore in the form of lumps, or fines made into balls, was piled in a shaft on a perforated arch or grate and heated by the products of combustion of a fire placed below. Shaft furnaces working continuously (Exeli, Langer, and Knox furnaces) succeeded, in which there was no grate to support the ore. The heating gases entered the shaft at the side some distance from the bottom. In a more recent type of continuous shaft furnace for treating coarse ore (Hähner, Valalta, Novak, and Spirek furnaces), there is no external fire, the ore being charged in mixed with charcoal.

In fine-ore shelf furnaces (Hüttner and Scott, Livermore, Czermak, and Czermak-Spirek furnaces) the ore passes down over a series of sloping shelves and is heated by the gases from an external fire. These furnaces are more economical than the coarse-ore furnaces and are in wide use. Reverberatory furnaces (Alberti, Exeli ironclad reverberatory, Czermak-Spirek reverberatory) are used in certain cases. Lastly there are the retort furnaces.

A more detailed description of some of these furnaces is appended.

Aludel or Bustamente furnace.—This old-fashioned form of furnace was still in use at Almaden in 1907 and is probably not yet entirely discarded. It is an intermittent shaft furnace, designed by Barba in Peru and introduced into Almaden by Bustamente in 1646. One form of Aludel furnace using wood as fuel is shown in elevation and plan in Figs. 1 and 2, and another and later form with a grate for coal is Figs. 3 and 4. In Fig. 1, *a* is the fire-door, *b* the fireplace, *c* a perforated brick arch above which is the circular distillation chamber, 4 feet 3 inches in diameter in the smaller furnaces, and 6 feet 6 inches in the larger. The ores are first charged in through the opening *d*, which is afterwards bricked up and charging is completed through the door in the top arch. The total height of the cylindrical shaft is from 20 to 26 feet. On the arch *c* is placed 2000 kilos. of quartz or of poor ore in large pieces so that the flames rise through them readily. This is covered with 10–14 tons of ore, beginning with ore of medium quality (*requiebro*, containing from 7 to 15 p.c. of mercury). Upon this is charged the poorer ores (*china*, containing about 1 p.c. of mercury), then the rich ore (*metal* containing over 15 p.c. of mercury), and lastly small ore of mixed quality (*vasisco*) made into balls.

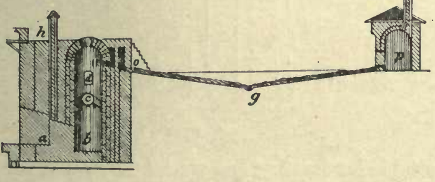


FIG. 1.

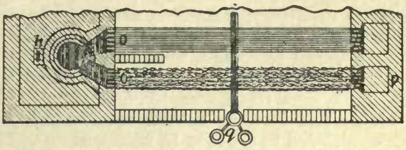


FIG. 2.

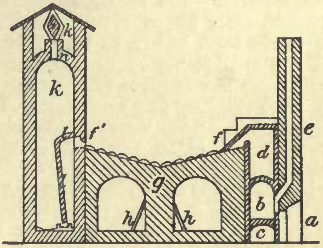


FIG. 3.

The furnace is then closed and the charging doors luted up, and the aludels are luted together in position. These are pear-shaped clay condensers, 18 inches long, glazed on the outside, and so shaped that the narrow end of each fits into the wider end of the next following one. They are arranged in 12 parallel rows each containing 40 to 45 aludels, lying in grooves on a sloping roof, *ff'*, Figs. 3 and 4. The aludels communicate with condensing chambers *k*, Figs. 3 and 4, *p*, Fig. 1. The products of combustion from the fire pass in part through the flue *h*, Fig. 1, *e*, Fig. 3, but mainly through the bed of ore. The mercurial vapours, sulphur dioxide, and the products of combustion of the fuel pass through the aludels where partial condensation takes place and into the chamber *k*, Figs. 3 and 4, passing below the partition *l*. The condensed mercury in part drains out of the aludels into cast-iron pans situated below (*q*, Fig. 2). In the coal furnace shown in Fig. 3, the mercury drains from the aludels at *g*, through the wooden pipes, *h*, to cisterns filled with water.

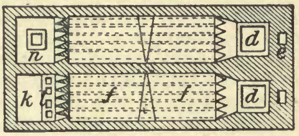


FIG. 4.

The fire is maintained for 10 or 12 hours, thus heating the column of ore sufficiently to enable the cinnabar, pyrites, and bituminous matter to burn in the current of air, which is raised to a temperature of 200°–300° by passing through the layer of quartz before it reaches the ore. The ores burn for 44 hours, a period during which the first aludel reaches a temperature of 245°–260°, and the last aludel one of 29° somewhat later (Kuss, Ann. des Mines, 1877, 13, 39; 1878, 15, 524). The furnace is then opened and the residues allowed to cool for 18 hours, after which they are withdrawn and the furnace recharged.

The aludels are cleaned out once in one or two months, according to position, and the soot collected and prepared for re-treatment. The losses of mercury, according to Langer (Berg. u. Hüttnm. Jahrb. Berg-Akad. 1879) amounted in 1879 to an average of 20 p.c. (*See* also Moreau, Le Génie Civil, 1884, 380; Eng. and Mng. Jour. 1881, 32, 335.)

Idrian furnace.—The aludel furnaces were introduced at Idria about 1750, but were soon altered into the form known as Idrian furnaces, in which the condensing apparatus consists of large brick chambers in place of aludels. These furnaces gave higher percentage losses than aludel furnaces but were worked more cheaply. They were discarded at Idria in 1870. (*See* Schnabel and Louis, *l.c.* ii. 352.) For description of older methods of ore treatment at Idria, *see* Mitter (Vortrag auf dem Bergmannstag zu Klagenfurt, 1893); also Agricola (De re Metallica, Lib. ix. 1556).

Exeli furnace.—The introduction of shaft furnaces fired continuously marked a great advance on the older forms. One of the earliest of these was the Exeli furnace, built at Idria in 1872 (Das K. K. Quecksilber bergwerk Idria in Krain, Vienna, 1881; Schnabel and Louis, *l.c.* 358), and introduced by Randol at New Almaden in 1874 (Egleston, *l.c.* ii. 857). It was surrounded by three external fireplaces and cased in wrought iron to prevent loss of mercury. It was afterwards altered by bricking up the fireplaces and charging charcoal with the ore at the top of the furnace. For the *Langer furnace*, see Schnabel and Louis, *l.c.* ii. 365, and for the *Knox furnace*, see Egleston, *l.c.* ii. 841.

Novak furnace.—This is a good example of a continuously working shaft furnace in which the ore and fuel come into direct contact. It is suitable for coarse ore in cases where charcoal can be obtained cheaply. The earliest shaft furnace of the kind was the Hähner furnace, used at Idria from 1849 to 1852 (Schnabel and Louis, *l.c.* ii. 407). It was replaced by the Valalta furnace (Berg. u. Hüttmn., Ztg. 1864, 284; 1868, 32; Eng. & Mng. Jour. 1872, 14, Nos. 11, and 12). The Novak furnace was introduced at Idria in 1892. One of these furnaces is shown in elevation and plan in Figs. 5 and 6, but three furnaces are united in a single block. The outer walls are cased in iron plates. The shaft *a* is rectangular, 7 metres in height and 2 metres by 2·4 metres in cross section at its widest part. There are four openings, *b*, *b*, for the removal of the residues. The brick shaft stands on a cast-iron plate, *c*, supported by legs and standing on a brick foundation, accessible also from below at *d*. Any loss of mercury in the foundations is thus prevented. The roof-shaped ridge *e*, in the bottom of the furnace, is pierced with many small holes for the supply of air. The charging hopper *f* is fitted with a water-joint and the pipe *g* leads to the condensers. Poor ore in lumps not smaller than 0·67 inch mesh and pressed soot are treated, one ton of ore together with 16 p.c. of its weight of charcoal being charged into the furnace every 2 hours. The condensers are of the usual Czermak type, see Fig. 11. The production of soot amounts to 0·5 p.c. and the loss of mercury to 7 or 8 p.c. With furnaces of this type the formation of soot is much less than in the fine ore furnaces about to be described.

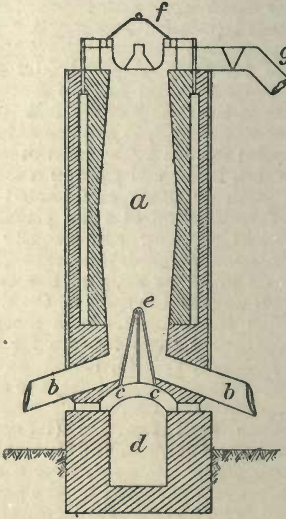


FIG. 5.

The modern Czermak-Spirek shaft furnaces used at Siele, Monte Amiata, in which the loss is only 2 or 3 p.c. of mercury, are described in the Mineral Industry for 1901, 10, 559. (*See* also Spirek, Sixth Internat. Cong. of Appl. Chem. Rome, 1906.)

Hüttner and Scott furnace (Schnabel and Loius, *l.c.* ii. 372; Egleston, *l.c.* ii. 864). This furnace was introduced at the New Almaden mines, California, in 1875, and was the earliest of the shelf furnaces, which are especially suitable for treating fine ore. At New Almaden the small ore of less than 1·2 inch cube was called *tierras*, and the larger ore of between 1·2 inch and 2·3 inch cube, was known as *granzitas*. These materials were treated in separate furnaces built on the same principle, with a large number of inclined shelves sloping at an angle of 45° in alternately opposite directions, upon which the fine ore slides down, filling up the spaces between

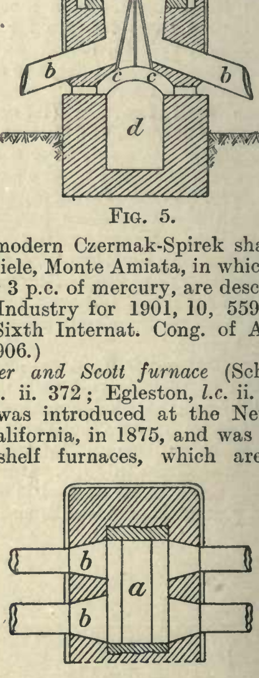


FIG. 6.

the shelves. The products of combustion of the fire pass horizontally between the under side of the shelves of each tier and the surface of the ore resting on the shelves of the next tier below. The ore is thus heated and roasted, and is finally discharged at the bottom of the furnace.

One of the newer forms of this furnace was built by Newcomb at Oat Hill, California, in 1898 (Mineral Industry, 7, 583). Fig. 7 is a vertical section through the furnace and the first section of the condensers; and Fig. 8 is a front view, with the furnace in section and the condensers partly in elevation. Fig. 9 is a horizontal section of the furnace on A, B, Fig. 8.

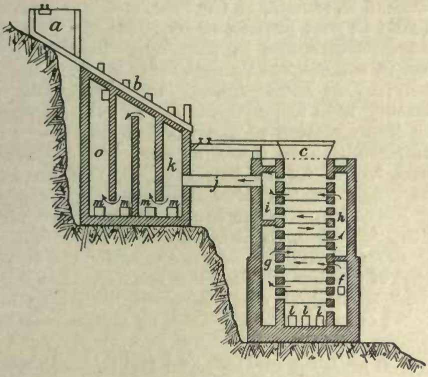


FIG. 7.

The ore is passed through 1·5 inch gratings before entering the ore-bin *a*, Figs. 7 and 8, whence it passes over a drying platform *b*, placed above the condenser, and is discharged into a hopper, *c*. The hopper is kept full of ore which acts as a seal when a slot is opened and some ore let fall into the furnace. Two tons of ore are thus charged in at intervals of one hour.

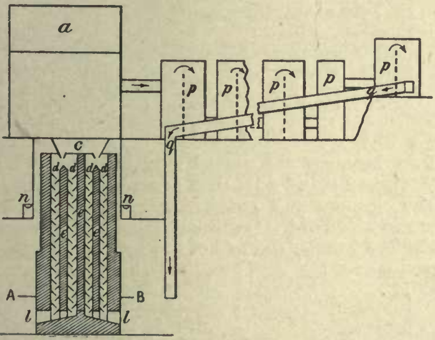


FIG. 8.

The furnace is of brick, 22 feet by 16 feet, and 37 feet high, outside measurements. The roasting chamber is divided into four compartments, *d*, Figs. 8 and 9, by three vertical partitions, *e*, and in each compartment is a series of 24 sloping shelves (*see* Fig. 8) consisting of fire-clay tiles which allow the ore to slide down in a zig-zag path. The ore piles up on the shelves bridging over the 6-inch spaces between them, so that the products of combustion from the fire-box *f*, Figs. 7 and 9, cannot rise vertically in the shaft but pass horizontally under the shelves from *f* to *g*, thence from *g* to *h*, following the course indicated by the arrows, and finally from *h* to *i*, whence they escape by two cast-iron exit pipes *j*, to the condenser *k*.

The spent ore is discharged by being raked, at intervals of 15 minutes, through the openings *l*, *l*, which are placed 5 feet below the level of the fire-grate, so as to enable the ore to be cooled before it is withdrawn. The furnace holds 40 tons of ore, so that the ore remains under treatment about 20 hours. The fuel used is 2½ cords of wood in 24 hours. The temperature is kept as low as possible, a cherry-red heat being aimed at, and hardly a trace of cinnabar is found in the material discharged.

FIG. 9.

The condensers are of brick with cemented floors sloping down to the discharge apertures *m*, *m*, Fig. 7, whence the metal runs to the quicksilver troughs *n*, *n*, Fig. 8. Very little mercury is condensed in the first compartment *k*, but the amount increases up to the last compartment *o* of the first condenser. After this, in passing through the remaining six brick condensers *p*, *p*, Fig. 8, the amount of mercury recovered decreases. The fumes next pass into the wooden flue condenser *q*, Fig. 8, eventually being discharged into the open air through a vertical flue in which an exhaust fan is placed. The length of travel in the condensers is 400 feet. About 30 p.c. of the total yield of mercury is obtained from the soot. The loss of mercury is estimated at about 5 p.c., and the labour required is 4 men per shift with a fifth during the day to attend to the soot-pan.

In California, the Hüttner-Scott furnaces are in general use, very coarse ore being crushed to enable it to be treated in these fine-ore furnaces. Shaft furnaces appear to have been discarded in California, as less advantageous than the shelf furnaces.

Czermak-Spirek continuous roasting furnace (Mineral Industry for 1897, 6, 572). This furnace is a modification of the Czermak furnace introduced at Idria in 1886 (*see* Schnabel and Louis, *l.c.* ii. 388). It is on the same principle as the Hüttner-Scott furnace, and is similar in being suitable for the treatment of fine ore.

It consists of a rectangular chamber of iron, with two fireplaces, one at each end. The fires are lighted alternately, only one being at work at any given time. The products of combustion pass into a wide flue or combustion chamber extending longitudinally in the middle line of the furnace near its base. Hot air from iron pipes used to cool the ore just before it is discharged is used for combustion, and an excess of air is supplied.

The ore is fed from above upon V-shaped tiles, with the apex upward, ranged in parallel lines, in such a way that the apex of each tile is opposite the space between two tiles in the layer next above (*see* Fig 10). The ore slips down the tiles and completely fills the space *a* between two successive layers of tiles. When part of the residues are withdrawn from the bottom of the furnace, there is a general subsidence of ore extending to the top. There is a regular system of oval openings in the sides of the furnace provided with movable covers, through which iron bars may be introduced to dislodge the sintered ore in case of necessity. The V-shaped tiles are supported on longitudinal walls made of perforated bricks.

The products of combustion and hot air from the combustion chamber circulate through the furnace by the passages *b*, between the tiles and the ore and pass out at the top of the furnace through cast-iron pipes into the condensers. The temperatures in the furnace are as follows: ore on discharge, 100°; air supplied for combustion, after being used to cool the roasted ore before it is discharged, 300°–360°; combustion chamber, 800°–900°; in the first tier of tiles of the roasting zone, 700°–800°; in the fourth and highest tier, 360°–400°; in the passage to the condenser, 260°–360°.

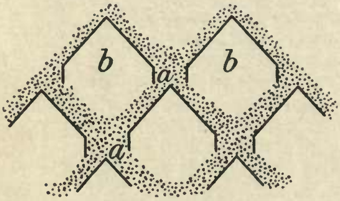


Fig. 10.

The condensers are of the usual Czermak pattern, consisting of cast-iron pipes of elliptical section (*a*, Fig. 11). In positions where the temperature is below 100° so that the acid vapours are condensed, the iron is lined with cement to avoid corrosion of the iron. Glazed stoneware is also used instead of cast iron. These condensers are cooled with water. The lower part *b* of the condensers is sometimes constructed of wood, and dips for about two inches into water contained in lined cast-iron or wooden boxes, *c*. The flue leading from the furnace is shown at *d*. The vapours escape into the wooden flue *e*. The large furnaces have two sets of condensers which can be cleaned alternately without stopping the work of the furnace. From the condensers, the vapours pass into flat wooden flues, or dust chambers, in which a poor soot is collected.

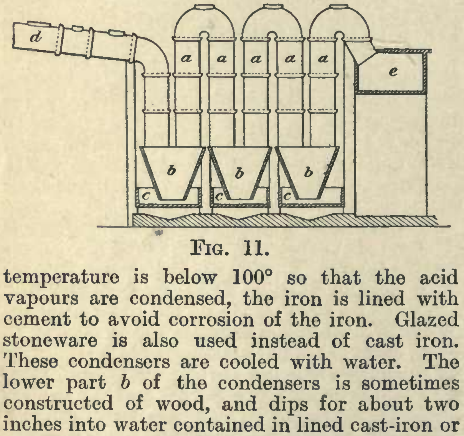


Fig. 11.

The pressure of the vapours within the furnace and condensers is kept below atmospheric pressure by means of a fan which provides an exhaust equivalent, according to Spirek, to a water column of about 4 mm. at the outlet or 1 mm. at the junction between the furnace and the condensers.

The capacity of the furnace depends on the nature of the ore, and in the case of the largest sized furnace at Siele varies from 16 to 26 tons per day. The ore remains in the furnace from 41 to 68 hours and is shifted by the withdrawal of a portion every 2 or 3 hours. The ore is roasted at a bright red heat until the last trace of mercury has been driven off. The condensation is also very good, about 90 p.c. of the mercury and soot collecting in the first 3 U-tubes, within a length of 4 metres. The greater part of the metal, and in the case of low-grade ores the whole of it, remains in the soot, and is recovered in part in soot presses, or by rubbing on an inclined surface and in part by redistilling the soot in a small continuous roaster of the same pattern. At Monte Amiata, the average loss of mercury with these roasters is 4 or 5 p.c., after the impregnation of the wooden condensers is completed. Two workmen per shift are sufficient to attend to this furnace, one on the charging floor, the other as fireman.

These furnaces are in use at Monte Amiata, Idria, Almaden, Nikitowka, and elsewhere.

Reverberatory furnaces are used for the treatment of fine ore which yields too much flue dust when treated in shelf furnaces, and also for coarse ore which decrepitates or sinters readily.

The first reverberatory was employed by Alberti at Idria in 1842, and the latest form is the Czermak-Spirek long-bedded calciner introduced in 1888 and shown in Figs. 12 and 13.

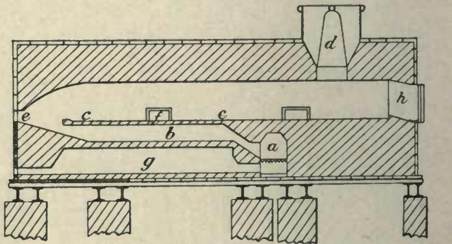


Fig. 12.

Two furnaces are placed side by side in one block and stand on a dish of riveted sheet-iron. The fire-grate *a* extends across almost the whole width of the furnace. The flame traverses the flue *b* under the bed of the hearth and then passes over the tiled hearth *c*, which is 5½ metres long and 2·4 metres wide. The charging hopper is at *d*, and there are five working doors at *e* and *f*. The residues are withdrawn every 2½ hours through the door *f* into the receptacle *g*. The gases and vapours pass through the

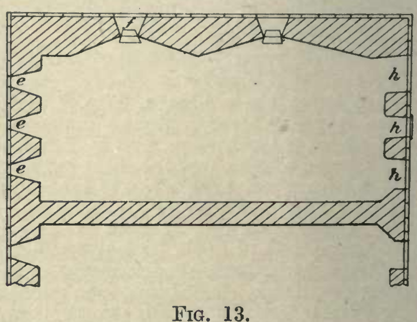


Fig. 13.

openings *h* into Czermak condensers of the usual pattern.

These furnaces treat 6·6 tons of poor ore and soot in 24 hours with a consumption of 148 cubic feet of wood per 10 tons of ore. The production of soot amounts to 1·9 p.c. and the loss of mercury to 8 or 9 p.c. (Schnabel and Louis, *l.c.* ii. 402).

For the description of a similar reverberatory furnace designed by Spirek for the treatment of mercury-lead ores, see Mineral Industry for 1902, 11, 548.

Retort furnaces were used for a time at Idria, Monte Amiata, and California, but are probably no longer in use in any part of the world except, according to Schnabel, at Littai, in Carniola. The ore is mixed with lime or iron and heated in cast-iron or clay retorts, which are pear-shaped or cylindrical in shape, and usually contain from 1 to 5 cwt. of ore. The method is suitable only for rich ore or soot, but even for such material the process gives no better results than the air-roasting process, and apart from cost, it has the disadvantage of producing concentrated vapours of mercury which have injurious effects on the workmen.

At Littai (Schnabel and Louis, *l.c.* ii. 421), cast-iron retorts are used, taking a charge of 2 cwt. of ore. The ore contains 2 or 3 p.c. of mercury, and 5 or 6 p.c. of lime is added. The retorting lasts 6 hours and the loss of mercury is stated to amount to from 5 to 6 p.c.

Soot or *Stupp*, the deposit on the walls of the condensers, consists of finely divided mercury and compounds of mercury, together with carbon, tarry matters, and ash from the fuel and dust from the ore, amounting in all, according to Spirek, to about 1 p.c. of the ore at Monte Amiata. The composition of soot varies largely. One sample from the condenser of a Czermak furnace was found to contain :

Metallic mercury	22·01 p.c.
Mercury as cinnabar . . .	6·75 ,,
Mercury as sulphates, chlorides, &c.	3·04 ,,
Total mercury . . .	31·80 ,,

(*See* Schnabel and Louis, *l.c.* ii. 425, where many analyses are given.)

The soot is usually treated mechanically to separate part of the mercury contained in it. It may be worked with hoes on an inclined surface until no more mercury flows off, as at Almaden (Berg u. Hüttnm. Jahrb. der K. K. Montanlehranstalten, 27, 46). When rubbed with lime, more mercury is separated.

At Idria and Monte Amiata, Exeli stupp presses are used. These are iron pans fitted with vertical knives fastened to the bottom. Revolving arms carrying similar knives stir the soot and press it against the stationary knives. Lime is added little by little to the extent of from 17 to 30 p.c. of the soot during the course of the operation, which occupies one or two hours in the case of rich material. When the soot is stirred and pressed, mercury separates from it and flows away through small openings in the bottom of the pan.

The soot residues after treatment still contain 10 p.c. or more of mercury and are treated mixed with ore in the same furnace as before, or mixed with other rich materials in similar furnaces of small size, or more rarely in retorts. Formerly where coarse ore furnaces were in use, the soot residues were moulded into bricks and treated with the ores.

Purification. Impure mercury is recognised by the fact that globules are pear-shaped with tails, instead of spherical, when made to run down a sloping surface, and may even leave a trail behind them on paper. Mechanical impurities are removed by squeezing through chamois leather or by filtering through punctured blotting paper.

Retorting at a low temperature with a cover of charcoal and lime will remove most of the impurities. Oxidisable impurities are best removed by the passage of a stream of air through the mercury which is covered with dilute nitric or sulphuric acid. The base metals are rapidly oxidised by the air and dissolved by the acid. Small quantities of impurities may be removed merely by digesting or shaking mercury with dilute nitric acid.

Mercury is kept in a glass or stoneware vessel under a layer of dilute nitric acid of sp.gr. 1·1 and drawn off as required by a stop cock at the bottom and washed with water before use.

Properties. Mercury is a silver-white liquid metal with a slight bluish tinge. In thin films it transmits violet light (Melsens). Its sp.gr. at 0° is 13·59545 when compared with water at 4° (Volkmann, Thiesen and Scheel). At −38·85° it solidifies (Balfour Stewart), contracting considerably and forming a tin-white, soft, malleable and ductile metal of sp.gr. 14·193 at its melting-point (Mallet, Phil. Mag. 1877, [v.] 4, 145). Its electric conductivity is 1·63, if silver =100 (Matthiessen), and its thermal conductivity is 1·83, if silver =100 (Angström, Gray). For thermal expansion *v.* Callendar and Moss, Phil. Trans. 1911, 211 A, 1.

It is volatile at ordinary temperatures and even at −44° (Merget); its b.p. is 357·25° at 760 mm. pressure (Regnault), forming a colourless vapour. (For its vapour pressures from 40° to 512°, *see* Ramsay and Young, Chem. Soc. Trans. 1886, 49, 37.)

It is unaltered in air, oxygen, nitrous and nitric oxides, carbon dioxide, &c., at ordinary temperatures. When heated to about 350°, it becomes gradually converted into the red oxide, HgO, which is decomposed below a red heat.

Mercury is not acted on by HCl, and is almost unaffected by dilute H_2SO_4, although dissolved by hot strong H_2SO_4. It is dissolved even by cold dilute HNO_3, and is rapidly attacked by hot or concentrated nitric acid. It is also dissolved by aqua regia.

When agitated with oils, turpentine, &c., or triturated with grease, fats, sulphur, certain sulphides, arsenides, &c., mercury is subdivided into minute globules, not easily reunited. This is known as the flouring, sickening, or deadening of mercury and is the cause of losses in the extraction of silver and gold from their ores by amalgamation. The coalescence of floured mercury can be effected with some loss by the action of nitric acid.

Vapours of mercury have a poisonous effect ('salivation') on the animal system. Among the remedies are cleanliness, fresh air, acid foods, and moderation in the use of alcohol. The use of potassium iodide is also recommended.

Uses. Mercury is used in the extraction of gold and silver from their ores, for the manufacture of vermilion (*v. infra*), of mirrors and of fulminates, in medicine, and in dentistry. The metal and its amalgams are used in small quantities for a variety of other purposes.

The consumption of mercury in silver milling was formerly very large when the pan amalgamation process was in wide use. In treating the ores of the Comstock lode, for example, 7 lbs. of mercury was formerly lost in the treatment of a ton of ore. In modern stamp-battery practice on gold ores, the loss is only 0·2 or 0·3 oz. of mercury per ton of ore. The progress of the cyanide process and the abandonment of the patio and pan amalgamation processes have caused a reduction in the amount of mercury required in the extraction of silver ores.

The *production* of mercury during the years 1907–1909 in metric tons was as follows (Mineral Industry for 1910, 19, 594):—

—	1907	1908	1909
Austria . .	527	572	637
Hungary . .	40	78	80
Italy . .	434	684	771
Mexico . .	200	200	200
Russia . .	130	47	(?)
Spain . .	1212	1068	1393
United States .	712	685	713
Total .	3255	3334	3794

Mercury is transported in wrought-iron flasks or bottles closed by screw stoppers. The weight of mercury in a full flask was formerly 76·5 lbs. but was reduced to 75 lbs. in Europe in 1903, and in California in 1904. The old sheepskin bag used to contain 55 lbs.

The price of mercury is usually between £8 and £10 per flask. T. K. R.

COMPOUNDS OF MERCURY.

Mercury forms two series of salts: the *mercuric* compounds, in which the metal is divalent, and the *mercurous* compounds, in which it is apparently monovalent.

The *mercuric salts* are often obtained when excess of acid acts on metallic mercury. Reducing agents convert them into mercurous salts, which may be further reduced to metallic mercury. The soluble salts are extremely poisonous and are acid to litmus.

The *mercurous salts* are produced when an acid acts on excess of mercury, or by the reduction of mercuric compounds. In solution they readily dissociate into metallic mercury and a mercuric salt (Hada, Chem. Soc. Trans. 1896, 1667). This reaction is reversible and ends with the establishment of equilibrium between the mercurous and mercuric ions present (Abel, Zeitsch. anorg. Chem. 1891, 26, 361).

Mercury forms three oxides, *mercurous oxide*, *mercuric oxide*, and *mercuric peroxide*.

Mercurous oxide Hg_2O is obtained as a blackish-brown powder by the addition of alkalis to a solution of mercurous salt, or by triturating a solution of alkali with calomel. It is washed, dried spontaneously, and kept in the dark. By the action of light or of a gentle heat it is decomposed into the red oxide and mercury, and it combines with oxygen at 100° (Colson, Compt. rend. 1899, 128, 1104). It may be obtained in colloidal solution by treating the aqueous solution of a mercurous salt with alkali salts of the albinic acids in presence of alkali hydroxide or carbonate (Hofmann, D. R. P. 185599, 1905; J. Soc. Chem. Ind. 1907, 1254).

Mercurous hydroxide does not exist at the ordinary temperature but is obtained as a bright-yellow precipitate by the action of alcoholic potash on alcoholic mercurous nitrate at −42° (Bird, Amer. Chem. J. 8, 826).

Mercuric oxide, *Red oxide of mercury, Red precipitate*, HgO. This oxide is slowly produced when the metal is heated in air to near the boiling-point. It may be obtained pure by pouring a boiling solution of mercuric chloride into an excess of boiling potassium carbonate solution and boiling till the precipitate is of the right colour (Dufau, J. Pharm. Chim. 1902, 16, 439). It is usually prepared by heating the nitrate until nitrous fumes cease to be evolved, but not sufficiently to decompose the oxide itself. When prepared slowly on the large scale the oxide is obtained in fine brick-red crystalline plates of sp.gr. 11·163 (Playfair and Joule).

By precipitating a mercuric salt with cold potash, the oxide is obtained as an orange-yellow powder of the same composition, but more easily acted on by reagents. With oxalic acid it produces the oxalate, whilst the crystalline oxide is not so affected. When heated with mercuric chloride solution it rapidly forms an oxychloride; the crystalline form is only slowly so converted. The amorphous oxide is also more easily decomposed by heat. It was formerly considered by many chemists that the red and yellow oxides differed only in the size of the particles (see *e.g.* Ostwald, Zeitsch. physikal. Chem. 1900, 34, 495; Schick, *ibid.* 1902, 42, 155). Schoch, however, has shown (Amer. Chem. J. 29, 319) that the crystalline form of the red is different from that of the yellow oxide, that the dissociation pressure of the yellow oxide at 300° is considerably greater than that of the red oxide, and that when heated at 250° it is converted into the red oxide with partial decomposition.

Mercuric oxide is a powerful poison. It dissolves in about 20,000 parts of water at 25° or about 2200 parts at 100° (Schick, *l.c.*). When heated it becomes of a bright red, and finally nearly black, but regains its colour on cooling. A superficial change of colour from bright red to brownish red is produced when the red oxide is exposed to light. When strongly heated, it is decomposed into mercury and oxygen. By this reaction, oxygen was first prepared by Priestley.

When heated with zinc, tin, or antimony filings, the oxide is reduced to metal with incandescence. When added to fused sodium the action is still more intense. The mixture with sulphur explodes violently when heated. Mixed with phosphorus it detonates when struck. At a red heat it is converted by chlorine into mercuric chloride, with liberation of oxygen. It dissolves in fused potash with formation of a double oxide, without evolution of gas.

Mercuric oxide is frequently used as an oxidising agent in chemical operations.

A colloidal solution of mercuric oxide is obtained when mercuric chloride solution is treated with the sodium salts of protalbinic or lysalbinic acids and caustic soda. A yellow solution is obtained which can be purified by dialysis and then gives on evaporation *in vacuô* at 40° red-brown plates of the stable hydrosol (Paal, Ber. 1902, 35, 2219).

Mercury peroxide HgO_2 is formed in small quantities during the catalytic decomposition of hydrogen peroxide by metallic mercury (Antropoff, Zeitsch. Elektrochem. 1906, 12, 585), and is prepared by the interaction of alcoholic mercuric chloride, hydrogen peroxide, and alcoholic potash (Pellini, Atti. R. Accad. Lincei, 1907, [v.] 16, ii. 408). Either method yields the anhydrous peroxide as an amorphous, brick-red powder, which is fairly stable in dry air. It is slowly decomposed by water, and with acids yields a mercuric salt and hydrogen peroxide: with hydrochloric acid chlorine is liberated.

Mercuric sulphide HgS occurs native as *cinnabar*, which is the principal source of the mercury of commerce. Cinnabar is found, granular or massive, in sub-transparent rhombohedral crystals which cause circular polarisation of transmitted light. It has a cochineal-red colour and gives a scarlet streak.

Mercuric sulphide exists in two forms (*a*) a red, crystalline variety, of which cinnabar is an example, and (*b*) a black, amorphous substance.

The black sulphide is produced by the action of hydrogen sulphide on solutions of mercuric salts, or by triturating or heating mercury with sulphur. Thus prepared it was formerly used in medicine under the name of *Æthiops mineral*. It occurs native in California (Moore, J. pr. Chem. 1870, [ii.] 2, 319).

Under the name of *vermilion*, the red variety is prepared on the large scale and used as a pigment. Native cinnabar cannot be so used because of impurities which affect the colour. Vermilion is prepared both by *dry* and *wet* processes.

Dry processes.—These all depend on the preparation of the black sulphide, usually by the combination of mercury and sulphur, and its subsequent conversion into the red variety by a process of sublimation. The following method was formerly largely used in secret in Holland. 1080 lbs. of mercury and 150 lbs. of powdered sifted sulphur are moderately heated in an iron pan with constant stirring, and the black *œthiops* obtained is cooled and powdered. This is introduced in charges of about 25 lbs. four times an hour into long subliming pots of refractory clay, each holding about 410 lbs., heated from below to about two-thirds of their height. As each charge is added it ignites, and a long flame escapes from the pot; when this has subsided, the pot is covered with an iron plate. The operation occupies about 36 hours. The pots are cooled and broken, and the vermilion, which is principally in the upper portions, is ground with water between stones, sifted, elutriated, and dried.

It is said that if 1 part of antimonious sulphide be added to the mixture of sulphur and mercury before sublimation, and the vermilion be digested with potassium sulphide, an improved pigment is obtained which contains no antimony.

At Idria, a mixture of 8 lbs. sulphur and 42 lbs. mercury is placed in a well-bound cask, which is rotated for some hours until the contents consist of a uniform brownish powder.

A number of vertical, cast-iron cylindrical retorts heated to dull redness are charged with the mixture, and immediately covered. When crackling has ceased the covers are replaced by stoneware necks, each connected with a tube and receiver. The fire is then increased to drive the whole of the sulphide from the retort.

When cooled the necks are taken off, and the cake of vermilion removed. That nearest the retort is best, whilst that in the receiver contains free sulphur, and is resublimed with a fresh charge. The cakes are broken, ground with water, boiled with sodium hydroxide solution, washed and dried.

The Chinese vermilion is celebrated for its fine colour, which inclines to carmine. It is said to be prepared as follows:—

About half a bottle (38 lbs.) of mercury and 17½ lbs. of sulphur are mixed in an iron pan, about 25 inches wide and 7 or 8 inches deep, and heated by charcoal. When melted, it is stirred with an iron spatula, and the remainder of the mercury is gradually added. When the metal has disappeared the mass is removed from the fire, cooled by the addition of a little water, rapidly stirred, and coarsely powdered. The reddish or black semicrystalline powder, which contains free mercury and sulphur, is placed in a fixed iron pan, and covered with porcelain tiles 8 inches diameter (many of which are broken), arranged in the shape of a dome. The whole is covered by a pan 4 inches less in diameter than the fixed one, to which it is luted by clay, leaving four holes in the luting for the escape of gases. The charcoal fire is then lighted and kept fiercely burning for 18 hours; blue flames are seen burning round the holes, showing loss of sulphur and of mercury. The fires are then allowed to die out and the pans to cool. Most of the vermilion is found adherent to the porcelain, and is removed. That attached to the iron is inferior, and is made with the other waste into cakes with alum and glue water, dried, and resublimed. The sulphide on the porcelain is blood-red and crystalline. It is powdered and ground with water in a hand-mill between stones, and washed into a vessel. At the close of a day's work a solution of alum and glue (1 ounce of each to 1 gallon of solution) is well stirred with the powder, and the whole is allowed to stand until morning. The glue tends to lengthen the period of deposition, and to render the stratification into the various qualities more perfect. The alum is said to improve the colour. The liquid is decanted, and the upper portions of the deposit are set aside. The lower parts are reground and treated as before, the grinding being sometimes repeated several times. The fine vermilion is stirred in water and settled, and the water is decanted. The residue is dried in the open air, powdered, sifted through muslin, and packed in papers holding about 1⅓ ounce each (*v.* Chem. News, 1884, 50, 77; J. Soc. Chem. Ind. 1882, 1, 195). It is used for making Chinese red-ink; for painting on porcelain and wood and colouring candles and paper. Most of the numerous temples throughout China are painted red, and everything lucky and pleasant among the Chinese is of vermilion colour (J. Soc. Chem. Ind. 1890, 9, 1047).

It is said that China imported in 1880 mercury to the value of 170,032 dollars, the whole of which was converted into vermilion.

Wet processes.—The processes most used depend on the action of alkaline sulphides on the amorphous mercury sulphide. The temperature adopted largely influences the colour.

The action of these sulphides is attributed by Ditte (Compt. rend. 98, 1380) to the alternate production and decomposition of a double sulphide of mercury and alkali. In the case of potassium sulphide the compound $K_2S{\cdot}5HgS$ is first produced, and is decomposed at about 45° (the temperature generally employed), with deposition of the *red crystalline* mercuric sulphide, whilst the liberated alkaline sulphide dissolves a further amount of the more readily attacked amorphous sulphide, and again forms the double sulphide, which is again decomposed as before.

In order to prepare a polysulphide free from hyposulphite (which is said to have an injurious effect on the colour), potassium sulphate is converted into sulphide by ignition with carbon. The mass is extracted with water, and boiled with sulphur out of contact with air.

Of this strong solution 2¼ kilos. is digested and agitated with 1 kilo. sulphur and 5 kilos. mercury at a gentle heat. The mixture gradually becomes heated, and in about 2 hours acquires a greenish-brown colour. After a further period of 2 hours it becomes of a rich brown, and is allowed to cool to 50°, and is maintained at that temperature for 3 or 4 days with frequent agitation. A fine-coloured vermilion gradually settles down; it is washed with potash, then with dilute nitric acid, and finally with water (Firmenich, Dingl. poly. J. 1864, 172, 370).

According to Liebig, a fine vermilion is produced by immersing recently precipitated *white precipitate* in a solution of ammonium polysulphide. The mixture at first produced is black, but when heated to about 45° gradually acquires a fine colour resembling that of Chinese vermilion. It may be digested with potash, and washed to improve the colour.

Hausmann (Ber. 1874, 7, 1746) adds excess of dilute ammonia to a solution of mercuric chloride, and dissolves the precipitated *mercuric ammonium chloride* in a slight excess of sodium hyposulphite. On warming to 70° or 80° the vermilion begins to precipitate. The heat is continued until the mass has become pasty, the sulphide is then separated as usual. The above temperature and the presence of the ammonia and ammonium chloride are said to be essential.

One of the best processes is that of Brunner (Pogg. Ann. 1828, 15, 593). A mixture of 100 parts mercury with 38 parts sulphur (flowers) is triturated for some hours, mixed with a solution of 25 parts potash in 150 parts water, and digested at a temperature below 45°, keeping the liquid at constant volume by adding water.

After 2 or 3 hours it becomes brownish, and then gradually brightens. The temperature must be carefully regulated and the volume kept constant, or the precipitate loses its pulverulent character and becomes inferior in colour. At the proper point, usually after about 8 hours, the heating is stopped and the contents are washed as quickly as possible, as the further action of the potash would produce a brown colour. It is lixiviated to separate any black sulphide, and dried.

The method of Gauthier Bouchard is strongly recommended. Concentrated ammonia solution is saturated with sulphuretted hydrogen, and 400 c.c. of the solution is digested in a stone bottle with flowers of sulphur, with production of a solution of ammonium sulphide of sp.gr. 1·034. This is mixed with 200 grams of sulphur and 1000 grams of mercury (as pure as possible) agitated well in a closed vessel for about 7 hours, and finally heated for 3 or 4 hours to 50°. The liquid is decanted and the residue is washed with water, followed by dilute nitric acid and finally by water.

The chief difficulty in all these methods is to free the vermilion from alkaline sulphides and sulphur, the presence of which is detrimental to the colour of the product. Picton and Linder therefore recommend (Eng. Pat. 5120, 1892) that the black sulphide, produced by one of the usual methods, be suspended in water and treated with a stream of hydrogen sulphide gas until it dissolves. This solution is then heated in a closed vessel to 160°–170° for several hours, when a very pure vermilion is deposited.

Vermilion is adulterated with red lead, red ochre, chrome red, red oxide of iron, and frequently with gypsum. These all remain on volatilisation of the vermilion in a glass tube. Dragon's blood, if present, gives a characteristic odour on heating; it also dissolves in alcohol with a red colour. Chinese vermilion usually contains a little glue, which is not, however, an adulteration. Mercuric sulphide is occasionally present in vulcanised caoutchouc (Frank and Jacobsohn, Gummi. Zeit. 1909, 23, 1046).

The sp.gr. of red mercuric sulphide is 8·12; that of the black sulphide is 7·5.

Mercuric sulphide when heated in the air is decomposed with production of the metal and sulphur, which is at once oxidised to sulphur dioxide. With lime, alkaline carbonates, or metals such as iron, copper, and tin, it is reduced with formation of alkaline or metallic sulphide. When heated with litharge both lead and mercury are reduced, the oxygen and sulphur combining, and passing off as sulphur dioxide.

If boiled in water with powdered zinc, metallic mercury is liberated. A similar but slower action occurs with copper.

Concentrated nitric acid has no action except after prolonged heating. It is then converted—especially if freshly precipitated—into a white insoluble compound containing both sulphide and nitrate of mercury. It dissolves easily in *aqua regia* and in cold concentrated hydriodic acid. Barium sulphide readily dissolves it.

The solubility of mercuric sulphide in solutions of alkali sulphides has been investigated by Knox (*v.* Abegg's Handbuch der anorg. Chem. Bd. 2, Abt. 2, s. 633; and Trans. Faraday Soc. 1908, 4, 29). The black sulphide is more soluble than the red sulphide and the amount of either dissolved per mol. of sodium sulphide increases with dilution. The compound Na_2HgS_2 exists in the solution but when evaporated over sulphuric acid it deposits yellow crystals of the composition

$$2Na_2S,5HgS,3H_2O.$$

The solubility of the sulphides in water is very small, $K_{25}=0{\cdot}01-0{\cdot}02\times10^{-6}$ (Name, Zeitsch. anorg. Chem. 1904, 39, 108).

Mercuric sulphide can be obtained in colloidal solution by washing the precipitated sulphide with a solution of hydrogen sulphide (Winssinger, Bull. Soc. chim. [ii.] 49, 452; Linder and Picton, Chem. Soc. Trans. 1892, 61, 123; see also Picton, *ibid.* 139). By saturating with hydrogen sulphide a solution of 12 grams mercuric cyanide in 100 of water, a deep brown solution is obtained which when dialysed gives an unstable hydrosol. If, however, the hydrocyanic acid is distilled off *in vacuô* an oily stable hydrosol is obtained (Lottermoser, J. pr. Chem. 1907, [ii.] 75, 293).

Mercurous sulphide Hg_2S is not known.

Mercurous chloride, *Calomel* Hg_2Cl_2, occurs native in small quantities as *horn-quicksilver*, crystallising in rhombic prisms. Artificially prepared calomel has been known from early times, and was used in the 16th century as a medicine under the names *Aquila alba*, or *Draco mitigatus.*

Mercurous chloride is formed by the union of its elements.

It may be prepared by addition of an alkaline chloride to a solution of mercurous nitrate or other mercurous salt. The precipitate is washed well to remove the alkaline chloride, which if allowed to remain would render the calomel slightly soluble. It may be prepared on the large scale by mixing 17 parts of corrosive sublimate with a little alcohol or water to prevent the escape of irritating fumes, and rubbing in 13 parts of mercury until *deadened.* The mixture is then sublimed in glass flasks, in the upper portion of which the calomel condenses as a solid, translucent, fibrous cake. The flasks are broken and the cake is removed, ground to a powder, washed repeatedly with boiling water to remove mercuric chloride, and dried. The powder has usually a slight yellowish tinge.

It is also prepared from the sulphate; 1 kilo. of mercury is mixed with 1·5 kilos. of concentrated sulphuric acid in an iron boiler, gently heated until the fumes of sulphur dioxide cease to escape, and evaporated to dryness. It is then mixed with 1 kilo. of mercury and 1½ kilos. of common salt until *deadened*, and is sublimed as usual.

Instead of condensing the calomel in a cake, the vapours may be led into chambers containing air or steam, in which it falls as a very fine powder, which requires no grinding. Sometimes the distillation is conducted in an iron tube connected with the condenser.

At Apothecaries' Hall, the proportions used are 62 parts of mercury sulphate, 40½ parts of mercury, and 34 parts of common salt.

The Japanese have long manufactured a very pure calomel, absolutely free from mercuric chloride, called '*keifun*' (light powder). Balls of porous earth and salt, soaked in 'bittern' (mother liquor of concentrated sea-water), are heated in iron pots lined with earth, each containing a little metallic mercury. Hydrochloric acid is formed from the magnesium chloride in the bittern and the mercury distils into the closely fitting, but unattached clay covers of the pots. Air enters by diffusion and the following reaction takes place:

$$4Hg+4HCl+O_2=2Hg_2Cl_2+2H_2O,$$

by which calomel is formed at a temperature below its subliming point and fills the cover with a network of micaceous particles (Divers, J. Soc. Chem. Ind. 1894, 13, 108).

In preparing calomel by the wet way, 9 parts of mercury are digested in 8 parts of nitric acid (sp.gr. 1·2) with the aid of heat towards the end, until no more dissolves. The decanted solution is mixed with a boiling solution containing 8 parts of common salt in 64 parts of water and a few drops of hydrochloric acid. The precipitate is *well* washed with water. This form is said to be more effective for medicinal purposes than that prepared in the dry way.

Calomel is also produced by the action of reducing agents upon solutions of mercuric chloride.

Calomel is a white, tasteless powder, of sp.gr. 6·56–7·41, crystallising in four-sided prisms terminating in pyramids. When heated it volatilises without previous fusion, giving a colourless vapour of sp.gr. 8·21 (air=1). This appears to indicate a molecular constitution HgCl, but Smith and Menzies (J. Amer. Chem. Soc. 1910, 32, 1541) have shown by quantitative measurements of vapour pressures that calomel vapour, even when saturated, is completely dissociated into mercury and mercuric chloride, and contains no molecules of the type HgCl or Hg_2Cl_2. The results also show that calomel is soluble in mercury and its molecular weight in that solution at 360°–400° corresponds to the monomolecular formula, HgCl. The boiling-point of calomel is 382·5°. (For methods used *v.* S. and M. *ibid.* 32, 1419; *cp.* also Harris and v. Meyer, Ber. 1894, 27, 1482.) Baker states (Chem. Soc. Trans. 1900, 646) that perfectly dry mercurous chloride can be vapourised without dissociation and then has a v.d. corresponding to the formula Hg_2Cl_2. Further, by cryoscopic measurements, Beckmann has shown that mercurous chloride dissolved in fused mercuric chloride has the formula Hg_2Cl_2 (Zeitsch. anorg. Chem. 1907, 55, 175).

By conductivity measurements, the solubility of calomel in water has been found to be about 0·4 mgm. per litre at 20° (Ley and Heimbucher, Zeitsch. Elektrochem. 1904, 10, 301).

By treatment with alkalis and alkaline carbonates it is converted into mercurous oxide, ammonia converts it into black mercurous ammonium chloride. By digestion with ammonium chloride it is partially decomposed, mercuric chloride passing into solution and metallic mercury remaining undissolved (Richards and Archibald, Zeitsch. physikal. Chem. 1902, 40, 385). Hydrochloric acid or sodium chloride acts less rapidly. The prolonged action of steam, hot water, or hot air has a similar effect.

Calomel is largely used in medicine. The usual adulterations or impurities are corrosive sublimate, ammonium and sodium chlorides, lead and calcium carbonates and barium sulphate. The last three may be distinguished by their non-volatility, the others by their solubility in water or alcohol. According to Bonnewyn, if the calomel be shaken with a little alcohol the presence of even $\frac{1}{50000}$ part of corrosive sublimate can be detected by the black deposit produced on a knife-blade inserted into the solution.

Mercuric chloride, *Corrosive sublimate* $HgCl_2$. Mercury is converted into this salt when acted on by chlorine or *aqua regia.*

On the large scale it is prepared by distilling mercuric sulphate with common salt. Mercury is gently heated with concentrated sulphuric acid in an iron boiler until sulphur dioxide ceases to be evolved. The whole of the metal having dissolved, a slight excess of sulphuric acid is added to ensure the absence of mercurous sulphate, and a portion is tested by the addition of sodium chloride. If a precipitate of calomel falls, more acid is added. The mixture is evaporated and thoroughly dried. 20 parts of the sulphate is mixed intimately with 8 parts of sodium chloride and 1 part of manganese dioxide (to minimise the production of calomel) and introduced into glass subliming pots which are placed on iron plates, surrounded by sand to the necks and gently heated to remove moisture, which passes, through hoods placed over the necks, into a flue.

The moisture being removed, the hoods are replaced by small inverted conical condensers. Sufficient sand is then removed to uncover the upper half of the flasks, and the heat is increased until the whole has sublimed. The heat is finally raised sufficiently to render the sublimate coherent, but not to melt it. When cooled, the upper half of the flask is cracked away and the cake of sublimate is removed. On the lower part of the cake is frequently found a small quantity of the less volatile *calomel*; this is removed and added to a subsequent sublimation.

Wagner (Dingl. poly. J. 186, 135) recommends for the preparation on the large scale the decomposition of *turpeth mineral* (*v. Mercuric sulphate*) with hydrochloric acid. Mercuric chloride is thus obtained in a solution of sulphuric acid containing excess of mercuric oxide and is removed by crystallisation:

$$HgSO_4{\cdot}2HgO+2HCl=HgCl_2+H_2SO_4+2HgO.$$

For the crude salt, he precipitates mercuric oxide by the addition of sodium hydroxide to mercuric nitrate and digests the precipitate with crude magnesium chloride (the mother-liquor from *carnallite*). Where the presence of potassium chloride is not injurious the carnallite itself may be used, in which case the crystals obtained on evaporation contain $KCl,HgCl_2,H_2O$.

Mercuric chloride occurs as a white, satiny, translucent mass, sp.gr. 5·403; or, when crystallised from solutions, as needles or four-sided prisms, belonging to the rhombic system (Mitscherlich, Pogg. Ann. 1833, 28, 118; Luczizky, Zeitsch. Kryst. Min. 1909, 46, 297). It fuses at 288° (Carnelley) and boils at 303° (Carnelley and Williams), giving a vapour of sp.gr. 9·8, corresponding to the normal molecular weight. The vapour condenses in triclinic crystals (Von Lang, Wien. Akad. Ber. 1862, 45, 119). The relations between the vapour pressures and the molecular volumes of the mercuric halides have been examined by Prideaux (Chem. Soc. Trans. 1910, 97, 2032).

100 parts of water dissolve at 10° 6·57 parts, and at 100° 53·96 parts of the salt. The solution is acid to test paper and gradually deposits calomel on exposure to light. Mercuric chloride is soluble in 3 parts of cold alcohol and in about 1·2 parts of boiling alcohol. It is soluble in 4 parts of cold ether and can be extracted from aqueous solution by this solvent. In aqueous solution, mercuric chloride undergoes electrolytic dissociation only to a very slight degree (Grotrian, Wied. Annalen, 1883, 18, 177; Luther, Zeitsch. physikal. Chem. 1904, 47, 107), but it is partially hydrolysed (Ley, Ber. 1897, 30, 2192). Sulphuric acid precipitates it from aqueous solution (Viard, Compt. rend. 1902, 135, 242), but it dissolves in the strong acid and in nitric acid without decomposition. Aqueous solutions of mercuric chloride decompose in the dark to form mercuric oxide, chlorine, and hydrochloric acid, or in the light to form only mercurous chloride and the acid (Verda, Chem. Zentr. 1907, i. 1392). Mercuric chloride is volatile with steam and the salt can be recognised in the vapour from its solutions by chemical tests, or by its action on a photographic plate (Kof and Haehn, Arch. Pharm. 1907, 245, 529; Zeitsch. physikal. Chem. 1907, 60, 367). The dry salt or its solution is easily reduced, first to calomel, and finally to metallic mercury, by arsenic, zinc, tin, &c.; or by stannous chloride, oxalic acid or other reducing agents (*v. e.g.* de Coninck and Dautry, Bull. Acad. roy. Belg. 1908, 55).

Corrosive sublimate has a sharp, metallic taste and is extremely poisonous. The best antidotes are egg-white, with which it forms an insoluble compound, or, in order of efficacy, sodium thiosulphate ('hypo'), hydrogen sulphide, sodium iodide, sodium bromide, and sodium chloride (Raimondi, Chem. Zentr. 1907, ii. 1807). It is used in medicine both internally and externally, especially in cases of syphilis, and in surgery as an antiseptic in the form of dilute solutions (usually 1 : 1000) and in gauzes and lint. (For the estimation of mercuric chloride in surgical dressing-materials, see Utz, Pharm. Post. 39, 785.) It is also used in preserving anatomical specimens and samples of milk, syrups, &c., for analysis.

Mercuric chloride forms numerous double salts and additive compounds. With the alkali chlorides it forms the compounds $KCl{\cdot}HgCl_2,H_2O$;

$$2KCl{\cdot}HgCl_2,H_2O\ ;\ KCl{\cdot}2HgCl_2,2H_2O\ ;$$

$2NaCl{\cdot}HgCl_2$; $NaCl{\cdot}HgCl_2,2H_2O$, and many others. Of the double salts with ammonium chloride only $HgCl_2{\cdot}2NH_4Cl,H_2O$ can be crystallised from water, but others are formed (Meerburgh, Zeitsch. anorg. Chem. 1908, 59, 136). To the formation of such compounds is due the increased solubility of mercuric chloride in solutions of alkali chlorides and in hydrochloric acid. In many cases, these solutions contain complex anions in which mercury is present (*v.* Shenill, Zeitsch. physikal. Chem. 1903, 43, 705). It forms additive compounds with alcohols and ketones, aromatic nitro derivatives (Mascarelli, Atti. R. Accad. Lincei, 1908, [v.] 17, i. 29), and with alkaloids. The latter compounds are frequently used in the purification of the alkaloids.

A series of *mercury oxychlorides* can be obtained from mercuric chloride by boiling its solution with mercuric oxide or by the action of potassium hydrogen carbonate or calcium carbonate upon it (Tarugi, Gazz. chim. ital. 1901, 31, ii. 313; Arctowski, Zeitsch. anorg. Chem.

1896, 12, 353). $2HgCl_2{\cdot}HgO$ crystallises in red monoclinic needles; $HgCl_2{\cdot}2HgO$ is a black crystalline precipitate and $HgCl_2{\cdot}3HgO$ occurs in glistening yellow scales as the mineral *kleinite* (Sachs, Sitzungsber. K. Akad. Wiss. Berlin, 1905, 1091). Hewitt states that when caustic soda solution diffuses into a solution of mercuric chloride and sodium chloride, very dark red crystals of the formula $Hg_6O_5Cl_2$ are produced (Chem. Soc. Proc. 1907, 23, 10; *v.* also Buttle and Hewitt, Chem. Soc. Trans. 1908, 93, 1405).

Mercurous bromide Hg_2Br_2 is obtained as a white precipitate by adding a soluble bromide to a solution of a mercurous salt, or by the prolonged action of bromine water on the metals. It crystallises from mercurous nitrate solution in white, pearly, tetragonal leaflets, sp.gr. 7·037, but is nearly insoluble in water. At 340°–350° it sublimes without decomposition.

Mercuric bromide $HgBr_2$ is formed from its elements with evolution of heat (Nernst, Zeitsch. physikal. Chem. 1888, 2, 20; Varet, Compt. rend. 120, 620), and is produced by dissolving mercuric oxide in hydrobromic acid. Cold water dissolves 0·4 p.c. and boiling water 2·5 p.c. of the salt, and on cooling it crystallises out in anhydrous glistening scales. From alcohol it crystallises in white rhombic prisms. Mercuric bromide melts at 244° (Carnelly and Williams, Chem. Soc. Trans. 1880, 127) (235° given for m.p. by Guinchant, Compt. rend. 1909, 149, 479). Like the chloride it is decomposed by boiling with water, *oxybromides* being formed (Fischer and Wartenburgh, Chem. Zeit. 1902, 26, 966).

It is occasionally administered in medicine instead of mercuric chloride, usually by hypodermic injection of a solution of the soluble compounds with sodium chloride $HgBr_2{\cdot}2NaCl$ or bromide, $HgBr_2{\cdot}2NaBr$ (Vicario, J. Pharm. Chim. 1907, [vi.] 26).

A double bromide of mercury and potassium has been used as a disinfectant (Cooke, Eng. Pat. 1530, 1905).

Mercurous iodide Hg_2I_2 is a green insoluble powder employed medicinally. It is prepared by triturating a mixture of 5 parts iodine and 8 parts mercury, moistened with alcohol; or by precipitation of a mercurous salt with potassium iodide. A purer product, obtained by boiling excess of iodine with a solution of mercurous nitrate containing nitric acid, crystallises in transparent, yellow, tetragonal plates, blackened by light. When heated it becomes first yellow, then red and finally garnet-red, and on cooling passes through the same colour changes in reverse order. It begins to sublime at about 190° and at 290° melts with decomposition (Stroman, Ber. 1887, 20, 2818; François, J. Pharm. Chim. 1899, [vi.] 10, 16; Compt. rend. 1895, 121, 888; 1896, 122, 190). It dissolves slightly in various oils. The best solvent is castor oil, of which 100 parts dissolves 2 parts of the iodide.

Mercuric iodide HgI_2. A mixture of 5 parts iodine and 4 parts mercury is moistened with a little alcohol, triturated, and sublimed. Dublanc pours 1 kilo. of alcohol upon 100 grams of mercury and adds 124 grams of iodine in 10 successive portions, triturating each time until the alcohol becomes colourless. The last 4 grams usually produce a permanent colour. The precipitate is then washed with alcohol and dried.

In the wet way, which is the best, a solution of 10 parts potassium iodide is added to a solution of 8 parts mercuric chloride, and the precipitate, which is salmon-coloured at first but soon becomes red and crystalline, is washed. A slight excess of either the chloride or iodide will redissolve a portion of the precipitate.

Mercuric iodide may be obtained in comparatively large crystals by the action of a mercuric salt on ethyl or methyl iodides (Bodroux, Compt. rend. 130, 1622); by the action of these iodides on the metal a very pure product may be obtained (Neogi, Chem. Soc. Abstr. 1907, ii. 772).

Mercuric iodide is dimorphous, existing in a red and a yellow form. The *red* variety is produced by the above methods of preparation. It crystallises from hot potassium iodide, alcohol, or nitric acid in tetragonal prisms and pyramids (Luczizky, Zeitsch. Kryst. Min. 1909, 46, 297), and is soluble in many organic solvents (Beckmann and Stock, Zeitsch. physikal. Chem. 1895, 17, 130). Its sp.gr. is 6·26. When heated to 126° it changes into the *yellow* modification with absorption of heat (Guinchant, Compt. rend. 1907, 145, 68). The yellow form melts at 253°–254° and volatilises without decomposition, the vapour density corresponding to the formula HgI_2. By cooling, the liquid or condensing the vapour (Gernez, Compt. rend. 1899, 128, 1516), the yellow modification is obtained in rhombic prisms of sp.gr. 6·06 which retain their form and colour when cooled to the ordinary temperature, but slowly (or immediately on rubbing) pass into the red variety. Nevertheless the yellow form may be kept at the ordinary temperature for many years (Gernez, Compt. rend. 1909, 148, 1015), and it separates from nearly all organic solvents in this form, though it is only stable above 126° (Kastle and Clark, Amer. Chem. J. 1899, 22, 473; Kastle and Reed, *ibid.* 1902, 27, 209; Gernez, Compt. rend. 1903, 136, 889); 129·5° (Reinders, Zeitsch. physikal. Chem. 1900, 32, 507). 1 litre of absolute alcohol at 18° dissolves 11·18 grams of the salt; 80 p.c. alcohol dissolves only 2·86 grams. It is almost insoluble in water; 1 litre at 17·5° dissolves 0·0403 grams (Bourgoin, Bull. Soc. chim. [ii.] 42, 620).

In potassium or other alkaline iodide, it dissolves freely with formation of a double iodide.

The solution in potassium iodide is a more powerful antiseptic than mercuric chloride. It has been employed in the preparation of an antiseptic soap (Thomson, J. Soc. Chem. Ind. 1888, 192). An alkaline solution of mercuric iodide in potassium iodide is employed as a delicate test for ammonia and its compounds, being known as *Nessler's solution.*

In mercuric chloride it dissolves readily, forming a double chloride and iodide.

Mercuric iodide forms a very large number of double salts (*v.* Duboin, Ann. Chim. Phys. 1909, [viii.] 16, 258). With alkali iodides and ether it forms both crystalline and liquid compounds, *e.g.* $KHgI_3{\cdot}3Et_2O$, and $KHgI_3{\cdot}4Et_2O$ (Marsh. Chem. Soc. Trans. 1910, 2297).

Mercuric iodide is much used in photography as an intensifier, a solution in sodium sulphite containing the proportions, $HgI_2 : Na_2SO_3$: water : : 1 : 10 : 100, being the best. For details see Lumière Bros. and Seyewetz (Monit. Scient. 1899, 13, 782; J. Soc. Chem. Ind. 1899, 1155).

Mercurous fluoride Hg_2F_2, produced by the action of hydrofluoric acid on the carbonate or of silver fluoride on calomel (Finkener, Pogg. Ann. 110, 142), is a yellow crystalline powder, hydrolysed by hot water and blackened by light.

Mercuric fluoride $HgF_2,2H_2O$, prepared by dissolving mercuric oxide in aqueous hydrofluoric acid (Finkener, Pogg. Ann. 110, 628) is a white crystalline salt. It is decomposed in air at 50° forming an *oxyfluoride* $HgF(OH)$; and in dilute aqueous solution is completely hydrolysed, but without formation of oxyfluorides (Jaeger, Zeitsch. anorg. Chem. 1901, 27, 22; Cox, *ibid.* 1904, 40, 146).

Mercurous sulphate $Hg_2(SO_4)_2$ is prepared by dissolving 2 parts mercury in 3 parts sulphuric acid with the aid of a gentle heat; or by the addition of sulphuric acid to a solution of mercurous nitrate; or by the electrolysis of sulphuric acid with a mercury anode (Hulett, Zeitsch. physikal. Chem. 1904, 49, 494). It is a white crystalline salt which with water yields first the basic salt $Hg_2SO_4 \cdot Hg_2O,H_2O$, and finally the oxide.

Mercurous sulphate is used in the standard cells of Clark and Weston.

Mercuric sulphate $HgSO_4$ is prepared by dissolving mercury in strong sulphuric acid with the aid of heat, or mercuric oxide in dilute sulphuric acid. Its preparation has been described under *Mercuric chloride.*

From its solution in sulphuric acid it crystallises in small, silvery, stellate plates. When strongly heated, it becomes reduced to mercurous sulphate with evolution of oxygen, mercury, and sulphur dioxide.

It is soluble in sodium chloride solution. When heated with water it produces a yellow basic sulphate $HgSO_4 \cdot 2HgO$, which turns red when heated, known as *turpeth* or *turbith mineral*, which is soluble in 2000 parts of cold and 600 parts of hot water. Turpeth appears to be the only basic sulphate which can exist in equilibrium with water at 25° (Cox, Zeitsch. anorg. Chem. 1904, 40, 165; Hoitsema, Zeitsch. physikal. Chem. 1895, 17, 651; Guinchant, Bull. Soc. chim. 1896, [iii.] 15, 555). A thiobasic mercuric sulphate, $4HgO \cdot 2HgS \cdot 3SO_3,4H_2O$, has been described by Estrup (Zeitsch. anorg. Chem. 1909, 62, 168).

Nitrates. Several nitrates of mercury are known. When excess of mercury is dissolved in a cold mixture of 1 part nitric acid and 4 parts water, the *mercurous* salt is formed. If the acid be sufficiently strong to effervesce, or be used in excess, or if the mixture be heated, *mercuric* nitrate is produced.

Mercurous nitrate $Hg_2(NO_3)_2$ forms monoclinic tables containing 2 molecules of water. They effloresce and become anhydrous in dry air and when heated to 70° melt to a clear liquid of sp.gr. 4·3 (Retgers, Jahrb. Min. 1896, ii. 183). The pure salt is immediately decomposed by water with formation of a basic nitrate, and when it is boiled with water mercury is volatilised and may be condensed in globules (Hada, Chem. Soc. Trans. 1896, 1667). Several basic nitrates are known (*v.* Cox, Zeitsch. anorg. Chem. 1904, 40, 174).

Mercuric nitrate $Hg(NO_3)_2$ is produced by boiling mercury with nitric acid until the solution no longer gives a precipitate with sodium chloride. Large crystals containing

$$2Hg(NO_3)_2,H_2O$$

separate on concentration.

The action of water at 25° on mercuric nitrate produces a basic salt, $Hg(NO_3)_2 \cdot 2HgO$, as a heavy white powder, which is decomposed on further treatment with water yielding the oxide (Cox, Zeitsch. anorg. Chem. 1904, 40, 159).

Mercurous nitrite $Hg_2(NO_2)_2$ is produced by the action of dilute nitric acid upon mercury and forms yellow needles which are partially decomposed by water. Dilute nitric acid slowly converts it into mercurous nitrate, and when heated it decomposes yielding nitric oxide, mercurous nitrate, mercury, and mercuric oxide (Rây, Zeitsch. anorg. Chem. 1896, 12, 365, Chem. Soc. Trans. 1897, 337; Rây and Sen, *ibid.* 1903, 491). The pure salt has sp.gr. 5·925 (Rây, Chem. Soc. Trans. 1908, 999).

Mercuric nitrite $Hg(NO_2)_2$ is obtained by the action of mercuric chloride on silver nitrite or by the decomposition of mercurous nitrate by water (Rây, Chem. Soc. Proc. 20, 57; Chem. Soc. Trans. 1897, 71, 337).

Mercuric hyponitrite HgN_2O_2, formed by the action of sodium hyponitrite on mercuric nitrite, is a buff-coloured powder which decomposes spontaneously into nitric oxide and mercurous hyponitrite (Divers, Chem. Soc. Trans. 1899, 119; see also Rây, *ibid.* 1907, 1404, 2031; Rây and Gañguli, *ibid.* 1399).

Mercury nitride N_2Hg_3 is produced as a brown powder by the action of potassamide on mercuric bromide in liquid ammonia solution. When dry it is very explosive (*v.* Franklin, Zeitsch. anorg. Chem. 1905, 46, 1).

Mercury acetylide (*mercury carbide*)

$$3C_2Hg,H_2O,$$

prepared by passing acetylene into a solution of mercuric oxide in ammonium hydrate and carbonate, is a heavy white powder, which is explosive (*v.* Plimpton and Travers, Chem. Soc. Trans. 1894, 264). For the action of acetylene on solutions of mercuric chloride and acetate, see Burkard and Travers (Chem. Soc. Trans. 1902, 81, 1271); Biltz and Mumm (Ber. 1904, 37, 4417), and Brame (Chem. Soc. Trans. 1905, 427).

Mercuric cyanide $Hg(CN)_2$ is prepared by boiling a solution of 1 part potassium ferrocyanide and 2 parts mercuric sulphate in 7 parts water:

$$2K_4Fe(CN)_6+7HgSO_4$$
$$=6Hg(CN)_2+4K_2SO_4+Fe_2(SO_4)_3+Hg.$$

It may also be prepared by adding 31 grams sodium cyanide dissolved in 50 c.c. water to 90 grams mercuric sulphate. Heat is evolved and the whole solidifies to a mass of granular mercuric cyanide which is extracted with boiling alcohol and finally recrystallised from water (Rupp and Goy, Apoth. Zeit. 1908, 23, 374).

It crystallises in white needles or tetragonal prisms soluble in 8 parts of cold water, insoluble in absolute alcohol. When ignited, it decomposes with evolution of cyanogen.

In aqueous solution mercuric cyanide only undergoes ionic dissociation to a very small extent, and therefore does not exhibit all the usual reactions of mercuric salts. For example, with potassium iodide it yields, not mercuric iodide, but a complex salt $Hg(CN)_2{\cdot}HgI_2{\cdot}2KCN$ (Rupp and Goy, Arch. Pharm. 1909, 247, 100). It is decomposed with formation of hydrocyanic acid by hydrochloric, hydrobromic, and hydriodic acids, or by sulphuretted hydrogen, but not by dilute sulphuric or nitric acids.

The aqueous solution readily dissolves mercuric oxide forming the basic salt $Hg(CN)_2{\cdot}HgO$, which is used as an antiseptic under the name of *mercuric oxycyanide* (Holdermann, Arch. Pharm. 1905, 243, 600; 1906, 244, 133; Rupp, *ibid.* 1906, 244, 1).

Mercuric thiocyanate $Hg(CNS)_2$ is prepared by the addition of an excess of mercuric chloride to a solution of ammonium thiocyanate. It forms a white crystalline precipitate which burns freely when ignited with evolution of mercurial vapours, and forms a most voluminous ash.

It is occasionally made into a thick paste with gum and worked into pilules which when dried are sold as *Pharaoh's serpents' eggs.*

It is soluble in a solution of ammonium thiocyanate and this solution, under the trade-name 'Agfa,' is used as an intensifier for photographic negatives (Eberhard, Photo. Mittheil, 1901, 38, 15; J. Soc. Chem. Ind. 1901, 387).

AMMONIACAL COMPOUNDS OF MERCURY.

Very many of these compounds have been described, but little is known as to their constitution because the ordinary methods for the determination of molecular weight are not applicable to them.

It is probable that there exist substitution products of ammonia of the type $(OHg_2)NH_2{\cdot}X'$ (*amino-mercuric compounds*); substitution products of ammonium compounds of the type

$$NHg_2X'{\cdot}H_2O$$

(*mercuri-ammonium compounds*); and additive compounds of ammonia and mercuric salts. (*See* Rammelsberg, J. pr. Chem. 1888 [ii.] 38, 558; Barfoed, *ibid.* 1889, [ii.] 39, 201; Pesci, Gazz. chim. ital. 1891, 21, 569; Zeitsch. anorg. Chem. 1899, 21, 301; *see also* Hofmann and Marburg, Annalen, 1899, 305, 198; Zeitsch. anorg. Chem. 1900, 23, 126; Franklin, J. Amer. Chem. Soc. 1907, 29, 35.)

Millon's base has the empirical formula $H_5O_3NHg_2$, and is regarded as *dihydroxydimercuriammonium hydroxide* $(HO{\cdot}Hg)_2:NH_2{\cdot}OH$, or as dimercuriammonium hydroxide

$$NHg_2{\cdot}OH{\cdot}2H_2O.$$

It is formed as a pale yellow powder when mercuric oxide is gently warmed with dilute ammonia. It deflagrates when heated.

Salts of Millon's base are formed by digesting the base with dilute acids, or by adding ammonia to solutions of mercuric salts of oxyacids. Anhydrous salts of the formula NHg_2X' have been obtained but are probably not true derivatives of Millon's base, but amino compounds of the type $Hg:N{\cdot}HgX'$ (Franklin, Zeitsch. anorg. Chem. 1905, 46, 1; *see also* François, Compt. rend. 1900, 130, 332, and 1022).

The iodide of Millon's base $(OHg)_2NH_2{\cdot}I$ (*oxydimercuriammonium iodide*) is formed by adding ammonia to a solution of mercuric potassium iodide (Nessler's solution, *v.* ANALYSIS), or by the action of excess of ammonia on mercuric iodide. It is a brown powder, fusible without decomposition.

Amino-mercuric chloride, *Infusible white precipitate* $NH_2{\cdot}HgCl$ (Hofmann and Marburg; Franklin), is prepared by the addition of ammonia to a solution of mercuric chloride. For medicinal purposes 1 ounce of mercuric chloride is dissolved in 3 quarts of water, and to the cool solution 8 fluid ounces of concentrated ammonia is added with frequent agitation, and the precipitate is washed and dried.

It is a white, inodorous, highly poisonous powder, totally volatile on heating to 360°, slightly soluble in boiling water, easily soluble in nitric, hydrochloric and sulphuric acids, insoluble in alcohol.

An analogous compound derived from ethylamine, $NH(C_2H_5)HgCl$, is known.

Fusible white precipitate $Hg(NH_3)_2Cl_2$ is produced by boiling the above compound with ammonium chloride solution, and form crusts of small regular dodecahedra.

MERCURY SALTS OF ORGANIC ACIDS.

Mercurous formate $Hg_2(HCO_2)_2$, obtained by adding sodium formate to mercurous nitrate solution forms white leaflets soluble in 250 parts of water at 17°. When boiled with water it is reduced to metallic mercury (Liebig, Annalen, 3, 207).

Mercuric formate $Hg(HCO_2)_2$, obtained by solution of yellow mercuric oxide in dilute formic acid, slowly changes to mercurous formate with liberation of formic acid and carbon dioxide (Varet, Compt. rend. 1905, 140, 1641).

Mercurous acetate $Hg_2(CH_3{\cdot}CO_2)_2$ forms white leaflets, more stable than the formate, soluble in 133 parts of water at 12°–15° (Lefort, Annalen, 56, 247).

Mercuric acetate $Hg(CH_3{\cdot}CO_2)_2$ also forms white leaflets soluble in 2·75 parts of water at 19° and in 1 part at 100°. The aqueous solution is acid, and on warming the salt is largely hydrolysed. Both these salts are used in medicine for the treatment of skin diseases.

Mercuric oleate and **stearate,** prepared by double decomposition, are used in pharmacy (Dott, Chemist and Druggist, 1909, 74, 785).

Mercurous oxalate $Hg_2C_2O_4$ is a white salt, very slightly soluble in water, insoluble in excess of oxalate (Schäfer and Abegg, Zeitsch. anorg. Chem. 1905, 45, 299). It has been used in gelatin emulsions for phototype printing (Castellani, Phot. Korr. 1906, 43, 281; J. Soc. Chem. Ind. 1906, 827).

Mercuric oxalate HgC_2O_4 is also sparingly soluble in water, but forms soluble double salts with many oxalates. In solution it is quantitatively reduced to mercurous oxalate by the action of light (Roloff, Zeitsch. physikal. Chem. 1894, 13, 324). This reaction is made use of in *Eder's mercury oxalate photometer* (*v.* Abegg, Zeitsch. Elektrochem. 1903, 9, 569). The sensitiveness of the solution to light is increased by the fluoresceins and their sodium salts (Jodlbauer and Tappeiner, Ber. 1905, 38, 2602).

Mercury fulminate $(C:N{\cdot}O)_2Hg,\frac{1}{2}H_2O$ is prepared by adding 17 parts of alcohol (90 p.c.) to a cold solution of 3 parts of mercury in 36 parts of nitric acid (sp.gr. 1·34), contained in a large flask. The mixture froths and turns black, and a very violent reaction takes place which is moderated by the addition of another 17 parts of alcohol. On the large scale the reaction is carried out by mixing in large glass balloons 1 part of mercury, 10 parts of nitric acid (sp.gr. 1·33), and alcohol (sp.gr. 0·833) in the proportion of 1 litre to each kilo. of acid. The reaction generally begins spontaneously and is allowed to proceed by itself (Beckmann, Ber. 1886, 19, 993; Lobry de Bruyn, *ibid.* 1370) (*v.* FULMINIC ACID).

On cooling the solution produced by either method, mercuric fulminate crystallises in shining white or grey coloured prisms, sp.gr. 4·42. It is insoluble in cold water, but fairly soluble in hot water and in aqueous ammonia (*v.* Steiner, Ber. 1876, 9, 779).

Mercuric fulminate explodes violently on percussion or when treated with sulphuric acid, and is much used as a detonator (*v.* EXPLOSIVES); but when ignited with a flame it burns with a reddish flame yielding carbon monoxide, nitrogen, and mercury.

Mercury gallate, prepared by triturating 37·6 grams gallic acid and 21·6 grams yellow mercuric oxide in 25 c.c. of water, is used therapeutically as an antisyphilitic (Brousse and Gay, Compt. rend. 1893, 117, 284).

Mercury tannate is prepared by triturating mercurous nitrate (20 grams) with tannin (12 grams), and is also used in medicine (Zdarck, J. Pharm. d'Anvers, 58, 98).

Mercuric *p*-phenolsulphonate is used medicinally under the name '*hydrargyrol*,' and its compound with ammonium tartrate is similarly used and known as '*asterol*.'

ORGANIC MERCURY DERIVATIVES.

Mercury can replace hydrogen in most organic compounds, and the substances so formed fall into two broad classes: (*a*) those in which mercury is attached to carbon, and (*b*) those in which it is attached directly to nitrogen. Generally, compounds of class (*a*) are non-electrolytes and in general chemical properties resemble the parent compounds. Compounds of class (*b*) are usually less stable and in solution show the reactions of the mercuric ion.

Mercury Derivatives of Aliphatic Compounds.

Mercury alkyl derivatives are of two classes:

(1) Monalkyl derivatives

$X{\cdot}Hg{\cdot}C_nH_{2n+1}(X{=}Cl,Br,I,\ etc.)$

(2) Dialkyl derivatives $Hg(C_nH_{2n+1})_2$.

(1) *Monalkyl mercury compounds* are prepared:

(*a*) By the action of mercury on alkyl iodides in sunlight.

(*b*) By the action of halogens, haloid acids, or mercury halides on the dialkyl derivatives.

The halogen compounds are usually colourless crystalline solids, which have a definite melting-point and can be sublimed and distilled in steam. Treated with moist silver oxide they yield hydroxy compounds which are thick liquids, soluble in water and alcohol, strongly basic in character and forming series of salts.

Methyl mercuric iodide $CH_3{\cdot}HgI$, forms colourless crystals, m.p. 143°, which sublime when heated (Frankland, Annalen, 85, 361).

Ethyl mercuric chloride $C_2H_5{\cdot}HgCl$. forms pearly leaflets, sp.gr. 3·48, subliming at 40° (Dünhaupt, Annalen, 92, 379; *see* also Buckton, *ibid.* 112, 221).

Ethyl mercuric hydroxide $C_2H_5{\cdot}HgOH$, produced by the action of moist silver oxide on the preceding compound, is a viscous caustic liquid which gives rise to a number of salts.

(2) *Mercury dialkyls* are prepared:

(*a*) By the action of sodium amalgam on alkyl iodides in presence of ethyl acetate (Frankland, Annalen, 130, 105).

(*b*) By the action of potassium cyanide on mercury alkyl iodides.

(*c*) By treating zinc alkyls with mercuric chloride or an alkyl mercuric chloride (*v.* also Buckton, *ibid.* 108, 103).

They are colourless heavy liquids, unchanged by air or water at the ordinary temperature. They have a peculiar faint odour, and are extremely poisonous (*v.* Hepp, Ber. 1887, Ref. 798). When heated in air they burn.

Mercury dimethyl $Hg(CH_3)_2$ has b.p. 93°–96° and sp.gr. 3·07. Hydrochloric acid converts it into mercuric chloride (Seidel, J. pr. Chem. [ii.] 29, 134).

Mercury diethyl $Hg(C_2H_5)_2$ has b.p. 159°, sp.gr. 2·44. Mixed mercury alkyls of the type $CH_3{\cdot}Hg{\cdot}C_2H_5$, have not been obtained (Frankland, Annalen, 111, 57; Buckton, *ibid.* 109, 222).

(For an account of the many known aliphatic compounds containing mercury, *see* Beilstein's Handbuch der Org. Chem. Bd. i. 1524–1526; suppl. i. 854.)

Mercuriethylene-diamine sulphate

$Hg(CH_2{\cdot}NH_2)_2{\cdot}H_2SO_4$

mixed with a molecular proportion of ethylene diamine is used as an antiseptic under the trade name '*sublamin*.' It does not precipitate soap, or coagulate albumen, and has a greater germicidal and a less toxic action, weight for weight, than mercuric chloride (Scordo, Chem. Soc. Abstr. 1907, ii. 713; Pesci, Gazz. chim. ital. 1909, 39, i. 143).

Mercury Derivatives of Aromatic Compounds.

Aryl mercuric compounds are formed with an ease comparable with that of sulphonation or nitration and the metal enters the usual position in the molecule (except in the case of benzoic acid, *v.i.*). They are usually prepared by boiling the aryl compounds with mercuric chloride solution. When acted on by stannous chloride in alkaline solution they yield mercury and mercury aryls of the type HgR_2 (Dimroth, Chem. Zentr. 1901, i. 449).

Mercury diphenyl $Hg(C_6H_5)_2$ is prepared by heating bromobenzene, mercuric chloride, and metallic sodium in benzene (Michaelis and Reese, Ber. 1882, 2876); or by heating bromobenzene with an equal volume of xylene, a little ethyl acetate and excess of sodium amalgam (Aronheim, Annalen, 194, 145). It is also obtained by the action of mercuric chloride on an ethereal solution of magnesium phenylbromide (Pfeiffer and Truskier, Ber. 1904, 37, 1125). It crystallises from benzene in white needles or rhombic prisms, m.p. 125°–126°, is easily volatile and gives a vapour irritating to the eyes. Mercury diphenyl has a therapeutic action equal to that of the fatty compounds, but it is less poisonous (Louise and Moutier, Compt. rend. 1905, 140, 1703).

Phenyl-mercuric chloride $C_6H_5{\cdot}HgCl$, made by the action of chlorine on mercury diphenyl, forms small white rhombic prisms, m.p. 250° (Dreher and Otto, Annalen, 154, 93).

Phenyl-mercuric hydroxide $C_6H_5{\cdot}HgOH$ is a strongly-caustic liquid and forms numerous salts (Otto, Ber. 1885, 246).

Mercury di-tolyls, di-xylyls, di-napthyls, &c., are known, and each forms similar series of compounds.

o- and *p-Hydroxyphenyl mercurioxides* and *hydroxy-phenylene-dimercuryoxides* are present in the so-called 'mercury phenate,' the *hydrargyrum carbolicum,* of the pharmacopœias (Dimroth, Ber. 1902, 35, 2853). This is obtained by precipitating a solution of mercuric chloride with sodium phenate (Merck, Apoth. Zeit. 1889, 4, 651; Andres, Pharm. Zeitsch. Russe, 27, 625), and is used medicinally in the treatment of syphilis.

o-Hydroxymercuribenzoic anhydride

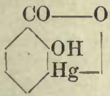
$$C_6H_4\left<\begin{matrix}Hg\\CO\end{matrix}\right>O$$

is the chief constituent of the 'mercury benzoate' used medicinally. It is prepared by digesting freshly precipitated mercuric oxide with benzoic acid and water and is formed by the action of dilute acids on the salts of *o-hydroxymercuribenzoic acid*

$$C_6H_4\left<\begin{matrix}Hg{\cdot}OH\\CO{\cdot}OH\end{matrix}\right.$$

o-Mercuridibenzoic acid $Hg:(C_6H_4{\cdot}COOH)_2$ is also known (Pesci, Atti. R. Accad. Lincei, [v.] 10, i. 413).

Anhydro-o-hydroxymercurisalicylic acid



is produced by boiling mercury salicylate with water for 15 minutes, and is therefore the main constituent of '*hydrargyrum salicylicum,*' which is prepared by digesting yellow mercuric oxide with aqueous salicylic acid. It is much used in the treatment of syphilis (Buroni, Gazz. chim. ital. 32, ii. 307; Dimroth, Ber. 35, 2872; *see* also Larin, Chem. Zeit. Rep. 1901, 25, 193).

(For further details of mercury aromatic compounds and a complete bibliography, *v.* Beilstein, Handbuch der Org. Chem. Bd. iv. 1703–1713; suppl. iv. 1208–1218.

For further information as to mercury compounds used in medicine, *v.* Hare, Caspari, and Rusby, National Standard Dispensatory (1905), 784.)

MESITOL *v.* PHENOL AND ITS HOMOLOGUES.

MESITYLENE *v.* CUMENES.

MESORCINOL *v.* PHENOL AND ITS HOMOLOGUES.

MESOTAN. Trade name for a yellowish oily liquid, $OH{\cdot}C_6H_4{\cdot}CO{\cdot}OCH_2{\cdot}OCH_3$, obtained by treating sodium salicylate with monochlordimethyl ether (*v.* SYNTHETIC DRUGS).

MESO-THORIUM *v.* RADIOACTIVITY and THORIUM.

MESOXALIC ACID *v.* KETONES.

META-ARABIC ACID *v.* GUMS.

METACETONE. By heating sugar with lime Fremy obtained a substance, b.p. 84°, to which he gave the name *metacetone* and the formula $C_6H_{10}O$. Fischer and Laycock find that this body is in reality a mixture of *propylaldehyde, dimethylfurfuran,* a third substance with the properties of a hydrocarbon, and a number of other lower and higher boiling homologues. Fischer and Laycock distilled 100 kilos. of sugar and 300 kilos. of burnt lime, and collected the distillate in fractions. Fraction *a*, distilling below 65°, combined partly with phenylhydrazine, yielding the phenylhydrazone of propylaldehyde. The distillate boiling at 25°–45°, consisted of furfuran, and that boiling at 45°–65° is probably methylfurfuran. Fraction *b*, distilling at 65°–115°, was treated like fraction *a*, phenylhydrazine being added, and the product distilled. The distillate consisted of a hydrocarbon and a substance which dissolved on heating with dilute hydrochloric acid to 170°, forming acetonylacetone, and which is probably dimethylfurfuran. The residue, which combined with phenylhydrazine is the phenylhydrazone of propylaldehyde. The fraction boiling above 115° is a complex mixture, consisting of higher homologues of furfuran and aldehydes, which could be removed with sodium bisulphite.

Fischer and Laycock have investigated wood tar, and found that this likewise contains propylaldehyde and dimethylfurfuran (Ber. 1889, 22, 101).

METACETONIC ACID *v.* PROPIONIC ACID.

METALDEHYDE *v.* ALDEHYDE.

METALLIC SOAPS *v.* SOAPS.

METALLOGRAPHY deals with the internal structure and constitution of metals and their alloys. The science is a comparatively young one, dating back only to 1864, when Sorby (Proc. Sheffield Lit. Phil. Soc. 1864) first applied the microscope to the study of metals and established the close analogy which exists between the internal structure of metals and of rocks. Sorby's pioneer work, however, remained neglected for a long time, and the microscopic study of metals and alloys was revived independently in Germany by Martens (A. Martens, Zeitsch. Ver. deut. Ing. 1878, 22, 11) and in France by Osmond (F. Osmond and J. Werth, Compt. rend. 1885, 100, 450). Since then the subject has developed rapidly, and now numbers many enthusiastic workers, among whom may be mentioned in England the late Roberts-Austen, Arnold and Stead; in France Osmond, Le Chatelier, Charpy, and Guillet; and in Germany Heyn, Wüst, Friedrich, and Tammann.

The metallographic study of metals and alloys is carried out by both microscopical and physical means, the most important of the latter being the thermal or pyrometric study of the behaviour of these bodies on heating and cooling. Other physical methods, such as measurements of thermal expansion, electrical resistance, solution potential, and many other quantities have also been employed. The pyrometric method is, however, at present far the most fruitful and important, and in the present article attention will be almost entirely confined to this one among the physical methods just referred to. In the majority of metallographic researches the pyrometer and the microscope are practically the only instruments used.

The pyrometric study of metals and alloys consists in observing the phenomena which occur in the heating or cooling of the substance between the ordinary or even an artificially lowered temperature, and a high temperature at which the metal or alloy is completely molten. The phenomena in question arise from the fact that when the substance undergoes either a change of state, an allotropic or polymorphic transformation, or a chemical reaction, these changes are almost universally accompanied by an absorption or an evolution of heat. A familiar example is found in the freezing of water to form ice, a process which is accompanied by the evolution of a very large amount of heat, viz. the latent heat of fusion of the water. If the cooling process of a body liable to such changes is followed with a suitable instrument for measuring temperatures, and the rate of cooling be observed it is found that the occurrence of a heat-evolution at any stage of the cooling process results in a retardation, and sometimes even in an entire cessation of the cooling process—the heat evolved by the transformation of the substance for a time balances the loss of heat due to radiation, conduction, &c., and keeps the temperature stationary. For this reason the temperature at which such changes occur are frequently referred to as 'arrest-points' in the cooling (or heating) 'curves' of the body in question. In the case of metals, these curves are obtained by means of a pyrometer, and generally some form of time-observation which enables the observer to record the rate of cooling over the whole range of temperatures involved. Such observations are most simply represented by plotting them in a curve having the temperature of the metal as ordinate and the time as abscissa, such a curve being known as a 'time-temperature' cooling (or heating) curve; on such a curve the arrest-points are shown as more or less marked flattenings of the curve (Fig. 1). If it is desired to plot such a curve on a large scale—and in practice the temperature range involved may be as much as 1000°—this mode of plotting is found cumbersome, and it is preferable to plot the observations in the form of an 'inverse rate' curve. The ordinates of this curve are again the temperatures of the metal, but the abscissæ are the time-intervals occupied by each successive decrement (or increment) of the temperature of the metal. Thus, during the steady cooling preceding the commencement of solidification, each fall in temperature of 3° might occupy, for example, 12 seconds; then the 3° interval including the commencement of freezing might occupy a time of 120 seconds, the next following fall of 3° might occupy 40 seconds, and the following one as little as 10 seconds; in the inverse-rate curve these observed intervals would be plotted against the mean temperature of each 3° interval. In these curves, uniform rates of cooling are represented by vertical lines, while arrest-points appear in the form of more or less sharp peaks, whose areas approximately represent the quantity of heat evolved by the transformation in question (W. Rosenhain, Observations on Recalescence Curves, Proc. Phys. Soc. London, 1908, 21, 180; *see* Fig. 2). Both types of curves represent observations of time and temperature; in another method of working, the temperature of a uniformly cooling body, such as a piece of pure platinum or porcelain, is used as one of the elements of the curve. Against the actual temperature of the cooling piece of metal is plotted the difference between its temperature and that of the neutral comparison body just mentioned; this method—known as the 'differential' or difference method of Roberts-Austen—has the advantage of extreme delicacy, but it is somewhat more laborious and requires more skill on the part of the observer in manipulating the apparatus, while it is also limited to the observation of heat-evolutions occurring at temperatures at which the metal in question remains solid. For all these methods of taking cooling or heating curves, the temperature observations are usually made by means of a thermo-couple whose E.M.F. is measured in some convenient way. The most widespread method of making this measurement is by reading the deflection of a galvanometer, usually of the moving-coil type, but this method has serious disadvantages, and for cases where any considerable accuracy is required the electro-motive force of the couple should be measured accurately by means of some suitable form of potentiometer (W. Rosenhain, The Metallographic Investigation of Alloys, Journ. Inst. Metals, 1909, i. 200; Observations on Recalescence Curves, Proc. Phys. Soc. London, 1908, 21, 180). The neglect of this condition has rendered a large amount of metallographic investigation unreliable.

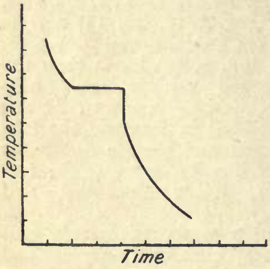


FIG. 1.

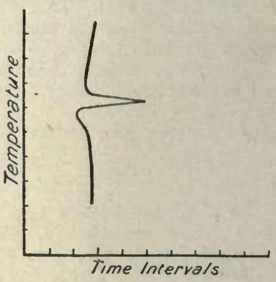


FIG. 2.

The cooling-curves of metals and alloys, taken from a temperature at which the metal is liquid downwards, always show as the highest arrest-point the initial 'freezing-point' of the metal; below this temperature, at which the liquid metal first begins to deposit solid crystals, the cooling-curves may show from one up to four or five further arrest-points, even in simple alloys containing two metals only. In studying such a 'binary' system of alloys, the arrest-points on the cooling-curve of each alloy are generally plotted as points on a diagram in which the concentration of the alloy is used as abscissa and the temperatures as ordinates, the result being a temperature-concentration diagram. If properly completed in such a manner as to indicate all the conditions in which alloys of the two metals can exist in equilibrium at all possible temperatures and concentrations, this diagram is termed the 'equilibrium diagram' of the binary system in question. As a rule, however, the mere plotting of observed arrest-points in the cooling-curves of a series of alloys is not enough to allow such a diagram to be drawn, the evidence of the microscope and of other physical methods being often required to allow of the correct interpretation of the arrest-points observed. The first and simplest line of such an equilibrium diagram is that known as the 'liquidus'; this is the boundary of the region in which the alloys are completely liquid; immediately below the 'liquidus' the alloys in general consist of a mixture of liquid with solid crystals, although in some cases the range of temperature over which such a mixture occurs is very short—in pure bodies, consisting entirely of one chemical entity (pure element or pure compound) the whole process of solidification occurs at a single definite temperature and no region of mixed solid and liquid exists. The liquidus line of the equilibrium diagram can, as a rule, be drawn definitely from pyrometric observations alone, although exceptions occur in the case of pairs of metals possessing either limited miscibility in the liquid state or where the formation of a definite compound takes place slowly in the liquid metal. In other cases, small breaks of continuity in the liquidus curve cannot be definitely located by pyrometric observations alone.

The process of solidification which follows, in any given alloy, upon the commencement of freezing at the temperature of the 'liquidus' curve depends, in the first place, upon the position of the alloy in the binary system to which it belongs and also upon the type which that system follows. This type depends again upon the manner in which the two component metals undergo mutual mixture, solution, combination, or separation during freezing and melting. A large number of these types can be distinguished, but only the most important can be mentioned here. The first and simplest type are those alloys in which the two metals, when they have reached their final equilibrium in the solid state, retain the condition of intimate mixture in which they existed in the liquid state at a higher temperature. In the language of metallography, two such metals form an unbroken series of solid solutions. In their final condition such alloys resemble pure metals in being built up of an aggregate of crystals which are all alike in composition and properties. In the cooling and freezing process, however, the alloys of such a series differ markedly from pure metals in showing at times a very wide range of temperature over which the freezing process is distributed. The equilibrium diagram of such a system of alloys is shown in Fig. 3. the line ACB representing the liquidus or line of commencing freezing, and ASB representing the line of complete solidification or 'solidus.' At temperatures lying between these two lines the alloys consist of a definite proportion of solid crystals in equilibrium with liquid alloy, but it is important to notice that the compositions of the crystals and of the liquid in equilibrium with them are not identical.

The opposite extreme to the type of alloys just described is found in those groups where the component metals are completely, or almost completely, immiscible in the solid state. A typical equilibrium diagram of this type is shown in Fig. 4, where the liquidus curve is represented by the lines ACB, forming a more or less deep V; the addition of the metal A to the metal B lowers the temperature of initial freezing, and this lowering is continued with increasing additions of B. Similarly successive additions of A lower the initial freezing temperature of B until a concentration is attained where the two branches of the liquidus curve meet at the point C, which represents the freezing-point of the most fusible alloy of the series. This alloy, both in the free state and when it occurs as a constituent of alloys of different composition, is known as the 'eutectic' alloy of the series, or more briefly as 'the eutectic' (Guthrie, Phil. Mag. 1884, [v.] 17, 462). This eutectic alloy shares with the pure metals and with pure inter-metallic compounds the property of undergoing complete solidification at one temperature instead of showing a 'freezing range.' The solidification of any alloy of intermediate composition, such as that represented by the line PQ, may be described as follows: when the cooling alloy reaches the temperature at which the lines PQ and AC intersect, solid crystals begin to separate, but these are crystals of the metal A. As a result of this separation, the residual liquid metal or 'mother liquor' becomes enriched in B; the residual liquid is now, in fact, an alloy lying further to the right than the line PQ. As the temperature falls, the temperature of initial freezing of this richer alloy is reached and a further quantity of solid A is separated, again increasing the concentration of B in the liquid. This process is continued until the concentration of the point C, and its temperature, are simultaneously reached. At that point the residual liquid has the composition of the eutectic alloy and solidifies as such. The alloy thus becomes completely solid on reaching the temperature of the line DE, which is usually called the eutectic line—this line (CE) is, therefore, in this case, the 'solidus' of the system, since it forms the boundary of the region of completely solid alloys. An alloy such as PQ, at all temperatures below that of DE consists of an agglomerate of crystals of the metal A embedded in a matrix of the eutectic alloy; if the composition of the alloy is such that the line PQ lies close to A, then the crystals of A in the solid alloy will be large and numerous, and little eutectic will be present, while, as the point C is approached, the proportion of eutectic

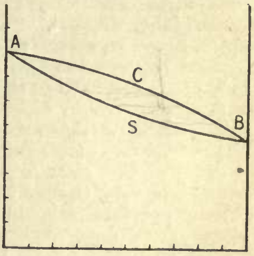


FIG. 3.

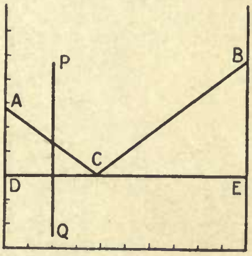


FIG. 4.

increases. On the other side of C, the alloys consist of crystals of B embedded in the eutectic, and these crystals increase in amount as we move from C to B. Actual examples of binary alloys strictly following this simple type are rare, if indeed they exist at all; so far as at present known the alloys of lead and antimony approximate closely to this type (Antimony-Lead, Gautier, Recherches sur la fusibilité des alliages metalliques, Bulletin de la Soc. d'Encouragement, 1896; Gold-Thallium, Levin, Zeitsch. anorg. Chem. 1905, 45, 31). The great majority of alloys, however, belong to a type which is intermediate between the two extremes which have just been described; this intermediate type consists of alloys in which the two component metals are mutually soluble in the solid state to a limited extent. The typical equilibrium diagram of this class is given in Fig. 5. The liquidus is very similar to that of type II., a eutectic point being again evident at C, but the eutectic line DE no longer crosses the whole width of the diagram. Alloys from O to F and from H to G behave as regards solidification exactly like alloys of type I., forming homogeneous crystalline aggregates which consist of only a single constituent. Alloys from F to G, however, behave like members of type II., but with the difference that the substance which commences to crystallise when these alloys reach the temperature of the line AC is not pure A, but a solid solution of B in A, or, if the alloy lies to the right of C, the crystals consist of a solid solution of A in B.

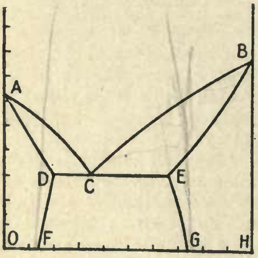


FIG. 5.

A considerable number of further types of binary series of alloys can be distinguished, but it is not possible to deal with these fully here. The only other class which need be mentioned are those in which a definite inter-metallic compound is formed. A typical equilibrium diagram of such a series is shown in Fig. 6, where the liquidus curve ACPDB shows a maximum (P) and two minima or eutectic points, C and D. The occurrence of a maximum in the curve of initial freezing, such as that shown at P, is a definite indication of the existence of an intermetallic compound, although the presence of such compounds is not always indicated in this way. The simplest way of regarding an equilibrium diagram of the type shown in Fig. 6, is to suppose it divided into two separate diagrams by the vertical line through P, the one half being thus a diagram of the alloys of A with the compound metal P, and the other half representing the alloys of B with P. In the diagram as drawn, the left-hand half then becomes a diagram of type II., while the right-hand half falls under type III. It should be mentioned, however, that in actual alloys the formation of the compound P may not take place quite completely, and the alloys may in reality contain some free B as well as A and P—the system thus becomes practically one of three components, to which reference is made below.

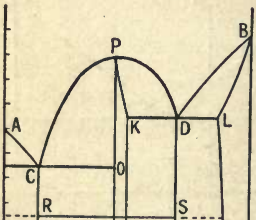


FIG. 6.

Equilibrium diagrams frequently contain lines other than those forming parts of the 'liquidus' and 'solidus' curves; these lines represent the occurrence of transformations or chemical reactions within the metal, frequently at temperatures well below those at which the alloys are completely solid. These changes are represented on the cooling curves by heat evolutions or absorptions, which are sometimes so faint as to escape detection by any but the most sensitive instruments, while in other cases they rival the freezing-point in intensity. These heat evolutions may represent either:

(1) An allotropic change in a pure metal or in the pure metal forming the basis of a solid solution or existing in the form of crystals in a eutectiferous alloy.

(2) A polymorphic change in an inter-metallic compound.

(3) A chemical reaction resulting in the formation or the decomposition of a compound or of a solid solution.

Two or more of these changes may occur together. An example of such a change is indicated in an imaginary case by the line RS in Fig. 6, which is supposed to represent the decomposition of the compound P. It will be seen that the line extends over the whole range of composition in which the compound P can exist, either as free crystals or as a constituent of the eutectics in which it occurs. As a rule, however, it is difficult, and sometimes impossible, to find any evidence—either pyrometric or otherwise—for the occurrence of such changes in alloys where the compound in question exists only as a constituent of a eutectic; the line of transformation is therefore shown as a full line only between the points R and S, where the compound exists in the form of primary crystals, and as a dotted line over the rest of the range of its existence. The interpretation of such a line of arrest-points in an equilibrium diagram will, as a rule, be based principally upon microscopic evidence, and this also applies to several of the other facts tacitly implied in such a diagram as that of Fig. 6; but before passing on to consider the microscopic study of alloys, certain other lines of pyrometric evidence must be mentioned.

The most important of these is the determination of the end-points of a series of arrest-points, and of the point of maximum intensity of such a series. The first of these is important for fixing the position of such points as D and E in Fig. 5, and O, K, and L in Fig. 6. Points D, E, K, and L serve to fix the limits of solid solubility of the metals and compounds in one another, while the point O assists in determining the exact composition of the compound P, since the maximum in the liquidus curve is not always very sharply marked. Probably the best method of determining the end-point of such a series of arrests consists in observing, by means of the most delicate pyrometric apparatus available, large samples of the alloys cooling at a slow rate, but it is also necessary in such cases to secure the complete equilibrium of the alloy at a temperature just above that of the arrest to be observed. For this purpose it is necessary, in some cases, to maintain the specimens of alloy at a definite, more or less high, temperature for prolonged periods—sometimes up to several weeks—and then to take the observations of cooling without having allowed the specimens to cool down intermediately (Rosenhain and Archbutt, Aluminium-Zinc Alloys, Phil. Trans. 1911, A, 211). The exact end-point found, however, will always lie a little short of the true end-point. For this reason a method of extrapolation is often employed. If the quantities of heat evolved at such a series of arrest-points were measured, the measurements being reduced to quantities of heat per gramme of alloy, then a curve could be plotted with concentration as abscissæ and quantities of heat evolved as ordinates. Provided that the measurements were strictly accurate, such a curve would simply be a straight line running from the concentration at which the heat-evolution was largest down to the two end-points of the series; even if not observed very close to these end-points, the line could be continued until it cut the axis, and this intersection would indicate the true end-point of the heat-evolutions. In practice this method is frequently applied, especially by Tammann and his school (Tammann, Zeitsch. anorg. Chem. 1903, 37, 303), both for the determination of end-points and of maxima of heat-evolutions; but unfortunately it is not possible to make the measurements of the quantities of heat evolved with any great degree of accuracy. The determination of the duration of the arrest itself or of the area of the peak of the inverse-rate cooling curves is usually employed, and it has been shown that this is only a rough approximation; the variation of specific heat with concentration of the alloys also affects the shape of these intensity curves, so that very great care is required in employing this method, which has more than once led to erroneous results (W. Rosenhain, The Metallographic Investigation of Alloys, Journ. Inst. Metals, 1909, i. 200; Observations on Recalescence Curves, Proc. Phys. Soc. London, 1908, 21, 180; Rosenhain and Tucker, Lead-Tin Alloys, Phil. Trans. 1908, A, 89; Rosenhain and Archbutt, Aluminium-Zinc Alloys, Phil. Trans. 1911, A, 211).

The above account of the pyrometric study of alloys and its diagrammatic representation has so far dealt only with alloys consisting of two component metals; in practice, however, alloys frequently contain three or more metals. Unfortunately the difficulty of making a complete metallographic study of a system of alloys increases very rapidly with the number of component metals; for fifty determinations required for the elucidation of a binary system of alloys, 1250 would be required for a system of three metals, while no attempt at the complete systematic study of a quaternary system (of four metals) has yet been made, but for corresponding completeness over 30,000 determinations would be needed. In the case of a ternary system (of three metals) it is still possible to employ graphic representation; the concentrations of a system of ternary alloys may be plotted in the form of an equilateral triangle, each corner representing one of the pure component metals, each side of the triangle then represents one of the three limiting binary systems, while the position of any point within the triangle represents the composition of an alloy of a ternary system, on the principle of trilinear co-ordinates. Upon this equilateral triangle as a base, the 'equilibrium diagram' can be erected as a three-dimensional model, ordinates representing temperature being erected upon each point of the area of the triangle. A few such equilibrium models of ternary systems have been more or less completely determined (Lead-Tin-Bismuth, G. Charpy, Compt. rend. 1898, 126, 1569; E. S. Shepherd, J. Phys. Chem. 1902, 6, 519; Lead - Cadmium - Mercury, E. Jänecke, Zeitsch. physikal Chem. 1901, 60, 399; Magnesium - Lead - Tin, A. von Vegesack, Zeitsch. anorg. Chem. 1901, 54, 367; Aluminium-Copper-Manganese, Rosenhain and Lantsberry, Ninth Report to the Alloys Research Committee, Proc. Inst. Mech. Eng. 1910), but the field is still largely unexplored. It is interesting to note, however, that no tri-metallic compound has yet been discovered.

The microscopic study of metals is always carried out by looking at suitably prepared surfaces illuminated by reflected light; the thin sections employed in petrography cannot be used in the case of metals as these are too opaque for such a purpose. The preparation of a suitable surface for examination by reflected light consists in three distinct processes, viz. the cutting and grinding of a small flat area, the fine-polishing of this surface in order to remove physical irregularities, and the treatment of this polished surface in such a manner as to indicate the nature of the structure of the metal beneath. The cutting and grinding process, in the first place, consists in preparing an area, as nearly flat as possible, which may range in size from a few square millimetres to several square centimetres—but the difficulty of the subsequent operations increases rapidly with the area to be treated, so that it is preferable to examine several small specimens rather than one very large one. The initial rough cutting and grinding is followed by some process of fine grinding, generally by the use of carefully graded abrasives, each stage reducing the depth of the scratches left on the surface.

The grinding operation is followed by that of fine-polishing. The purpose of this process differs essentially from that of the ordinary polishing process, the object of which is solely the production of the most brilliant surface; in most ordinary polishing processes this is largely accomplished by a species of 'burnishing' action, in which there is much surface flow of the metal, the previously existing scratches being largely 'smeared over' and filled up. For metallographic purposes this action should be avoided as far as possible, since scratches or holes thus hidden immediately become conspicuous under subsequent treatment (etching). It follows that for this work the entire processes of cutting, grinding, and polishing, should be conducted as gently as possible, particularly in the case of the softer metals. For polishing purposes a material which acts as an exceedingly fine abrasive is indeed much preferable to one which, though more rapid in action, tends to cause flow. The polishing materials most widely used consist of the oxides of such metals as aluminium, magnesium, and iron, alumina being probably the best.

A perfectly polished metallic specimen shows, under the microscope, a featureless surface, which will appear either uniformly bright or uniformly dark, according as the light falling upon it is or is not reflected into the objective of the microscope. In order to obtain a sectional view of the structure of the metal it is necessary to employ some method of 'etching.' As a rule, this consists in exposing the specimen to the action of some reagent, such as a weak acid, which gradually dissolves the metal. It is found that this solution does not take place uniformly over the surface of the metal, and that, in fact, it differentiates clearly and consistently the various constituents of metals and alloys. In the case of pure metals and of certain alloys which consist of a single constituent or phase, the etching agent cannot, of course, act by differentiating two or more distinct constituents; but in that case a differentiation occurs between the different crystals of the same constituent, the rate of attack being apparently dependent upon the orientation of the particular section of the crystal exposed to the solvent. Such a 'homogeneous' metal consists, in fact, of an aggregate of minute crystals which have grown together in such a manner that the boundary of each crystal is determined not by the natural symmetrical surfaces commonly associated with the term 'crystal,' but by the surfaces of mutual interference of adjacent crystals—each crystal has grown until checked by meeting its neighbour. In section such a structure exhibits a network of roughly polygonal areas, and the etching reagents employed in metallography attack these various areas at different rates, thus producing both differences of level and varieties of surface texture which readily reveal the arrangement of the constituent crystals. In the case of alloys possessing a duplex or more complex structure, although each of the constituents is still built up of such aggregated crystals, the differences of solubility between the various constituents are very much greater than those between adjacent crystals of the same constituent. Consequently the resulting surface pattern generally shows all those areas which represent sections of crystals of one of the constituents as comparatively deeply etched or eroded, while those corresponding to the other constituent remain practically untouched. In duplex alloys, therefore, etching reveals the distribution of the constituents rather than the crystal structure of any of them.

The specimens of metal thus prepared can be examined by means of almost any good ordinary microscope if it is provided with certain special accessories, but for the greatest convenience and for more refined purposes it is desirable to employ one or other of the specially designed 'metallurgical' microscopes. Two general types of such instruments have been evolved for this special purpose. In the one type, which is generally used by British workers, the ordinary arrangement of the microscope is adhered to, but the stage is provided with a focussing movement, while the body-tube is provided with one of the devices known as 'vertical illuminators.' In the most highly specialised instrument of this kind (Rosenhain, On an Improved Form of Metallurgical Microscope, Journ. R. Microscopical Soc. 1906) the body-tube is entirely fixed to the limb and all the focussing, both coarse and fine, is done by movements of the stage; further, the illuminating arrangements are made integral with the main tube of the instrument, while in other microscopes they are removable and are only screwed on at the lower end of the tube. The function of the 'vertical illuminator' is simply that of sending a beam of light down the tube of the microscope in such a way as to fall upon the back lens of the objective, and then, after being concentrated by the objective, to fall upon the specimen and to illuminate the portion of the surface which is under examination. Such a vertical illuminator consists essentially of a reflector, which may be a thin disc of glass or an opaque reflector or a totally reflecting prism so placed as to cover one-half or less than one-half of the aperture of the objective. The path of the light-rays in both cases is shown diagrammatically in Fig. 7. It will be seen that under this mode of illumination the light falls upon the surface of the specimen in a direction more or less parallel to the optical axis of the microscope, and as this is sometimes placed vertically, this mode of illumination has received the name of 'vertical illumination,' although 'normal illumination' is a more rational term, since the light remains normal to the surface of the specimen whatever the position of the microscope. Under this mode of illumination it is evident that flat, bright surfaces will appear light, while sloping surfaces, or areas rendered rough so as to scatter the light which falls upon them, will appear dark—since the light reflected from such regions will be more or less completely thrown outside the aperture of the obective of the microscope. With lenses of moderate power, which leave a certain amount of space between the lens and the specimen, the surface under examination may be illuminated directly by a beam of light falling obliquely upon the surface of the specimen, in the manner indicated in Fig. 8. With such lighting, plane polished surfaces will appear dark, while those with a suitable slope and those roughened so as to

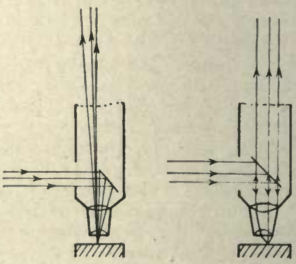


Fig. 7.

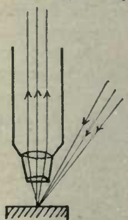


Fig. 8.

PLATE I.

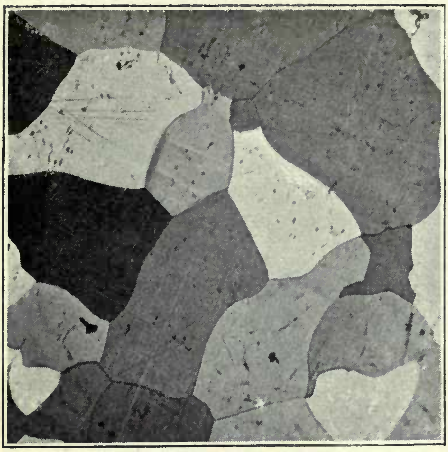


FIG. 9.

FIG. 10.

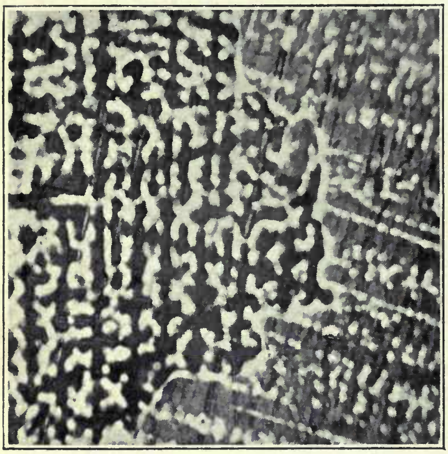


FIG. 11.

FIG. 12.

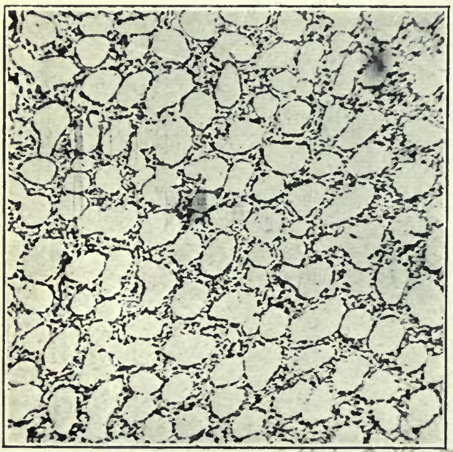


FIG. 13.

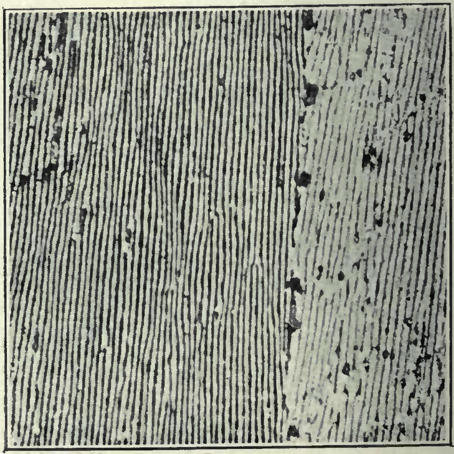


FIG. 14.

[To face p. 461.

scatter the incident light, will appear more or less bright; the consequence is that in many respects the image as seen by ‘oblique illumination’ bears to that seen by ‘normal illumination’ a relationship like that of a photographic negative to its positive. Oblique illumination, however, is much more searching, particularly as regards minute holes and scratches, while it also tends to reveal the natural colours of the various constituents much more definitely than normal light. On the other hand, its application is generally limited to magnifications not much greater than 200 diameters, while normal illumination is readily employed with the highest powers of the microscope.

The use of the vertical illuminator, whether as a permanent or a more or less temporary attachment to the microscope, entails a special arrangement of the source of light. Whether this be an ordinary lamp or some more or less elaborate optical system, it must be so placed that the light coming from it enters the aperture of the illuminator at the desired angle. This requires a definite relative position of the source of light and the illuminator itself. In any ordinary microscope where focussing is done by moving the tube of the instrument, the position of the illuminator will vary with every adjustment of the focus, and this would entail corresponding re-adjustment of the source of light. By using a focussing stage and leaving the body-tube with the illuminator attached to it in a fixed position, this difficulty is overcome, and this arrangement is the essential feature of the majority of metallurgical microscopes. For certain purposes, of course, special provision for taking large and heavy specimens, for complete rotation of the specimens, and for other special requirements is desirable and can be obtained.

The second type of metallurgical microscope originated with H. le Chatelier (Le Chatelier, Étude des Alliages, 1901, 421), and its use is widely extended in France and Germany. The observation tube of this instrument is horizontal, and directly in line with a tube carrying condensing lenses through which light from a suitable source is concentrated upon the specimen. The stage of this instrument is a table provided with a small hole, and the specimen is placed over this hole, polished face downwards. The objective of the microscope faces upwards towards the specimen, and the incoming light as well as the rays forming the image are turned off at right-angles by means of two totally reflecting prisms. In its most recent forms this instrument presents many points of great convenience, but it also possesses certain very marked limitations and disadvantages from which the more ordinary type of microscope is free.

The observations of the structures of metals and alloys made by such microscopes are readily recorded by means of photography. If the beam of light employed for illuminating the specimens is made sufficiently powerful, and particularly if the ordinary eyepiece of the microscope is replaced by one of the well-known ‘projection eye-pieces’ now available, the image of the surface under examination can be projected upon a screen, and this image can be made large enough and bright enough to be visible even to an audience of moderate size. Instead of projecting the image upon a large screen it can equally well be focussed upon the ground glass of a suitably placed camera, and there photographed in the ordinary manner. The manipulation requires some experience and skill, particularly when very high magnifications are attempted, but in principle it does not differ materially from ordinary photography, except that the microscope with its system of lenses is used in place of the ordinary camera lens.

The typical micro-structures met with in metals and alloys may now be briefly considered. We have already indicated that a pure metal is an aggregate of minute crystals whose sections, in the form of irregular, more or less polygonal areas, are revealed by etching a polished surface. In such metals as cast lead or tin the crystals are often very large, and can be seen without the aid of the microscope, but in iron and copper they are usually very small and require magnifications ranging from 100 to 400 diameters to be readily observed. Seen under normal illumination, the crystals of iron appear as illustrated in Fig. 9, Plate I.; the same field of view seen under oblique light is shown in Fig. 10, Plate I. The appearance there seen arises from the fact that the etched surface of each crystal is covered with a number of minute facets all similarly oriented over the whole area of the same crystal, but differing in orientation from one crystal to the next. Oblique light falling on a surface thus constituted picks out those areas where the facets are so placed as to reflect the light into the microscope, and these areas accordingly appear bright, while others, situated unfavourably, appear more or less dark. A rotation of the specimen on the stage of the microscope alters these relative positions, and different crystals appear bright in turn.

The description of the typical structure of a pure metal which has just been given applies equally to the structure of those alloys which consist either entirely of a definite intermetallic compound in a state of purity, or of a homogeneous ‘solid solution.’ The term ‘solid solution’—sometimes called ‘mixed crystals’—implies a state of mutual admixture or solution existing in the solid state which is as intimate as the condition of liquid solutions; probably the best interpretation of the conception is to regard the crystals of a solid solution as being built up of molecules of both the solvent and the solute indiscriminately. Where the two metals are completely isomorphous, these composite crystals may be built up of two kinds of molecules indiscriminately in any proportion, and we then have a series of alloys consisting of solid solutions only; in other cases the number of molecules of the solute which can be incorporated in the crystals of the solvent is limited, and in that case there is a limit to the ‘solid solubility’ of the two metals. While the final condition of a solid solution is thus simply that of an aggregate of homogeneous crystals resembling in appearance and character the structure of a pure metal, this final condition is not at once arrived at during the solidification of such an alloy. The central part of each individual crystal of such a solid solution when first formed contains considerably less of the solute than the liquid alloy from which it is being deposited, and as solidification proceeds this core of relatively dilute solution is surrounded by successive layers of more and more concentrated solution. Ideally the concentrations of these layers should be continually equalised by diffusion of the solute from the more concentrated to the less concentrated regions, but this is a slow process, and generally remains incomplete during the ordinary cooling of an alloy from fusion. Samples of alloys consisting of a single solid solution when taken from castings which have not been subjected to prolonged annealing, therefore always show traces of the original 'cores' within the polyhedral crystals. An example of this kind in the case of cast brass is shown in Fig. 11, Plate I. When this alloy has been reheated and subjected to such a process as rolling into bars or rods, these 'cores' are obliterated, and a homogeneous polyhedral structure is then found, such as that illustrated in Fig. 12, Plate I.

We may now consider the micro-structure of such an alloy as that represented by the line PQ in Fig. 4. In accordance with the nature of the freezing process of such an alloy, which has already been described, the microscope shows that it consists of two very distinct constituents; as a rule one of these, which represents the crystals of the pure metal A, remains practically unaffected by the etching reagent, while the other, which represents the eutectic, is more or less eroded and darkened. The relation between the two constituents is readily followed if a series of alloys are considered, commencing with one very rich in A and gradually increasing the concentration of B. At first the micro-structure closely resembles that of a pure metal, but the boundaries between adjacent crystals are seen to be thicker than the fine lines observed in pure metals. With a very slightly higher concentration of B the presence of a dark-etching constituent between the crystals of A becomes evident, and as the concentration of B increases the proportion of this dark-etching constituent (the eutectic) increases, while the crystals of A become mere islands. Ultimately, as the concentration of the point C is reached these islands of A disappear entirely, and the whole field is occupied by the eutectic. An example of such a eutectiferous alloy lying midway between the pure metal and the pure eutectic is shown in Fig. 13, Plate I., while the typical structure of a pure eutectic is shown, under much higher magnification, in Fig. 14, Plate I. It will be seen that the 'dark etching' eutectic is not uniformly etched, but itself exhibits a duplex structure, which is very characteristic of these bodies, although it is not one of their essential characters. The eutectic, as it crystallises from the residual mother-liquor along the eutectic lines, such as DE, Fig. 4, is really the product of the simultaneous crystallisation of both the constituents, and we thus generally find it with a laminated structure consisting of alternating layers of the two constituents. It was formerly thought that these were simply minute independent crystals deposited side by side, but later research has shown that most eutectics crystallise in the form of the predominating constituent, the crystals of the other metal being forced into the interstices of the other, the whole arrangement frequently adopting the spherulitic form (Rosenhain and Tucker, Lead-Tin Alloys, Phil. Trans. 1908, A, 89).

The great majority of alloys exhibit in their micro-structures varieties of the three types illustrated and described above, but in a certain number of cases special structures are met with.

In the course of metallographic investigations it is frequently necessary to adopt special methods for determining the exact temperature at which the solidification of a given alloy is completed. For various reasons it has been found that the best available method of making this determination is by a process of quenching small pieces of the alloy from a series of suitably chosen temperatures. By the micro-structure of the quenched specimen it is then possible to determine whether the alloy contained any liquid at the moment of quenching. The rationale of this process lies in the fact that while that part of the alloy which was solid at the instant of quenching had solidified slowly, and had, therefore, been allowed to form relatively large crystals, any liquid metal present when the specimen was suddenly cooled would be forced to solidify very rapidly and would, therefore, form extremely minute crystals. Thus in a series of specimens quenched from successively higher temperatures, it is found that the resulting specimens show the ordinary typical and comparatively large-scale structure of the alloy until the quenching temperature exceeds a certain limit, but that beyond that point small areas of very minute crystals are found. It may then be concluded that the limiting temperature in question is that of the final solidification of the alloy. The first traces of 'liquid' in such specimens appear as minute dots or 'fusion spots,' but with slightly higher temperatures the original solid crystals of the alloy are seen to be embedded in a matrix which had obviously been fluid at the moment of quenching.

When such a quenching process is employed for locating one of the lines of an equilibrium diagram, it is of great importance that the exact temperature of the specimen at the moment of quenching should be accurately known, and that the small specimens should be protected from oxidation as far as possible during the progress of the experiment in order to avoid changes of composition and structure. In all earlier investigations quenching was carried out by heating the specimens in a small furnace, and when the desired temperature had been attained, withdrawing them by means of a rod or wire and quickly throwing them into water or other quenching fluid. More recently an apparatus has been devised (Rosenhain, The Metallurgical and Chemical Laboratories in the National Physical Laboratory, Journ. Iron and Steel Inst. 1908, I.) in which the specimen is heated electrically while contained in an exhausted tube made of fused silica; when the desired temperature has been reached, water is admitted into this exhausted tube through a wide-bore tap, and the powerful stream of water, driven by the pressure of the atmosphere, quenches the specimen, and carries it out of the furnace with it; the quenching is thus carried out very rapidly at an accurately known temperature, and without any exposure to the atmosphere.

Apart from the processes of solidification, a great many metals and alloys undergo transformations which are frequently accompanied by thermal phenomena shown on the cooling-curves, and, as a rule, these transformations are accompanied by more or less striking changes in micro-structures. In the case of pure metals these changes occurring at temperatures below that of solidification are generally regarded as being 'allotropic'; in the case of alloys, however, these transformations or 'inversions' may arise from a variety of causes, such as the formation or decomposition of a compound, an allotropic change in one of the components resulting in the rejection of the other component from solid solution, or the rejection from solid solution of a phase the limit of solubility of which has been reached owing to a variation of solid solubility with temperature. Typical examples of these and similar changes are met with in such systems of alloys as iron-carbon, copper-tin, copper-zinc, copper-aluminium, aluminium-zinc, and others, and some of these will be referred to in connection with the equilibrium diagrams of these systems.

The equilibrium diagrams and general metallography of some of the more important alloys will now be briefly described. Among alloys forming uninterrupted series of solid solutions (type I. above) perhaps the most important are the iron-manganese and the copper-nickel series, whilst iron-nickel and copper-manganese probably also belong to this type. The equilibrium diagram of the copper-nickel series is given in Fig. 15, these alloys being important on account of their electrical uses (resistance alloys) and also as forming the basis of such industrially important metals as German silver and Monel metal. The diagram is of the simplest type, and the micro-structures met with in the alloys are correspondingly simple—in the cast alloys some core-formation is visible, but in the worked materials, such as sheet or wire, complete homogeneity is attained, the resulting structure being very similar to that of brass (*see* Fig. 12, Plate I.), but usually on a more minute scale.

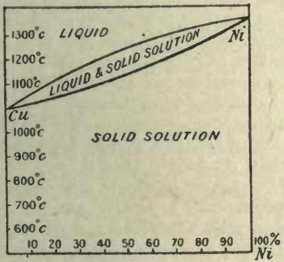


Fig. 15.

A typical example of another type of equilibrium diagram is that of the alloys of lead and tin, which are important on account of their use as solder, pewter, &c., and also because they form the basis of important ternary and quaternary alloys such as certain anti-friction alloys and type-metal. The diagram given in Fig. 16 (Rosenhain and Tucker, Lead-Tin Alloys, Phil. Trans. 1908, A, 89) shows the typical V-shaped liquidus with a long eutectic line running up to, or very nearly up to, the tin end of the series, but stopping some little distance (at about 18 p.c. of tin) from the lead end. Formerly the line was supposed to run up to the lead end also, but this was an error arising from the fact that these alloys take up their equilibrium condition very slowly, so that alloys cooled from fusion in the ordinary way show eutectic practically up to the lead end; this, however, disappears on prolonged heating of the alloys at a temperature near 170°. Below the solidus this diagram shows a line indicating an inversion occurring in the alloys from 18 to 63 p.c. of tin at a temperature of 150°, but with lower tin-contents the temperature at which this change occurs falls rapidly, and the inversion cannot be traced at all at concentrations of less than 8 p.c. of tin. This inversion is accompanied by a partial rejection of the tin from solid solution, and involves a change of density.

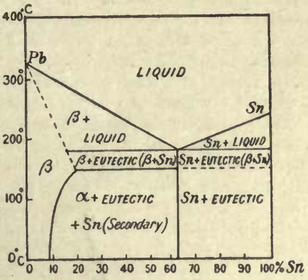


Fig. 16.

As typical of a comparatively simple system exhibiting a maximum in the liquidus corresponding to a definite compound, the alloys of aluminium and magnesium may be taken (G. Grube, Alloys of Aluminium and Magnesium, Zeitsch. anorg. Chem. 1905, 45, 225). Of this series those near the aluminium end are employed under the name 'Magnalium,' while they also enter into the composition of special light alloys used for constructional purposes, notably 'Duralumin,' which contains over 90 p.c. of aluminium and 0·5 p.c. of magnesium, the rest being copper, manganese, and iron. The aluminium-magnesium diagram, as far as at present known, is given in Fig. 17. The liquidus has four branches: Al–I. corresponding to the commencement of the deposition of aluminium containing only little magnesium in solid solution, with a corresponding eutectic line AI.; I.–II. corresponding to the formation of a series of solid solution of very narrow freezing range and ending at the freezing-point of the

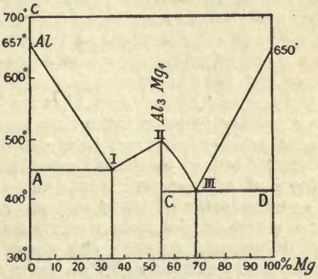


Fig. 17.

definite compound Al_3Mg_4; II.-III. corresponding to the deposition of crystals of Al_3Mg_4, with a eutectic line CD, and the branch III.-Mg, corresponding to the deposition of crystals of nearly pure magnesium. The micro-structures of the alloys from A to I. show crystals of aluminium, often developed as beautiful dendrites, embedded in eutectic; those from I. to II. are homogeneous crystalline aggregates, while those from II. to III. and from III. to D show crystals of the compound or of magnesium, as the case may be, embedded in eutectic. In connection with this diagram it is interesting to note that inter-metallic compounds, such as the body Al_3Mg_4, are almost always exceedingly brittle bodies, even when their constituent metals are so soft and ductile as aluminium and magnesium—compounds of copper with such metals as tin and aluminium furnish equally striking examples of this fact. It follows that in those binary alloys where a definite inter-metallic compound is formed, over a considerable range of composition on either side of this compound the alloys are usually so brittle that they cannot be used for any technical purpose; this removes the greater part of the ranges of most binary systems from all practical usefulness, and in fact it is found in the great majority of cases that industrially useful alloys rarely contain much more than 15 p.c. of substances other than the predominating metal. The only real exceptions to this rule are to be found in the alloys of zinc with such metals as copper and aluminium; apparently the addition of zinc can be pushed much further without producing serious brittleness than is the case with any other metal, and industrially useful alloys containing over 40 p.c. of zinc are well known. The alloys of lead and tin furnish another example, but in their case practical utility does not depend upon mechanical strength; similarly in certain anti-friction or bearing metals large proportions of added elements are sometimes employed, but these alloys are intended to meet special requirements and a considerable degree of brittleness is permissible.

Probably the most widely used of all non-ferrous alloys are those of copper and zinc, which include the whole series of 'brasses,' although in many industrial varieties of brass other metals besides copper and zinc are met with in varying proportions. It should perhaps be mentioned here that a considerable degree of confusion at present exists in the nomenclature of such alloys, the terms 'brass' and 'bronze' being used very loosely or even indiscriminately; in the present article, however, it is proposed to use the term 'brass' to denote approximately pure alloys of copper and zinc, while alloys consisting principally of these two metals, but with one or more added elements, will be described as 'special brasses,' or with the name of the most important third element, as, for instance, 'manganese brasses,' 'aluminium brasses,' or 'tin brasses.' The term 'bronze,' on the other hand, is to be confined to copper-tin alloys.

The equilibrium diagram of the copper-zinc alloys, as worked out by Shepherd (Copper-Zinc Alloys, E. S. Shepherd, J. Phys. Chem. 1904, 8, 421), and modified in accordance with the work of Carpenter and Edwards (Copper-Zinc Alloys, H. C. H. Carpenter and C. A. Edwards, Journ, Inst. Metals, v. 1911), is given in Fig. 18. In this diagram each of the six Greek letters indicates a definite phase; according to Shepherd these are all solid solutions, but it appears probable that each of these solid solutions owes its separate existence to some definite compound associated with it—there is some evidence for the existence of the two compounds Cu_2Zn and Cu_2Zn_3. It will not be necessary to discuss the whole of this diagram in detail, since the industrially important alloys consist either of pure α, or a mixture of α and β, and in special cases of either pure β or of β with a little γ; in accordance with what has been stated above in general terms, the β phase is decidedly harder and stronger, but also much more brittle than the α phase, while the γ phase is very brittle, and at the same time weaker than the β body. As indicated by the diagram, alloys containing up to 37 p.c. of zinc, when solidified and in equilibrium, consist of the pure α phase; this is a ductile body whose characteristics closely resemble those of copper itself, but with increasing zinc-content the strength increases while the ductility diminishes slightly. The micro-structure of these alloys closely resembles that of copper; in the cast state they consist of the usual aggregate of roughly polygonal crystals, similar to those illustrated in Fig. 11, Plate I.; as these alloys, however, consist of solid solutions of considerable concentration, they show a strong tendency towards the formation of dendritic 'cores,' as described above. In alloys as ordinarily cast this structure is very prominent, and tends to obliterate the ordinary polygonal structure so far as to suggest to the observer, at first sight, that he is dealing with a truly duplex alloy. Annealing, however, entirely removes this appearance from the micro-structure, and leaves the alloys perfectly homogeneous; if the annealing has been accompanied by or associated with mechanical work, the disappearance of the 'cores' is accompanied by the formation of numberless 'twinned' crystals which indicate their presence on the micro-sections by the appearance of crystals with rectilinear edges and crossed by one or more parallel bands showing a distinct orientation, as shown in Fig. 12, Plate I. These structures, it may be added, are also characteristic of the α body met with in other alloys of copper, such as those with tin, aluminium, manganese, &c., although in each class of alloys the range of existence of the α phase may be widely different—thus in the copper-aluminium series the range of the pure α phase is only slightly over 7 p.c.

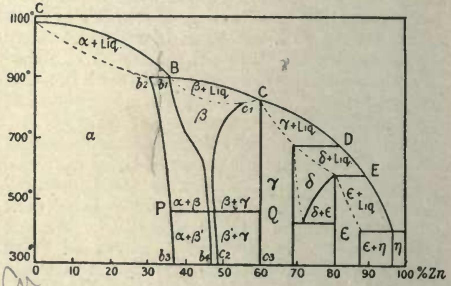


FIG. 18.

It will be seen that in the equilibrium diagram of the copper-zinc series the region of the pure α phase is bounded on the right by the curved line b_2b_3; immediately to the right of this line lies the region in which the alloys consist of a mixture of the α and β phases. If we consider the cooling from fusion of an alloy containing, for instance, 34 p.c. of zinc, we see that it will begin to solidify at a temperature of about 915°, depositing α crystals until the temperature of the line b_2b_1 is reached at about 880°. At that temperature the remaining liquid solidifies in the form of β crystals, which fill up the interstices between the previously deposited α crystals; if quenched from a temperature just below this line, such an alloy is found to exhibit the duplex structure of α and β thus indicated. On further cooling, however, the alloy crosses the line b_2b_3 and passes from the region of mixed α and β into that of pure α. If time enough is allowed to permit of the establishment of full equilibrium, the whole of the β present in the alloy will be transformed into α and the alloy will become homogeneous in accordance with the indications of the diagram; with most ordinary rates of cooling, however, this transformation is not completed, and the alloy retains some of its original β in that condition, remaining in what is known as 'meta-stable equilibrium.' In such a case the tendency for the β phase to undergo transformation is always present, but it is held permanently in check by the internal resistance of the metal to such rearrangements—this resistance being very considerable at low temperatures, but diminishing rapidly when the temperature is raised. All metals and alloys in which a transformation or 'inversion' of any kind has been prevented by rapid (or insufficiently slow) cooling, are thus in a meta-stable state, and the attainment of stable equilibrium only requires a raising of the temperature. Alloys which have been quenched are usually intentionally thrown into a meta-stable condition. In the present case it follows that the rate of cooling, in the first instance, or the subsequent application of heat, as in annealing, will make a very great difference to the character of the alloy and to all its physical and mechanical properties, since in the meta-stable state the relatively hard, strong, but brittle β body is present, while in the annealed state this body is absent.

To the right of the line b_2b_3 we have first the region of α and β, and then, to the right of the line b_1b_4, the region of pure β, while beyond that again is the region of $\beta+\gamma$. The industrially important Muntz metal, containing about 60 p.c. copper and 40 p.c. zinc, lies in the region of $\alpha+\beta$, and accordingly always exhibits a very definite duplex structure which is not removed by annealing, in this respect differing from a typical brass such as that used for condenser tubes, which contains 70 p.c. copper and 30 p.c. zinc, and therefore lies in the region of pure α. Study of the curves of the diagram will at once show that the alloys containing the β body during cooling undergo a decomposition on passing through the temperature of the line b_1b_4 or c_1c_2 respectively, breaking up from pure β into α plus β or β plus γ respectively. These decompositions are also readily prevented by somewhat rapid cooling, so that the final state of the alloys depends a good deal upon the rate at which they have been allowed to cool from fusion or from subsequent heating.

Some reference is required to the horizontal line in this diagram, running from P to Q through the entire region of the alloys in which the β phase occurs. This line represents a series of heat-evolutions, which, originally observed by Roberts-Austen (Roberts-Austen, Fourth Report to the Alloys Research Committee of the Inst. Mech. Eng. 1897, 31–100), have been redetermined by Carpenter and Edwards (H. C. H. Carpenter and C. A. Edwards, Journ. Inst. Metals, v. 1911). The nature of the change indicated by these arrest-points is not quite clearly established; the authors just named suggest the interpretation that at this temperature the β phase undergoes decomposition into α and γ, and they quote some microscopical and mechanical evidence in support of this view. There are, however, serious difficulties in the way of this explanation, and the writer prefers to regard the change, for the present, as a transformation in the β phase; the critical points in question, however, appear to be of some importance in the thermal treatment of brass.

Before leaving the metallography of the copper-zinc alloys the effect of heat-treatment on the micro-structure of these metals must be mentioned. It has been shown that even at the ordinary temperature the crystals of brass which have previously undergone severe mechanical distortion undergo a gradual rearrangement, resulting in the formation of larger crystals of normal shape (E. Cohen, Revue général des Sciences, Paris, 1910); at higher temperatures this recrystallisation is decidedly rapid, the size of the resulting crystals depending upon both the highest temperature reached and on the duration of heating, although at each temperature there appears to be a limiting size of crystal structure, which is gradually attained, but is not exceeded on prolonged heating at that temperature. For practical purposes the scale of crystal structure is important, because it is a universal law in metals and alloys that increasing size of crystals brings with it decrease in strength and increase in brittleness or fragility. It follows that in brass, as in most other metals, prolonged heating, or heating to an excessive temperature, tends to injure the metal, which becomes 'overheated,' and if the heating is very excessive, may become 'burnt,' a stage where the injury to the internal structure has become so severe that it cannot be eradicated by any treatment short of re-melting.

The influence of the most frequent impurities on brass has received much attention, both from the mechanical point of view and from that of the effect on the micro-structure. A very frequent, and in many respects very injurious, impurity is lead. This metal apparently does not remain in solid solution in the α body of the copper-zinc series, and in all ordinary brasses, therefore, appears as a distinct micro-constituent whose presence can be recognised, in the form of minute dark globules, which are readily seen before the specimen is etched, when present to the extent of not less than 0·2 p.c. When the specimens are etched in the more usual manner by means of ferric chloride solution, these minute dark specks are no longer very conspicuous; on the other hand, their presence can be made very obvious by etching the specimens with concentrated nitric acid, applied in the form of a single drop, and immediately washed off in a rapid current of water. This reagent develops a more or less deep and irregular pit in the surface at the spots previously occupied by lead globules, and the etched specimen accordingly appears to be deeply pitted. It may be mentioned that the presence of lead—at all events when present in quantities exceeding 0·40 p.c.—tends to produce 'pitting' by corrosion of the brass around the lead globules, a process which frequently leads to the rapid failure of such objects as condenser tubes, &c. The method of etching a polished specimen with strong nitric acid mentioned above thus furnishes an approximate guide to the probable behaviour of such metal—a brass which pits deeply under such etching is likely to pit rapidly in service. It should, however, be mentioned that these minute lead globules are not the only impurities which cause pitting under the action of strong nitric acid, minute globules of oxide behave in the same manner, although their appearance before etching is different from that of the lead particles.

With regard to other impurities, it may be stated generally that the less injurious or non-injurious ones are rarely if ever visible as distinct constituents under the microscope; in fact, the question whether a given impurity is injurious or not is very largely a question of whether it does or does not form a distinct micro-constituent. Thus arsenic (in small amounts), nickel, silver, &c., all remain in solid solution in the α body—some of these, indeed, as well as manganese and tin and iron are deliberately added to certain 'special' brasses in order to obtain valuable ternary alloys. The constitution of these ternary alloys has not yet been studied sufficiently to make it possible to discuss their metallography in detail, although much work has been done on them (*see* L. Guillet, Alliages Métalliques, ch. x.).

The alloys of copper and tin constitute one of the most complex of the binary series, but their constitution has been exhaustively studied and the results are embodied in the diagram reproduced in Fig. 19. Space does not permit of a full description and discussion of this diagram (Heycock and Neville, Phil. Trans. 1903, 202, A, 1; Giolitti and Tavanti, Gazz. chim. ital. 1908, 38, ii. 209; Shepherd and Blough, J. Phys. Chem. 1906, 10, 630), and attention must again be confined to that end of the series which embraces the industrially useful alloys, which, with the exception of 'speculum metal,' contain less than 14 p.c. of tin.

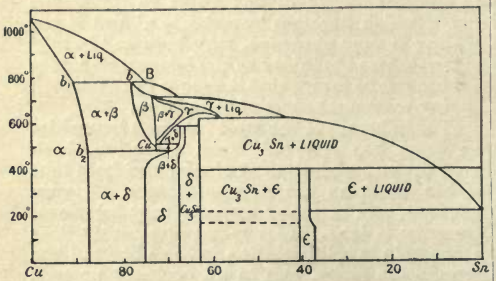


FIG. 19.

The industrially important alloys are entirely included among those which begin to solidify along the branch AB of the liquidus; these alloys begin to solidify by the deposition of crystals of the α body, which is a simple solid solution of tin in copper. Those alloys which contain more copper than the concentration indicated by the abscissa of the point b_1 (about 92 p.c. of copper) completely solidify in the α form and undergo no further changes on cooling to the ordinary temperature. This α body of the copper-tin series is, it may be remarked, somewhat similar in character to the corresponding body of the copper-zinc and copper-aluminium series, *i.e.* a tough ductile body of gradually increasing strength and hardness as the proportion of the added element is increased; there is, however, a marked difference between the three series as regards the relative influence of various proportions of the added element—the concentration of the point corresponding to b_1 in Fig. 19 being in the copper-zinc series approximately 70 p.c. of copper. This may be expressed by saying that the effect of 7 or 8 p.c. of tin is equivalent to that of 30 p.c. of zinc. It is interesting to note that this relatively feeble action of zinc is met with in other alloys of this metal.

Alloys still belonging to the group represented by the line AB, but containing more than about 8 p.c. of tin, do not solidify completely until they reach the temperature of the line b_1bB (just below 800°), and at that temperature the remaining liquid solidifies in the form of the β constituent. In the field $bb_1b_2c_4$ the alloys thus consist of a mixture of the two phases α and β, but if they are cooled sufficiently slowly, the β body disappears entirely. In the case of alloys lying between 92 and 87 p.c. of copper, the cooling alloy crosses the line b_1b_2, which is exactly analogous to the line of the copper-zinc diagram; on crossing this line the β body disappears and the alloys again consist entirely of α. Since in these as in all similar alloys, the β body is much more brittle than the α, this transformation has a powerful effect on the mechanical properties of the alloys. A still more important change takes place in the alloys containing rather less than 87 p.c. of copper; in these, along the line b_2c_4 the β body is transformed into the δ phase, and this phase is considerably harder and very much more brittle than the β phase. When these alloys are slowly cooled in the ordinary course, these transformations occur only to a limited extent, and the resulting structure shows a mixture of transformed and unchanged constituents, while the mechanical properties are also intermediate. By quenching the alloys containing less than 87 p.c. of copper from a temperature just above the line b_2c_4, however, the $\beta = \delta$ change can be entirely prevented, very much to the advantage of the strength and ductility of the alloys.

Copper-tin alloys to which other metals or metalloids have been added include a number of important 'special bronzes,' many of which are known under trade names. Among the special bronzes, the class of alloys known as 'phosphor bronze' are perhaps the most important. The

PLATE II.

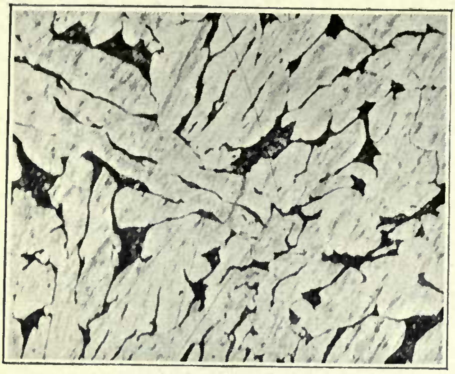


FIG. 21.


FIG. 25.

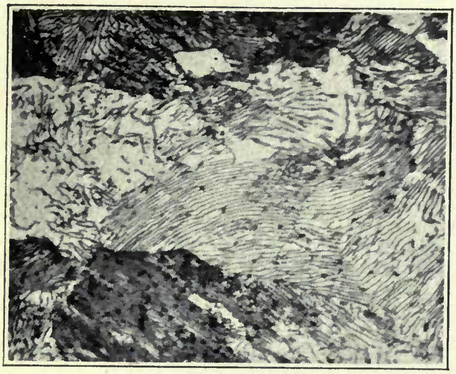


FIG. 26.

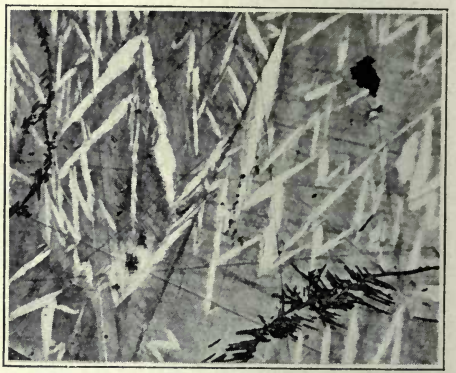


FIG. 27.

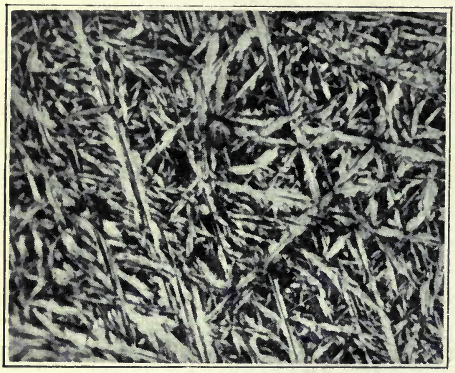


FIG. 28.

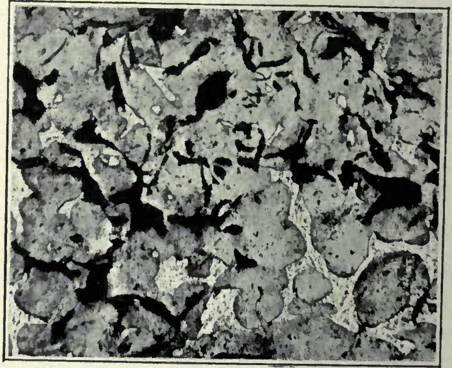


FIG. 29.

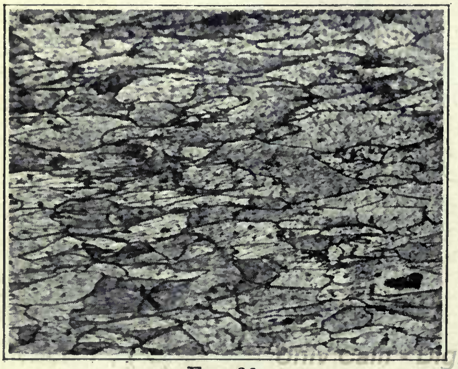


FIG. 30.

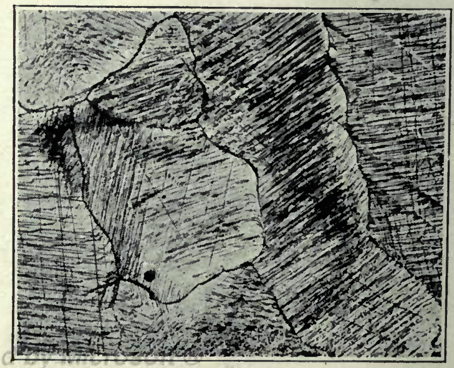


FIG. 31.

[*To face* p. 467.

addition of phosphorus to copper-tin alloys is usually made in the form of either phosphor-copper or phosphor-tin alloys previously prepared. The quantity of phosphorus introduced varies according to the purpose for which the alloy is intended. In a great many cases the object of adding the phosphorus is simply to free the metal from oxide of tin, which is apt to occur in ordinary bronze in the form of small angular crystals the presence of which reduces the strength and ductility of the alloy. Phosphorus thus added merely as a de-oxidising agent passes almost completely into the slag, and mere traces are found in the resulting 'phosphor bronze.' In other cases it is desired to retain a certain amount of phosphorus, probably in the form of the hard and brittle compound Cu_3P in the resulting alloy, in order to increase its hardness and to give it the special properties desired in a bearing metal—properties which are obtained by alloys consisting of crystals of a hard brittle constituent embedded in a soft and comparatively plastic matrix. The constitution of the copper-tin-phosphorus alloys has been studied to some extent, but the reader must refer to the original paper of Hudson and Law (Hudson and Law, A Contribution to the Study of Phosphor-Bronze, Journ. Inst. Metals, iii. 1910, 1, 161) for further details.

The alloys of copper with aluminium (aluminium bronzes) can only be very briefly considered here. The equilibrium diagram, as given by Carpenter and Edwards (Carpenter and Edwards, Eighth Report to the Alloys Research Committee of the Inst. Mech. Eng. 1906), is reproduced in Fig. 20. Again, industrially useful alloys are only found near the extreme ends of the series, but in this case the light alloys of aluminium containing up to 4 p.c. of copper are of importance, as well as the heavy alloys rich in copper (89 p.c. copper and over). The remarkable properties of these alloys and of others directly derived from them have been closely studied (Carpenter and Edwards, Eighth Report to the Alloys Research Committee of the Inst. Mech. Eng. 1906; Rosenhain and Lantsberry, Ninth Report to the Alloys Research Committee of the Inst. Mech. Eng. 1910). From the point of view of constitution and micro-structure, the copper-aluminium series is closely related to the copper-zinc and copper-tin series. Near the copper end of the series we have again an α body consisting of a solid solution of aluminium in copper and gradually increasing in strength and hardness with increasing content of aluminium, but with the important difference that the degree of combined strength and ductility obtainable by the aid of aluminium is much greater than that found in either of the two other series named. An additional property of very great value is the high resistance of these alloys to corrosion. In the copper-aluminium series we again have a β body, which is hard and comparatively brittle, while great brittleness, rendering the alloys industrially useless, appears with the occurrence of the third phase of the series.

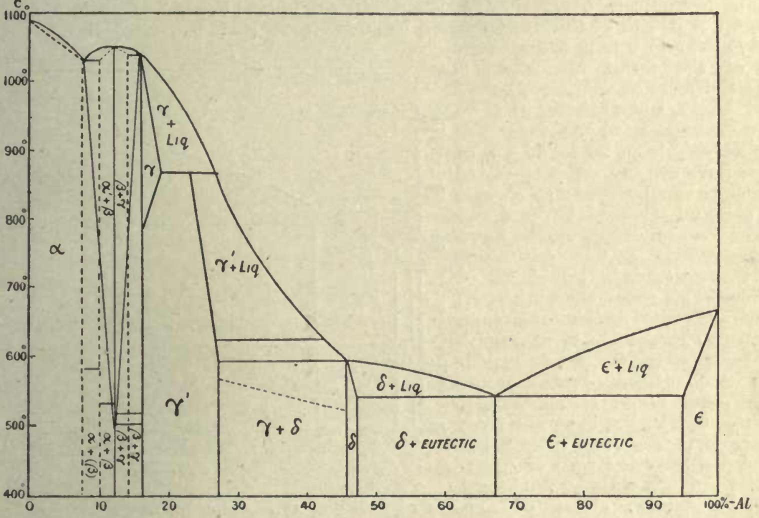


FIG. 20.

The micro-structures of all the copper alloys which have been described above are very similar. Those alloys which consist of the α constituent alone show a structure closely resembling that of pure copper, and already illustrated in the case of brass in Figs. 11 and 12, Plate I. Where the β phase is present, etching usually does not reveal the crystal boundaries of the α phase at all, the β constituent being merely darkened and eroded. A typical example from the copper-aluminium series is given in Fig. 21, Plate II. It should be remembered that the scale of this micro-structure will depend, in any given alloy, upon the heat treatment which the metal has received; prolonged heating, especially at high temperatures, produces a coarse structure, and this coarsening of the micro-structure is accompanied by a degradation of the mechanical properties.

The alloys of aluminium have acquired a considerable degree of importance which later developments tend to increase. Only a few of the most important ones can be discussed here. The alloys of aluminium with copper have already been mentioned; their constitution is represented by the right-hand side of the diagram of Fig. 20. It has been found that aluminium possesses a small, but not definitely ascertained power of dissolving copper in the solid state; at concentrations above 5 p.c., however, the copper forms a eutectic alloy with aluminium, the copper being present in this eutectic in the form of the definite compound $CuAl_2$, which—like almost all inter-metallic compounds—is an exceedingly brittle body. Alloys of aluminium containing as much as 3 and 4 p.c. of copper contain small quantities of this eutectic, and as a consequence they are harder and stronger, but also far less ductile than pure aluminium. When the copper content exceeds 4 p.c. the degree of brittleness becomes too great for most purposes, and the alloys can no longer be rolled into bars or sheets, even when hot.

The alloys of aluminium with manganese have not been studied sufficiently for the construction of a complete equilibrium diagram, but sufficient is known of their constitution to state that in the alloys near the aluminium end of the series, manganese is present in the form of the hard, brittle compound Al_3Mn, and additions of more than 2 p.c. appear to be injurious. Alloys containing from 30 to 60 p.c. of manganese have the curious property of disintegrating spontaneously; a cast ingot of such an alloy, whilst hard and sound when first solidified, breaks down spontaneously into a fine crystalline powder, in some cases in the course of a few hours. This process is not accompanied by any considerable oxidation, and appears to be the result of a polymorphic change of the compound Al_3Mn. Similar spontaneous disintegration occurs in certain other alloys of aluminium, notably those of iron, but in certain cases this change is permanently inhibited if an ingot of the alloy is forged or otherwise worked soon after casting. Certain other, more complex, alloys of aluminium exhibit a process of spontaneous change leading to gradual weakening in the course of several years, so that aluminium alloys should only be employed after a careful study of the properties of the particular combination in question. As regards many of the better-known alloys of aluminium, such as those with copper, copper-manganese, and zinc, this study has already been carried out, so that reliance can be placed on these materials.

The structure and constitution of ternary alloys of aluminium with both copper and manganese has been studied (Rosenhain and Lantsberry, Ninth Report to the Alloys Research Committee of the Inst. Mech. Eng. 1910), but the matter cannot be dealt with here. An interesting development from the alloys of this group is represented by the material known as 'Duralumin,' a patented alloy of aluminium with copper, manganese, and a small amount (about ½ p.c.) of magnesium. Treated in the ordinary manner this alloy is very similar in properties to the simple aluminium-copper alloys, but after heating to a definite temperature lying in the neighbourhood of 400° the alloy undergoes an ageing process occupying 8–10 hours, in the course of which it increases nearly 100 p.c. in strength and hardness without a corresponding loss of ductility. The metallographic explanation of this phenomenon has not, as yet, been arrived at.

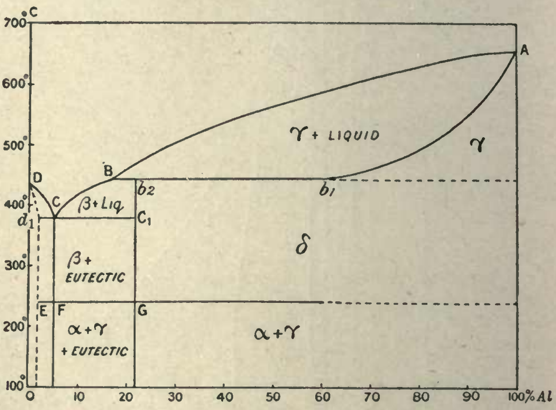


Fig. 22.

The alloys of aluminium with zinc, and derivatives of these alloys, have received much attention (Rosenhain and Archbutt, Aluminium-Zinc Alloys, *v. supra*). The equilibrium diagram of the aluminium-zinc series is given in Fig. 22. Owing to the fact that zinc is soluble in solid aluminium up to a considerable concentration (exceeding 40 p.c.) a considerable range of these alloys is industrially useful, and even the more brittle members of this series may be of practical utility as casting alloys on account of their comparative lightness and cheapness. The liquidus curve of the aluminium-zinc series is given by the line ABCD (Fig. 22). Along AB a solid solution of zinc in aluminium begins to crystallise; up to about 40 p.c. of zinc the solidification is completed in this form (the γ phase) along the curved solidus Ab_1. The break in the liquidus at B, however, indicates that beyond this point the liquid alloys deposit a new phase (β), which is probably the definite compound Al_2Zn_3; along the line Bb_2b_1 this compound is formed by a reaction between the solid γ phase already present and the residual liquid; since the solid crystals become encased in sheaths of the compound, the completion of this reaction is very slow, and in fact only takes place when the alloys are annealed for several hours at a temperature just below that of the line Bb_1. At the point b_2 the alloy possesses the composition of the compound, and the whole of the solid solution reacts with the whole of the residual liquid to form the compound; to the right of b_2 there is an excess of the original solid solution, and this forms an unbroken series of solid solutions with the compound—*i.e.* the compound and aluminium are mutually soluble in all proportions. To the left of the point b_2 there is an excess of liquid, and this solidifies as the eutectic of zinc and the compound along the line d_1c_1. The compound (β) is, however, again decomposed—throughout the entire range of its existence, even in the state of solid solution—on reaching the temperature of the line EFG (256°), when it breaks up into its constituents, viz. the α and γ phases, which are simply saturated solid solutions of aluminium in zinc and *vice-versâ*. An interesting feature of this decomposition, however, is that the two products arrange themselves in the form of fine laminæ closely resembling the typical structure of a eutectic alloy, but on a much smaller scale. This phenomenon presents a striking analogy to the formation of 'pearlite' in steel (*v. infra*), and is of importance because of its rarity. How far this decomposition occurs in those alloys of most industrial importance (viz. those containing less than 30 p.c. of zinc) is not yet definitely known, but it is probable that the phenomena in question affect the behaviour of these alloys on heating and cooling.

Iron and Steel. The iron-carbon system is, from the metallographic point of view, one of the most complex groups of alloys; although a range of only 5 or 6 p.c. of carbon-content is to be studied, since alloys richer in carbon cannot at present be prepared, and although probably a larger amount of investigation has been expended on these alloys than on any other system, it cannot be said that their metallography is as well understood as that of such alloys as copper-zinc or copper-tin. The reason probably lies in the difficulty of studying the constitution of these alloys at high temperatures —difficulties which are due to the rapidity with which they undergo oxidation at high temperatures, and the rapidity with which many of them undergo transformations on cooling through certain temperatures. Quenching such alloys fails to maintain them entirely in the condition which it is desired to study, and a series of complex transition products are accordingly met with, which vary in character according to the exact circumstances, and have consequently given rise to much controversy The metallography of the iron-carbon series will be described from the standpoint of the so-called 'allotropic theory,' which is now almost universally accepted, but it is desirable to mention the fact that somewhat divergent views are held in some quarters; these divergences, however, affect only the interpretation and not the actual facts of iron and steel metallography.

The equilibrium diagram of the iron-carbon series, somewhat modified from that originally drawn up by Roozeboom (Roberts-Austen, Fifth Report to the Alloys Research Committee of the Inst. Mech. Eng. 1890; Roozeboom, Zeitsch. physikal. Chem. 1900, 34, 437; Goerens, Erstarrungs und Erkättungsvorgäuge bei Eisenkohlenstofflegierungen Halle, 1907; Carpenter and Keeling, Journ. Iron and Steel Inst. 1904, I) is shown in Fig. 23. It should be remarked at once, however, that this diagram represents what is not in reality a diagram of completely stable conditions; the stable equilibria are indicated by the dotted lines in the diagram, and will be dealt with later, but the meta-stable equilibria represented by the full lines occur with such persistence, especially in the alloys containing less than 2 p.c. of carbon, that they are of greater interest and importance than the conditions of true stability, which are met with in practice only in the case of cast iron and pig irons generally.

The liquidus curve of the iron-carbon alloys, within the limits open to investigation, consists of two branches, AB and BC, the former representing the commencement of solidification of a solid solution of carbon or of iron carbide in iron; the branch BC as drawn in Fig. 23 represents the solidification of carbide of iron (or ('cementite'). This branch of the curve probably tends to a definite maximum at a concentration corresponding to the formula Fe_3C, but this portion of the curve cannot be pursued up to that point, principally because with these high concentrations of carbon the stable system, in which iron carbide or cementite has no place, tends to predominate, and the liquidus curve becomes that representing the separation of graphite according to the dotted line B′C′. Along the line b_1BC$_1$ the eutectic of the solid solution (AB) and of cementite (C) separates, while the curved solidus line Ab_1 represents the completion of solidification of the alloys containing up to 2·2 p.c. of carbon. The exact position of this line has only recently been determined (Gutowsky, Metallurgie, 1909, 6, 512), and it is of considerable practical importance since it indicates a superior limit above which steel may not be heated without permanent injury due to 'burning'—steel which has been heated to the point of incipient fusion (*i.e.* above the line Ab_1) appears to be permanently spoilt in such a way as to be unfit for any use except re-melting. It may be added that even at considerably lower temperatures steel may be rendered weak and brittle, but if the injury has not gone too far the quality of the metal can be restored by suitable treatment.

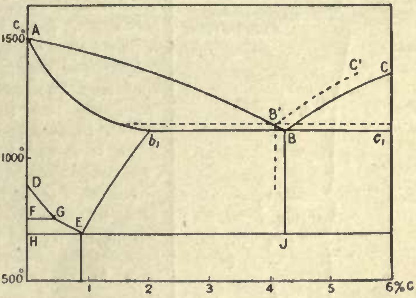


FIG. 23.

To understand the lower portion of the diagram of Fig. 23, *i.e.* the portion comprising the lines DE, Eb_1, FG, and HEJ, we must first consider the transformations undergone by pure iron in cooling from a temperature above 900° down to the ordinary temperature. The cooling-curve of electrolytic iron nearly free from impurities is shown in Fig. 24. At or near the temperature of 900° there is the first arrest-point in the cooling-curve; then the cooling proceeds regularly down to a temperature of 750° (point F in Fig. 23), where there is a second arrest-point which sometimes exhibits a double peak; if even a trace of carbon is present there is a third very slight arrest-point at or about 700°, and after that the iron cools normally. The interpretation to be placed on these arrest-points is that at the temperatures in question the iron undergoes a transformation or rearrangement of the constituent atoms of its molecule, which liberates a considerable quantity of latent heat, thus producing the arrest of cooling. These transformations or molecular rearrangements are analogous to similar phenomena observed in such elements as sulphur, selenium, &c., and are described as 'allotropic' transformations. In the case of iron, the form which is stable—in pure iron—at temperatures above 900° is called γ iron, and the arrest-point which indicates the transformation of γ iron is called Ar_3 (Osmond, Journ. Iron and Steel Inst. 1890, 1). The form of iron which exists between this arrest-point and the next (Ar_2) is called β iron, while the form which exists below Ar_2, down to the ordinary temperature, is called α iron. No marked difference in crystalline form has as yet been demonstrated between the three allotropic modifications of iron, but the point Ar_2 coincides with the disappearance of magnetic permeability, so that β and γ iron are generally regarded as being non-magnetic. It has been shown, however, that the transition of nearly pure iron from the α into the β form is accompanied by a marked and sudden increase in hardness and tensile strength (Rosenhain and Humfrey, The Crystalline Structure of Iron at High Temperatures, Proc. Roy. Soc. 1910), and it is also known that the allotropic transformations are accompanied by sudden changes in volume. It further follows from the equilibrium diagram of Fig. 23 that while γ iron can hold carbon or carbide of iron in solid solution to a considerable extent, both β and α iron have little or no power of dissolving carbon or carbide of iron.

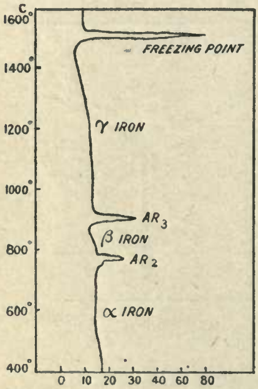


Fig. 24.

The area $ADEb_1$ of the diagram of Fig. 23 thus represents a region in which the alloys consist of a solid solution of carbon or more probably carbide of iron in γ iron. On cooling, this solid solution behaves very much like a liquid solution of two metals; along the line DG crystals of β iron are deposited, leaving the solid solution richer in carbon; along the line GE this process is continued except that the crystals which separate are now α iron; along the line Eb_1, on the other hand, crystals of cementite (carbide of iron) are deposited, leaving the residual solid solution poorer in carbon than it previously had been. If we follow the cooling of a steel containing from 0 to about 0·45 p.c. carbon, we find it passing first through the line DG, and then commencing to deposit crystals of β iron; these crystals increase in quantity until the line FG is crossed, when the whole of the β iron is transformed into α iron, and the quantity of this α iron now continues to increase, the carbon becoming increasingly concentrated in the residual solid solution. This concentration continues in such a way that at any instant if a horizontal line be drawn representing the temperature of the alloy, then the abscissa of the point where this line crosses the line DGE indicates the concentration of the residual solid solution. Accordingly, when the steel has reached the temperature of the line HEJ, the residual solid solution has at the same time reached both the concentration and the temperature of the point E. This point, and, indeed, the whole line HEJ, corresponds closely to the eutectic line of a simple system of eutectiferous alloy, such as the line DE of Fig. 4. At the temperature of the line HEJ the remaining γ iron of the residual solid solution undergoes transformation into α iron, and rejects the carbide which it held in solution up to that temperature; the result is that the residual solid solution breaks up into two phases, viz. α iron and cementite, giving rise to a regular laminated eutectic-like structure, which is called a 'eutectoid.' The micro-constituent corresponding to this decomposition is called 'pearlite,' from the pearly appearance which its laminated character gives it under certain conditions of illumination. The α iron, on the other hand, which has previously separated, is known micrographically as 'ferrite,' since it is practically pure iron. The microscopical appearance of pure ferrite has already been illustrated in Figs. 9 and 10, Plate I.; Fig. 25, Plate II. shows the structure of a very mild steel, containing about 0·15 p.c. carbon and consisting of ferrite (light) and pearlite (dark). Fig. 26, Plate II. shows the 'eutectoid' structure of pearlite more highly magnified.

Alloys lying between the concentrations of points E (0·9 p.c. C), and b_1 (2 p.c. C) undergo a somewhat similar series of changes, but here it is cementite which is separating out at all temperatures below the line Eb_1, while the residual solid solution is lowered in carbon content until the temperature of the line EJ, and the concentration of the point E are again simultaneously reached. The alloys of this group accordingly consist, when slowly cooled, of crystals of cementite embedded in the eutectoid pearlite.

Alloys lying to the right of the point b_1, so far as they follow the equilibria of the cementite system at all, consist, immediately below the line Bb_1, of crystals of the solid solution of cementite in γ iron embedded in a true eutectic of cementite and solid solution. The subsequent behaviour of these alloys is similar to that of the group just previously described, the solid solution behaves exactly like that of an alloy having the concentration b_1, the additional cementite remaining unchanged throughout. After slow cooling through the line EJ these alloys consist of two kinds of cementite, viz. that derived from the original eutectic solidification and that deposited by the solid solution during cooling, the latter being embedded in pearlite.

The constitution of the iron-carbon alloys at high temperatures, as indicated by the equilibrium diagram, is of special importance, owing to the wide use in the arts and industries of the process of hardening steel by quenching. It has already been explained that the effect of quenching is to inhibit the occurrence of those changes which take place in the metal in the course of normally slow cooling; this inhibition may be more or less complete according to the vigour of the quenching process employed. A very rapid cooling, as by quenching in water or even in iced brine, prevents the transformations more completely than more moderate rates of cooling caused by plunging the hot steel into oil or mercury (Benedicks, Journ. Iron and Steel Inst. 1908, ii. 152).

The iron-carbon alloys in the region ADGEb_1 of the diagram consist, as has already been stated, of a homogeneous solid solution of carbide of iron in γ iron. This solid solution, so far as it is known in micro-sections, has received the name of 'austenite.' In the case of certain alloy steels containing considerable proportions of such elements as nickel or manganese, this austenite solid solution remains stable down to the ordinary temperature, or may be retained by moderate quenching. In pure carbon steels it is never preserved unchanged by quenching, but it has been observed by etching steel surfaces at a temperature of over 1100° by means of hydrogen chloride acting in an atmosphere of hydrogen (Baykoff, Révue de Métallurgie, 1910). In quenched carbon steels, austenite is only met with if the carbon content is over 1 p.c., the quenching temperature over 1000°, and the quenching a vigorous one. Even then the austenite is always accompanied by some of the transition products which are intermediate between the unaltered solid solution (austenite) and the normal final decomposition product, pearlite. Among these transition products, three definite stages are observed. The first of these is the constituent known as 'martensite.' This always accompanies austenite in severely quenched carbon steels, and appears in the form of jagged areas showing a minute structure of fine interlacing needles or laminæ, generally crossing at angles approaching 60°. An example of the austenite-martensite structure of severely quenched carbon steels is shown in Fig. 27, Plate II. In the case of steels of lower carbon content, this constituent, martensite, may appear entirely without austenite, and it may occupy the entire area of the specimen. A photograph of a typical martensite structure is shown in Fig. 28, Plate II. This constituent is the hardest body met with in carbon steels; it is distinctly harder than austenite, but while austenite appears to be non-magnetic, martensite is distinctly magnetic, and it is, in fact, this constituent to which the large coercive force of hardened steel is due. The nature of martensite has been much discussed, but a rational view appears to be that the acicular structure arises from a partial decomposition of the austenite along the cleavage planes of its crystals, the whole process, however, being complicated by the changes in volume which accompany the allotropic transformations of iron. Austenite being principally γ iron, is capable of transformation into both β and α iron, the condition of the dissolved carbide being correspondingly altered. Although β iron cannot exist as a stable constituent of steel containing more than about 0·45 p.c. of carbon, yet it is very probable that γ iron in breaking down passes through the β condition before reaching the α stage, although the β condition is itself meta-stable. Martensite being the first stage in the breaking down of austenite, it is reasonable to suppose that the former constituent consists of or contains β iron. This view is supported by the fact that it has been shown (Rosenhain and Humfrey, The Crystalline Structure of Iron at High Temperatures, Proc. Roy. Soc. 1910) that β iron is decidedly harder and stronger than α iron. As regards the magnetic properties, it is admitted that β iron at high temperatures has only a small magnetic permeability, but it is quite possible that this property in this material has a high temperature-coefficient, so that if β iron could be obtained in the cold it might possess sufficient magnetic permeability to account for the magnetic properties of hard steel. Martensite may thus be regarded, provisionally at all events, as containing a considerable proportion of β iron, and as owing a considerable share of its great hardness to the presence of that form of iron. The hardness of martensite, however, is also due in part to two other causes; one of these is connected with the change of volume which is associated with the allotropic transformation; this change is to some extent inhibited by quenching, and severe internal stress is set up, and such a stress contributes materially to the hardness of the metal. The presence of carbon also plays an important part; in the first place the presence of carbon is essential in order that any process of quenching shall retain the iron in the γ or β state. This action of carbon is evident when an attempt is made to harden iron free, or nearly free, from carbon; no hardness comparable with that of steel can be obtained in that case. Carbon is said to act as a species of 'brake' on the allotropic transformations, and the nature of its action may be understood when it is considered that the transformation of pure iron from one allotropic form to another merely involves a rearrangement of the atoms within the molecule, or at most the interchange of atoms between closely adjacent molecules. When the γ iron contains dissolved carbide of iron, however, the allotropic change of the iron involves the expulsion of the carbide from solution, and, for completion, its rejection from the crystals of iron. This rejection involves a transfer of the carbide molecules across distances which are very large compared with molecular dimensions, and it is not difficult to understand that such a transfer occupies time, and that it is, therefore, more or less readily inhibited by the action of quenching.

In the case of martensite the rejection of the carbide from its state of solution in the γ iron of the austenite has only just begun, and the carbide probably exists in a separated form only on the cleavage planes of the original γ iron crystals. When the rate of cooling has been somewhat slower, however, the rejection of the carbide, as well as the allotropic transformation of the iron itself, are allowed to go somewhat further, and as a result a further transition product is found in the micro-sections. This is the dark-etching body known as 'troostite,' found in oil-hardened and in many tempered steels. In this constituent the rejection of the carbide is practically complete, but the carbide is in a state of extremely fine division, according to some views, indeed, in a state of ‘colloidal solution’ or suspension in the iron (Benedicks, Journ. Iron and Steel Inst. 1905, ii. 352, and 1908, ii. 217). In troostite it appears probable that while some of the iron still retains the original γ condition, and a large proportion is in the hard β condition, some has already passed into the soft α stage, with the result that steel containing troostite is distinctly softer than that consisting entirely of martensite. When the quenching or tempering is so adjusted that the whole of the γ iron has just disappeared, the proportion of troostite would attain its maximum, this being the state of tempered steel called ‘osmondite,’ by Heyn (Heyn and Bauer, Journ. Iron and Steel Inst. 1909, i. 109). Further tempering, or still slower cooling, leads to the appearance of a further transition product, which is not very sharply differentiated from troostite on the one hand, and from pearlite on the other. This is known as ‘sorbite.’ Here the iron has reached the α stage, and the carbide has begun to segregate into masses which are at first too minute to be seen under the microscope; but with further tempering, or less vigorous cooling, the segregation of the carbide reaches the point where it can be resolved under the microscope into granular or laminated pearlite. Steel containing sorbite is not really hard in the ordinary sense, although it possesses distinctly greater hardness and tensile strength than the same steel in the pearlitic state. Rail and other comparatively low-carbon steel is sometimes so treated as to render the carbonaceous constituent sorbitic, and in this condition the steel exhibits specially valuable physical properties.

The hardening of steel may be summarised metallographically as follows :—

Fully hardened steel = Martensite or austenite-martensite.
Moderately hardened or slightly tempered = Martensite-troostite.
Tempered steel = Troostite with either martensite or sorbite.
Slightly hardened or much tempered = Sorbite.

The causes which produce hardness in quenched steel may be summarised as :

(1) The retention of iron in the γ and β state.

(2) Internal stress set up by the partial retention of carbide in solution under conditions where stable equilibrium would require the separation of the carbide.

(3) Internal stresses and strains caused by the partially suppressed volume changes which accompany the allotropic transformations of iron.

It is desirable to mention at this point that, according to a rival theory, the hardness of quenched carbon steels is due to the existence of a definite iron-carbon compound (containing about 0·9 p.c. of carbon); on slow cooling this compound is said to decompose into pearlite, while quenching retains it in existence as ‘hardenite.’ This theory has, however, met with so little general acceptance and presents so many inherent difficulties that it could not be dealt with in the limits of this article.

A large and increasingly important class of alloys are those produced by the addition of various metals, such as nickel, chromium, manganese, and the rare metals such as vanadium, tungsten, molybdenum, and others, to iron and to certain grades of steel. The metallography of these steels is, however, so complex that it cannot be described here. Broadly speaking, these ‘special’ steels may be divided into four large classes, the class to which any particular steel belongs being dependent upon the total proportion of alloyed elements present. The first class of the special steels are those containing relatively small proportions of the added elements; these possess a simple structure of ferrite and pearlite, very similar to that of pure carbon steels, although differing in minor details; their mechanical properties are frequently markedly superior, and notably those containing nickel, chromium, and vanadium are finding much technical application. The second class of the alloy steels show a structure resembling that of martensite; they are hard and practically unworkable, but their existence is utilised in certain special cases, as in the production of case-hardened objects without quenching in the cementation of certain grades of nickel steel. The third class of alloy steels are those containing still larger proportions of alloyed elements, as, for example, a nickel steel containing about 25 p.c. of nickel. They exhibit a simple polyhedral structure, which is that of austenite, but in this case the solid solution contains the alloyed elements as well as the γ iron and carbon. These steels are non-magnetic, and possess remarkable mechanical properties, notably a high degree of ductility combined with great tensile strength. In some cases, however, they possess the peculiar property of being converted into steels of the previous class (martensitic) by mechanical work; such a steel, when first cut by a saw, for instance, is quite soft, but it rapidly hardens under the tool, until it can no longer be cut at all. This property is, however, confined to steels lying near the border-line of the two classes. A further increase in the proportion of the alloyed elements brings the steel into the fourth class, in which the presence of a carbide of the alloyed element can be detected in the micro-structure. For most general purposes such steels are useless, but certain of them appear to be capable of use as high-speed cutting tools. This highly important type of alloy steels cannot, however, be discussed in detail here. It can only be mentioned that while in ordinary carbon steels the temperature required for tempering, and therefore softening the steel is as low as 400°, these special steels can be made to withstand temperatures as high as a dull red heat without losing their hardness; they are thereby enabled to maintain their cutting edge at speeds which render the tools almost red hot. The manner in which the presence of the alloyed elements effects this behaviour can be approximately understood when it is mentioned that the critical points of an ordinary carbon steel are to some extent displaced, according to the temperature to which the steel has last been heated. The presence of an alloyed element not only itself displaces the normal position of the critical points—in the case of nickel steels, for example, extending the range of stable existence of γ iron down to the ordinary temperature—but the alloyed element also increases the extent to which the critical points can be displaced by heat treatment. In the case of high-speed tool steels it is found that by heating the steel to a temperature of 1200° or higher (a white heat), and allowing it to cool in a current of air, the critical point on next heating is raised to so high a temperature that a dull red-heat does not affect the 'temper' of the steel.

The micro-structure of steel has so far been described as the result of either 'normally slow cooling' or of quenching. For the steels containing higher proportions of carbon this classification is practically sufficient, but for the class of 'mild' steels containing up to 0·70 p.c. of carbon the effects of quenching need scarcely be considered, except in the case of the 'sorbitic' steel mentioned above. On the other hand, for these steels the temperature and duration of annealing, and the application of work by rolling, pressing, or forging is of vital importance, both to the micro-structure and to the mechanical behaviour of the material. Metallographic methods have cleared up the greater part of this field, but only general results can be mentioned. Thus it may be taken as a fundamental fact that coarse and well-defined micro-structures imply undesirable mechanical properties, especially as regards behaviour to shock, while a fine, close structure offers the best prospect of good quality in the metal. It is, however, a universal tendency of crystals forming an aggregate such as iron or steel, to grow; *i.e.* certain of the constituent crystals of the aggregate tend to increase in size at the expense of their neighbours. In the case of such comparatively 'refractory' metals as iron or steel, this growth of crystals is *nil*, or exceedingly slow at ordinary temperatures, although in the case of lead (Ewing and Rosenhain, The Crystalline Structure of Metals, second paper, Phil. Trans. A, 1900) and brass (*see* L. Guillet, Alliages Métalliques, ch. x.),such growth takes place measurably even without the application of heat. When iron or steel is heated, however, the tendency for crystal growth rapidly asserts itself, and, indeed, it is to this process of growth, or of 're-crystallisation,' that we owe the power of annealing or softening metal which has been rendered hard and brittle by the application of cold work. In the case of steel, when the temperature of a critical point is passed (on heating) the transformation occurs at a number of centres which behave as centres of crystallisation, and a new system of crystals begins to grow from each of these centres, although to some extent the new set of crystals tends to follow the outlines of those previously in existence. With rising temperature the rate of crystal growth increases, and the ultimate size of structure attained is thus a function of both the time of heating and of the temperature attained. When steel which has been thus heated is allowed to cool slowly, although there is a distinct tendency for rearrangement to occur on passing through the critical points, yet the coarse structure is very apt to persist, and if the heating has been carried too far we have a coarse, weak structure typical of 'overheated' steel. To some extent this coarse structure may be removed by heating the steel for some time to a temperature just above the critical point, and then cooling it somewhat rapidly through the critical point down to the ordinary temperature. A more effective method, however, consists in exposing the steel to hot working (rolling, forging, &c.). This process deforms the existing crystals in a manner described below, and these deformed crystals are unstable, *i.e.* crystal growth starts afresh in them, and can no longer follow the previous outlines; the result is an entirely new and much more minute system of crystals. The exact analogue of this process has been watched, in the case of lead, taking place at the ordinary temperature.

Cast iron, Pig iron. The equilibrium diagram and constitution of iron-carbon alloys has so far been discussed only in reference to alloys containing less than 2 p.c. of carbon, and usually known under the name of 'steel.' The alloys richer in carbon must now be dealt with; these are met with industrially in the shape of a large variety of cast and pig irons, but it must be remembered that while the better kinds of steel consist essentially of almost pure iron-carbon alloys, the cast and pig irons generally contain very considerable proportions of impurities, such as silicon, sulphur, phosphorus, &c. In addition, a large number of these higher-carbon alloys differ essentially from steel by containing carbon in the form of graphite. The equilibrium diagram of the iron-carbon system given in Fig. 23 represents, as has already been mentioned, what is in reality a meta-stable condition of the iron-carbon system; if sufficient time at a suitable temperature be allowed it is probable that carbide of iron would decompose completely into iron and graphite. Apparently it is also possible for free carbon (graphite) to separate as primary crystals from the molten iron-carbon alloys containing over 4·3 p.c. of carbon. If it is true—as seems probable—that in the liquid alloys the carbon is dissolved in the form of only slightly dissociated carbide, then in these high-carbon alloys the carbide (cementite) in certain conditions, and notably in the presence of silicon and in the absence of manganese, is liable to undergo decomposition at a temperature near that of incipient solidification, one of the products of decomposition being graphite, which thus appears as a solid phase in the shape of crystals separating from the liquid. The equilibrium diagram of this ultimately stable system (Fig. 23, dotted lines) thus contains the liquidus branch corresponding to the separation of the γ iron solid solution, but this is carried to a eutectic point differing slightly from the γ iron-cementite eutectic, and corresponding to a γ iron-graphite eutectic; below the temperature of this eutectic the alloys are completely solid, and consist, to the left of the eutectic-point (B) of γ iron embedded in the graphite eutectic, while to the right of the point B they should consist of primary graphite crystals embedded in the eutectic; owing to the low density of the graphite, however, this substance does not remain embedded in the liquid metal from which it is separated, but floats to the surface in the form of 'kish.' On further cooling the behaviour of these alloys should theoretically lead to the complete decomposition of all the cementite, including that contained in the γ iron solid solution, but the exact circumstances in which such decomposition occurs are not fully ascertained. The lower part of the dotted-line diagram of Fig. 23 has not, therefore, been filled in.

In practice certain varieties of cast and pig iron tend to follow the system of solidification just indicated, but they rarely, if ever, do so completely; whilst, if the rate of cooling is rapid, and especially if the iron contains little silicon and much manganese, the decomposition of the cementite is more or less completely prevented, and the iron cools with the formation of little or no graphite, forming what is known as 'white iron'; iron which contains much graphite and little cementite is known as 'grey,' whilst intermediate varieties are known as 'mottled.'

Microscopically, all varieties of iron may, in accordance with the above, be regarded as mixtures of steel with a certain amount of graphite. The 'steel' portion will have the characteristic structure of an iron-carbon alloy whose carbon content corresponds to the amount of 'combined' carbon, *i.e.* of undecomposed cementite, present in the iron. Thus an iron containing, for instance, 0·5 p.c. of combined carbon, together with 3 p.c. of graphite (total carbon 3·5 p.c.), will show a structure of ferrite and pearlite corresponding to that of a 0·5 p.c. carbon steel, together with a considerable amount of graphite. A typical example of the micro-structure of a 'grey' iron of this type is shown in Fig. 29, Plate II., but the presence of impurities, particularly of phosphorus, very materially affects the appearance of such micro-structures, since the phosphorus forms, with the iron, a definite compound Fe_3P, and this compound forms with the iron a well-defined and characteristic eutectic, which may be mistaken for pearlite under the microscope. This phosphide eutectic can, however, be readily distinguished from pearlite by exposing the specimen to a moderate degree of heat which causes a slight surface oxidation, and in consequence a differential tinting of the various constituents.

Increasing total carbon-content, with constant amount of combined carbon, merely causes an increase in the amount of graphite found in the micro-sections; an increase in the proportion of combined carbon, however, causes the 'steel' portion of the iron to move up the carbon-scale, first producing an increase of the amount of pearlite, and finally the appearance of cementite in place of ferrite. In the case of 'white' irons produced by chilling high-carbon cast iron, the graphite disappears entirely, and the resulting micro-structure consists entirely of cementite and pearlite, together with the constituents due to impurities. As regards mechanical properties, it is obvious that the presence of plates of graphite, destroying the continuity of the 'steel' matrix, largely reduces the strength of the material as compared with a steel of equal combined carbon; on the other hand, the iron will be 'soft' or 'hard,' according to the micro-structure of the 'steel' matrix, an iron containing ferrite and pearlite will be much softer and less brittle than an iron containing cementite and pearlite. These latter constituents are responsible for the great hardness of 'chill' iron castings.

For certain purposes castings are treated in such a manner as to be deprived of their graphite content more or less completely by a process known as the production of 'malleable' castings. This process consists in heating or annealing the castings for a considerable time, generally while packed in an oxidising material, such as iron oxide. To a considerable extent decarburisation occurs, while much of the combined carbon is deposited in the form of a very finely divided graphite known as 'temper carbon.' The softening effect of the process depends partly upon the actual removal of carbon by oxidation and partly upon the effect produced by prolonged heating upon the arrangement of the graphite which remains in the metal. While in ordinary castings it is present in the form of plates and veins, in 'malleable' castings it is found in small nodules and patches which do not affect the strength and ductility of the material to anything like so great an extent.

A converse process, for producing surface hardness in articles made of iron or mild steel is that known as 'case hardening.' In this process the iron or steel is heated for a considerable time in contact with carbonaceous matter, preferably also containing nitrogenous matter. The iron takes up carbon and forms a hard external layer rich in cementite, which, therefore, has the power of being hardened by quenching. Micro-sections of case-hardened articles readily show the depth and nature of the hard 'case,' and the structure of the underlying softer and tougher material.

Deformation, fracture, and fatigue in metals. Microscopic metallography has made it possible to determine the mechanism by which metals undergo plastic deformation, and incidentally to explain the mode of fracture under tension, shock, and 'fatigue.' It has already been indicated that when a piece of metal is forced to change its shape, as by hammering, rolling, pressing, &c., the component crystals of the metal also undergo a corresponding change of shape, although subsequently if the temperature is high enough to permit of sufficient molecular mobility in the particular metal in question, the crystals tend to rearrange themselves into more normally shaped forms. If a bar of metal be forcibly stretched, the constituent crystals will be found to be stretched also. Thus cold-rolled iron shows the structure illustrated in Fig. 30, Plate II., where the ferrite crystals are seen to be lenticular in section in place of the normal polyhedral shape. The manner in which metallic crystals undergo such changes of shape becomes evident if a surface of a specimen of metal is prepared for microscopic examination (*i.e.* polished) before the piece of metal is subjected to the change of shape. The crystals which, before deformation, appeared as practically featureless polygonal areas, after the application of the strain, are seen to be cross-hatched by systems of fine lines. In the case of highly plastic metals, such as lead or copper, the lines are seen to be characteristically straight and regular, while in the harder metals, such as iron, the lines appear more or less branched and curved. It has been possible, however, to observe the formation of these lines in iron at high temperatures (up to 1100°) (Rosenhain and Humfrey, The Crystalline Structure of Iron at High Temperatures, Proc. Roy. Soc. 1910), and in those circumstances they are as straight and regular as those of copper. The typical appearance of these lines is shown in Fig. 31, Plate II. Their nature has been elucidated by a long series of experiments, including the preparation of transverse sections of specimens of metal upon which the lines had previously been developed, and the conclusion arrived at is that they are in reality minute steps in the surface arising from the fact that the adjacent portions of the crystal have slipped over one another along the cleavage or gliding planes of the crystal. It may be accepted as abundantly proved that the polygonal grains seen in the micro-sections of metals are true crystals, possessing all the essential features of crystals as regards the regular and symmetrical arrangement of the constituent molecules, although these crystals have grown together into an aggregate without allowing the individual members to develop their characteristic external shape. Such crystals, then, may be regarded as built up of minute elements or groups, much as a stack of bricks is built up of individual bricks. It has been shown (Ewing and Rosenhain, The Crystalline Structure of Metals, Bakerian Lecture, Phil. Trans. A, 1899; Rosenhain, Deformation and Fracture in Iron and Steel, Journ, Iron and Steel Inst. 1906, I.; Rosenhain and Humfrey, The Crystalline Structure of Iron at High Temperatures, Proc. Roy. Soc. 1910) that these crystal 'bricks' or units are themselves never deformed or changed in shape (excepting the temporary 'elastic' deformations which are left out of consideration here), and that the crystals which are built up of these units accommodate themselves to changes of shape imposed upon them by allowing the 'bricks' to slide over one another along at least three sets of gliding planes. Where these planes of slip reach the surface of a crystal forming part of the previously polished face of the specimen, the result is the formation of a minute step in the surface, and the short sloping surface of such a step, when viewed by 'normal' light, appears as a fine dark line. Illumination by oblique light, on the other hand, shows the lines shining brightly against the dark background whenever the short sloping surfaces are turned so as to face the incident light. On account of their mode of formation these lines have been called 'slip bands.'

In certain metals, notably in copper and its α alloys, and also in lead and many other plastic metals and alloys, the process of deformation by slip as just described is also accompanied by what is known as 'mechanical twinning.' In this process a certain portion of the crystal, in order to accommodate itself to the circumstances created by the application of plastic strain, swings over into an entirely new orientation, which is, however, definitely related by crystallographic laws to the orientation of the parent crystal; this process usually occurs in a series of parallel bands. The presence of crystals showing regular alternating bands of similar orientation is always an evidence of 'twinning,' and since twinned crystals rarely occur in cast metals, this feature is generally evidence of the application of work to the specimen in which it appears. Where deformation by slip and by mechanical twinning occur together, the slip-bands change their direction on passing the edge of the twinned area, and a stair-like shape of the bands results.

The process of deformation by slip obviously implies that the metal retains its truly crystalline character after it has undergone a permanent change of shape, and it is found that, unless the amount of deformation has been very large, this is actually the case.

A further series of phenomena must, however, be considered; these relate to the changes which occur in the structure of the crystal at and in the immediate neighbourhood of the surfaces upon which slip has taken place. It has been shown that when the surface of a piece of metal is rubbed or polished (G. T. Beilby, The Hard and Soft State in Metals, Phil. Mag. 1904; G. T. Beilby, Hurter Memorial Lecture, J. Soc. Chem. Ind. 15, 1903), some of the molecules in the surface layer of the metal are torn away from their crystalline arrangement, and are left upon the surface in a state of relative freedom, which allows them to behave in a manner resembling a thin film of viscous liquid. It is by the spreading out of such a film under the action of pressure and of polishing media, that polished surfaces are formed. The material of this thin surface film, however, is no longer in the crystalline condition; its condition resembles that of an exceedingly viscous liquid, and is therefore to be regarded as being truly 'amorphous,' and it has been shown that in this amorphous condition, although temporarily mobile, the material is much harder and also much more brittle than the same substance in the crystalline state. Now in the interior of the crystals of a metal which undergoes deformation by slip, metal surfaces move over one another under very considerable pressures, and it follows that an action very similar to that which occurs upon a surface which is being polished will take place on every gliding plane; *i.e.* a thin layer of molecules will be disturbed from their normal position in the crystalline arrangement, and a layer of temporarily mobile, amorphous material will be formed. Now it has been shown that if this layer is thin, the directive forces of the adjacent crystalline systems are sufficient to cause the disturbed molecules to reassume the orientation of the system, and in that case the surface on which slip has taken place may be said to have 'healed up.' On the other hand, two different cases may occur. In the first case the process of slip may be carried so far that the disturbed layer becomes too thick to allow of complete and almost immediate recrystallisation, and then each surface of slip remains as a species of 'scar' within the metal, taking the form of a thin layer of hard, amorphous material. The presence of these hard layers tends to render the metal both harder and stronger, but also more brittle, and it is well known that this is the universal result of the application of cold work or plastic deformation to ductile metals. If the process of plastic deformation is carried to an extreme, as in the hammering of thin metal foil, a large proportion of the metal may ultimately be present in the amorphous condition; but this condition is unstable, and a very moderate amount of heating is sufficient to induce recrystallisation. This stage, however, is only reached in special circumstances; more usually the application of stress results first in a certain amount of plastic deformation (by slip), followed by a local and rapid deformation—also by slip—which results in fracture at some point where the amount of slip has carried the adjacent parts of a crystal out of contact. The fracture resulting from such a mode of breaking has a fine silky fibrous appearance, owing to the fact that all the minute surfaces of slip along which fracture has occurred are inclined at small angles to the direction of stress, but the metal has remained essentially crystalline; indeed, apart from non-metallic inclusions, such as the 'cinder' in wrought iron, there is no true 'fibrous' structure or condition in metals.

The second class of circumstances which do not permit of the immediate re-crystallisation of the layer of disturbed molecules, which are formed on surfaces of slip arise when the stress which has produced a small amount of slip is reversed; such a reversal of the stress will, if it comes soon after the first occurrence of the slip, cause the reversal of the slip itself, and the layer of disturbed molecules will still be in the mobile condition, and will serve as a species of lubricant to facilitate the return slip. At the same time, the reverse motion will produce an increase in the number of disturbed molecules, and the disturbed layer will grow in thickness with each reversal. After a large number of such reversals of stress some of this disturbed material will be forced—in its temporarily mobile state—out of the space between the adjacent sections of the crystal, and what was before a surface of slip will thus become an actual fissure, which spreads rapidly through the whole mass. The resulting fracture will show comparatively large bright facets representing the planes on which slip has occurred, so that the fracture will have a 'crystalline' appearance, although the metal itself is neither more nor less crystalline than it was at the beginning. The view that metals 'become crystalline' under alternating stresses or under vibration is thus entirely without foundation. It should be said that the explanation of the manner in which metals fracture under 'fatigue,' *i.e.* under the repeated alternation of stresses which would fail to fracture the material at a single prolonged application, which has been given here is no longer to be regarded as of a speculative character, since every point in the explanation has been definitely observed and verified by several independent observers (Ewing and Humfrey, The Fracture of Metals under Repeated Alternations of Stress, Phil. Trans. A, 1903, 200; Stanton and Bairstow, The Resistance of Iron and Steel to Reversals of Direct Stress, Proc. Inst. C.E. 1907).

The methods of metallography, although they have so far been described largely from the point of view of affording a clearer insight into the nature and constitution of metals and alloys, are also capable of direct practical applications. These applications include, in the first place, the control of metallurgical operations, particularly of the temperatures employed in thermal and mechanical treatment of all kinds and the investigation of new alloys. There is also an important field of usefulness for these methods, and more especially for the microscopic examination of metals in conjunction with exhaustive mechanical tests, in the investigation of cases of failure or breakage either under test or in service, including such questions as apparently mysterious fractures, unduly rapid wear or corrosion and similar problems. Although it would be too much to claim that metallographic methods are always capable of finding the correct solution of problems of this class, a great deal of light can often be thrown upon the causes which have led to the failure, and, in many instances, the true cause of failure can be discovered. A considerable number of such investigations have been described (W. Rosenhain, The Study of Breakages, Engineering, Sept. 1908), but the greater number are—for obvious reasons—never allowed to reach the public. It is, however, to be borne in mind that it is largely by the investigation of cases of unexpected breakage or other failure that fresh knowledge on the properties of our engineering materials can be obtained. In a number of actual cases it has been found that the metal had been damaged by modes of treatment which had been regarded as harmless. Metallography is therefore a science which has not only placed in the hands of metallurgists a mass of valuable and detailed knowledge of the internal structure and constitution of metals and alloys, but it has also furnished them with methods of investigation which are probably destined to elucidate many of the still 'mysterious' features in the behaviour of the materials of engineering. W. R.

METANIL YELLOW *v.* AZO- COLOURING MATTERS.

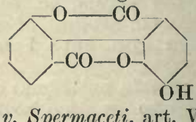
METARABIN *v.* GUMS.

METAXYLORCINOL *v.* PHENOL AND ITS HOMOLOGUES.

METELLAGIC ACID. Metellagic acid $C_{14}H_6O_5$ is prepared by the oxidation of *m*-hydroxybenzoic acid with potassium persulphate and sulphuric acid. It crystallises from pyridine in colourless prismatic needles, and when distilled with zinc dust gives fluorene. The acetyl derivative

$$C_{14}H_5O_5(C_2H_3O)$$

colourless needles, melts at 269°–271°. According to Perkin and Nierenstein (Chem. Soc. Trans. 87, 1425), metellagic is related to ellagic acid, and possesses the following constitution:



METHAL *v. Spermaceti,* art. WAXES.

METHANE. *Methyl hydride* (*v.* METHYL COMPOUNDS).

***p*-METHOXYBENZENEDIAZO CYANIDES** *v.* DIAZO- COMPOUNDS.

METHYL CH_3 is a univalent, compound radicle, not known in the free state. The compound C_2H_6 discovered by Frankland and Kolbe (Chem. Soc. Trans. 1, 60) was called methyl, and believed to be the free base, and even when its molecule was recognised as dimethyl $(CH_3)_2$, it was at first thought to be distinct from ethane, the gas obtained by Frankland from ethyl iodide by heating with zinc and water. It was, however, proved to be identical with that body by Schorlemmer (Chem. Soc. Trans. 17, 262).

METHYL COMPOUNDS.

Methyl acetate *v. Alkyl acetates,* art. ACETIC ACID.

Methyl alcohol CH_3OH. *Methyl hydrate, hydroxymethane, wood spirit, pyroxylic spirit, wood naphtha*, 'Columbian spirit,' 'Colonial spirit,' 'kakol' (proprietary names in U.S.A.), (Ger. *Holzgeist*). B.p. 64·56°/760 mm. (J. Gyr, Ber. 1908, 4322); sp.gr. 0·796472 at 15°/15° (Klason and Norlin, Chem. Soc. Abstr. 1906, i. 821; Gyr, Ber. 1908, 4322; Doroschewsky and Roschdestvensky, Chem. Soc. Abstr. 1909, i. 868); 0·81000 at 0°/4° (Young and Fortey, Chem. Soc. Trans. 1902, 735); H.C. = 170·6 (Stohmann, Kleber, and Langbein, J. pr. Chem. [ii.] 40, 341); H.F. = 61·4 (S., K., and L.).

Boyle found that the liquid obtained by distilling wood contained two constituents, an acid portion and a neutral spirit.

Various conjectures were made as to the nature of this 'spirit,' the first investigation of which was made by Dumas and Peligot in 1834 (Ann. Chim. Phys. 58, 5; 61, 193). They gave it the name 'methyl alcohol' (μέθυ, wine; ὕλη, wood).

Formation.—By the dry distillation of wood, of beet-sugar molasses (Vincent, Bull. Soc. chim. [ii.] 27, 148), or of calcium formate (Paternò and Lieben, Annalen, 167, 293; Friedel and Silva, J. 1873, 526). Methyl alcohol occurs in the free state in plants (Gutzeit, Maquenne, Geuther). It is also recovered from the waste water of the steamed wood pulp in paper manufacture, by allowing the liquors to concentrate through repeated use and subsequently distilling (Alkier, Eng. Pat. 1514, 1890).

Preparation.—Methyl alcohol is prepared on the large scale from the distillate from wood, which contains various tarry matters, acetic acid, and the methyl alcohol. The distillates from the wood are allowed to stand for some time, when the tarry, resinous, and oily matters precipitate; the supernatant liquid is then filtered through gravel into another vessel, from which it is either distilled at once or after previous neutralisation with lime. The distillation is effected in the first case in copper stills, and heat is applied by coils of copper pipes conveying steam; in the second case boilers of sheet iron are employed, and the heat applied by the direct fire.

The distillate is then purified by repeated redistillations from caustic lime, and lastly, from a little sulphuric acid (in order to remove NH_3 and amines). In some cases chalk is used instead of lime, and sometimes chalk and sodium bicarbonate.

The distillation is carried on in copper stills heated by steam coils, or the retorts are guarded by iron jackets, and heated over the fire. The crude spirit thus obtained is colourless, and its sp.gr. varies from 0·87 to 0·82.

The disagreeable-smelling constituents are sometimes got rid of by Wildsmith's process, which consists in the application of oxidising agents, *e.g.* potassium dichromate, aided by the action of light, to the crude spirit, by which means the hydrocarbons, &c., are destroyed, and a colourless, almost odourless, liquid obtained.

The usual yield of pyroxylic spirit is from 1 to 3 gallons from each ton of wood distilled, but the quantity depends upon the kind of wood employed, and also upon the proper regulation of the temperature during distillation. The best yields are obtained by using a mixture of oak, beech, and hornbeam (Barillot, Compt. rend. 122, 469).

Large quantities of methyl alcohol are now made by the distillation of kinasse (residues obtained by the evaporation of the spent wash in the preparation of ordinary alcohol from beet-sugar molasses). The distillate contains ammoniacal compounds, methylamine, methyl cyanide, and methyl alcohol. After neutralising with sulphuric acid the mixture is evaporated, the vapours being condensed; these contain methyl cyanide and methyl alcohol; the former is decomposed by rectification over lime, and the distillate, which contains dilute methyl alcohol, is dehydrated by means of lime.

Commercial wood spirit contains very variable proportions of the pure alcohol, from as low as 35 p.c. to as high as 95 p.c. It contains acetone, methyl acetate, and often, various empyreumatic bodies; these have considerable influence, not only upon its density, but also upon its solvent powers for shellac and other resins. The purest spirit is always preferred for use in lamps as a fuel, but for the use of the varnish-makers and polishers some of the impurer varieties, containing essential oils, &c., are sometimes chosen.

The following process for the production of methyl alcohol from wood is patented by F. J. Root (U.S. Pat. 713552, 1902). In the destructive distillation, a pressure is maintained in the apparatus slightly lower than that of the atmosphere. The readily condensable gases are condensed in primary condensers, whilst the gases which are not readily condensable are mixed with a definite proportion of steam and the acids thus set free are recovered in a secondary condenser. The degree of vacuum and the supply of steam required for mixing with the less condensable gases are obtained by means of a steam exhauster situated beyond the primary condensers. This exhauster is regulated automatically by the volume and tension of the gases generated so that both functions are kept constant. The introduction of superheated air, containing only a little oxygen and a good deal of steam, which increases the yield of volatile products in the ordinary destructive distillation, is patented by Zwillinger (Eng. Pat. 18823, 1889).

A variant of the ordinary method of destructive distillation of wood consists in first adding strong sulphuric acid. 100 kilos. of wood, containing 35 p.c. of moisture, with 20 kilos. of strong sulphuric acid on distillation up to 160° and rectifying the distillate, yield wood alcohol 3 kilos., acetic acid 7 kilos., oil of turpentine 2 kilos., and 40 kilos. of wood charcoal of good quality (Orljavacer, Chem. Fabrik, Fr. Pat. 357432, 1905).

Hofer and Moest find that a good yield of methyl alcohol is obtained by the electrolysis of sodium acetate solution containing sodium chlorate (Annalen, 323, 284; D. R. P. 138442, 1901).

The conversion of methane, which often occurs in large quantities near oil fields, into methyl alcohol or other commercially useful articles, is a problem which is still undergoing examination. Lance and Elworthy (Eng. Pat. 7297, 1906) claim the use of hydrogen peroxide (with or without ferrous sulphate or monopersulphuric acid) and monopersulphuric acid alone. Von Unruh has utilised atmospheric air as an oxidising agent with bark as a catalyst, but in this case methyl alcohol is the subsidiary product, the oxidation proceeding farther and producing formaldehyde chiefly. 24 litres of methane by this process, when mixed with 180 litres of air at 45°, yield in the apparatus described, 1565 grams of formaldehyde in 12 hours (U.S. Pat. 891753, 1907; *see also* Hausmann & Co., D. R. P. 214155, 1906).

Purification.—According to a method patented by Piper and Rotten of Berlin (D. R. P. 36827, 1886), the wood spirit is first distilled with lime and then by fractional distillation the acetone is reduced to 1 or 2 p.c. To remove the remaining acetone the spirit is heated to boiling (with reflux condenser), and dry chlorine is passed into it; portions are tested from time to time by distilling, and testing the distillate for acetone by the iodoform reaction (*see also* Rotten, J. Soc. Chem. Ind. 1901, 604). Treatment with bleaching powder is also sometimes adopted. When this reaction is no longer given the passage of the chlorine is stopped, and the methyl alcohol separated by fractional distillation from the high boiling chlorinated acetone, and purified by distillation over lime from traces of chlorine. The methyl alcohol thus obtained is perfectly free from acetone; the chloracetone can be reconverted into acetone by reducing agents. Methyl alcohol purified in this way invariably contains some chlorinated impurities, which may be removed by heating under a reflux condenser with lime.

In order to obtain pure methyl alcohol, the oxalic or formic ester is prepared, and then decomposed by heating with water (Wöhler, Annalen, 81, 376), or ammonia (Grodzki and Krämer, Ber. 7, 1494). Methyl benzoate when heated with a solution of 1 part sodium hydroxide in 5 parts of water yields methyl alcohol (Carius, Annalen, 110, 210). Pure methyl alcohol may be prepared by treating 10 parts of commercial wood spirit with 1 part of iodine, and then adding caustic soda until the colour of the iodine disappears, and distilling (Regnault and Villejean, Bull. Soc. chim. [ii.] 42, 255). 100 c.c. of the crude spirit are digested with 150 grams of solid caustic soda, and afterwards distilled, 500 grams of oxalic acid are mixed with 200 c.c. of sulphuric acid, and then 400 c.c. of the purified alcohol are added, and the mixture is heated on the water-bath; the crystals of methyl oxalate are dried by pressure and saponified by heating with water at 70°. The distillate is then dehydrated by means of baryta, lime, and anhydrous copper sulphate (Dittmar and Fawsitt, Trans. Roy. Soc. Edin. 33, 509). Apparatus for the purification of wood spirit is best constructed of aluminium or an aluminium alloy free from copper. Copper heavily coated with tin, or iron or copper lined with earthenware may also be used with connecting pipes of earthenware. Air should be excluded as completely as possible as this oxidises the methyl alcohol to formaldehyde, acetaldehyde, and methylal, the reaction being readily catalysed by copper vessels. Aldehyde resin is likely to form in the still if the alkaline reagent has been added to the crude wood spirit (P. Pikos, J. Soc. Chem. Ind. 1909, 1118).

The following is a continuous method of preparing pure concentrated wood spirit. The crude spirit is distilled and the vapours passed first through lime water, then warm concentrated alkali solution (15°–20° Beaumé), afterwards washed with stearic or other fatty acid, and finally with alkali again. This treatment removes all aldehydic resins, higher alcohols, ketones, &c. (J. Farkas, D. R. P. 166360, 1904).

The purest anhydrous methyl alcohol is prepared from the best acetone free commercial article by first heating for some time with freshly burnt lime, then leaving in contact with ignited potassium carbonate for some weeks, and finally distilling several times from metallic calcium. The most accurate criterion of dryness is the esterification constant which, for the anhydrous alcohol and phenyl acetic acid, is 3·556. One-twentieth of a p.c. of water by volume lowers this to about 0·532 and ordinary pure dry methyl alcohol from methyl oxalate is often as low as 0·465 (J. Gyr, Ber. 1908, 4322).

Other processes are patented by Rosencrans (U.S. Pat. 793542, 1905); Chute (U.S. Pat. 824906, 1906); and Schmidt (U.S. Pat. 885183, 1908).

Detection and estimation.—The recognition of methyl alcohol itself is a somewhat difficult matter but its oxidation products, formaldehyde and formic acid, are more readily characterised. Of its compounds, the most characteristic is the *oxalate*, which is a crystalline solid melting at 54°. Mulliken and Scudder (Amer. Chem. J. 1899, 21, 266; 1900, 24, 444; J. Amer. Chem. Soc. 1905, 892), Barbet and Jandrier (Chem. Soc. Abstr. 1898, ii. 265), Jandrier (Chem. Zentr. 1899, i. 1296), Leach and Lythgoe (J. Amer. Chem. Soc. 1905, 964), Scudder and Riggs (*ibid.* 1906, 1202), Franz Utz (Chem. Zentr. 1905, ii. 1467), Hinkel (Analyst, 1908, 417), Voisenet (Bull. Soc. chim. 1906, [iii.] 35, 748), Trillat (Compt. rend. 1899, 127, 232), Vorisek (J. Soc. Chem. Ind. 1909, 823), and others have all made contributions to the vexed question of the most reliable test for methyl in the presence of ethyl alcohol. As an outcome, the following official test of the U.S. Pharmacopœia has been adopted for quantities of 2 p.c. and upwards: the liquid is diluted so as to contain about 10 p.c. total alcohols. About 3 c.c. is oxidised by plunging a red hot copper spiral five or six times into it while it is kept from boiling away by being surrounded by a beaker of cold water. It is then filtered and boiled till free from the smell of acetaldehyde, After cooling, 1 drop of 0·5 p.c. resorcinol is added and sulphuric acid poured into the test tube so as to form a layer. It is allowed to stand for 3 minutes and gently rotated. If no rose-red ring appears, methyl alcohol is below 2 p.c. Quantities from 2 p.c. down to 0·1 p.c. may be detected by fractionating 50 c.c. three times through a good fractionating head. The first two distillations should proceed till about 35 and 20 c.c. respectively in the case of a strong spirit, or 20 c.c. and 10 c.c. with a weak one, have passed over. The first 3 c.c. of the third distillation is tested as above.

The detection of methyl alcohol in the presence of formaldehyde necessitates first the removal of the formaldehyde. This may be done in several ways. Gnehm and Kaufler (Chem. Soc. Abstr. 1904, ii. 520; 1905, ii. 209) recommend combining it with sodium sulphanilate. Stritar (*ibid.* 1904, ii. 686) uses ammonia. Bamberger (*ibid.* 786) prefers sodium hydrogen sulphite. The best reagent for this purpose is probably potassium cyanide, as proposed by Leffmann (Chem. Zentr. 1905, ii. 1467). The methyl alcohol is subsequently distilled off and estimated by the sp.gr. of the distillate. *See* also Duyk (Chem. Soc. Abstr. 1902, ii. 110) and Blank and Finkenbeiner (Ber. 1906, 1326).

Table showing percentage of methyl alcohol in aqueous solutions at 15° (*Klason and Norton, Arkiv för Kemi Mineralogi och Geologi, vol.* 2, *No.* 27).

Sp.gr. 15°/15°	P.c. methyl alcohol by wt.	P.c. methyl alcohol by vol.
0·7964	100·00	100·00
0·7975	99·64	99·77
0·8000	98·75	99·18
0·8025	97·85	99·59
0·8050	96·96	98·01
0·8075	96·07	97·41
0·8100	95·18	96·80
0·8125	94·28	96·18
0·8150	93·39	95·55
0·8175	92·50	94·92
0·8200	91·60	94·28
0·8225	90·70	93·63
0·8250	89·80	92·98
0·8275	88·88	92·31
0·8300	87·97	91·64
0·8325	87·06	90·97
0·8350	86·16	90·29
0·8375	85·23	89·60
0·8400	84·29	88·88
0·8425	83·34	88·13
0·8450	82·39	87·40
0·8475	81·44	86·64
0·8500	80·47	85·88
0·8525	79·50	85·09
0·8550	78·51	84·27
0·8575	77·50	83·44
0·8600	76·50	82·61
0·8625	75·50	81·76
0·8650	74·49	80·89
0·8675	73·49	80·02
0·8700	72·48	79·13
0·8725	71·44	78·23
0·8750	70·38	77·31
0·8775	69·31	76·39
0·8800	68·25	75·43
0·8825	67·18	74·43
0·8850	66·09	73·41
0·8875	64·98	72·39
0·8900	63·86	71·34
0·8925	62·76	70·28
0·8950	61·65	69·23
0·8975	60·52	68·17
0·9000	59·36	67·09
0·9025	58·20	65·97
0·9050	57·01	64·82
0·9075	55·82	63·65
0·9100	54·64	62·46
0·9125	53·49	61·27
0·9150	52·31	60·04
0·9175	51·10	58·80
0·9200	49·84	57·54
0·9225	48·54	56·20
0·9250	47·20	54·79
0·9275	45·84	53·36
0·9300	44·49	51·92
0·9325	43·15	50·48
0·9350	41·79	49·01
0·9375	40·40	47·53
0·9400	39·00	45·94
0·9425	37·54	44·29
0·9450	36·03	42·66
0·9475	34·51	41·03
0·9500	32·95	39·35
0·9525	31·38	37·61
0·9550	29·79	35·81
0·9575	28·14	33·89
0·9600	26·44	31·82
0·9625	24·66	29·83
0·9650	22·89	27·83
0·9675	21·14	25·76
0·9700	19·38	23·67
0·9725	17·63	21·54
0·9750	15·85	19·40
0·9775	14·03	17·25
0·9800	12·27	15·12
0·9825	10·60	13·04
0·9850	8·94	11·03
0·9875	7·32	9·06
0·9900	5·72	7·13
0·9925	4·18	5·30
0·9950	3·01	3·84
0·9975	1·39	1·69
1·0000	0·00	0·00

For the estimation of methyl alcohol, in the absence of other materials than water, a reference to the table of sp.gr. is the most rapid method, but Zeisel's well-known methyl iodide method is very reliable. The latter is only interfered with by acetal or ethyl alcohol. In the presence of ethyl alcohol the most accurate method is that due to Thorpe and Holmes (Chem. Soc. Trans. 1904, 1), depending on the fact that when oxidised with dichromate and sulphuric acid, ethyl alcohol gives rise to acetic acid and a minute quantity (about 0·5 p.c.) of carbon dioxide, whilst methyl alcohol is completely oxidised, under the stipulated conditions, to carbon dioxide and water. The process is as follows: the sample is mixed with water in such proportion that 50 c.c. of the mixture shall contain not more than 1 gram of methyl alcohol, and in the presence of ethyl alcohol not more than 4 grams of the mixed alcohols. Fifty c.c. of this mixture are then introduced into the oxidation flask, 20 grams of potassium dichromate, and 80 c.c. of dilute sulphuric acid (1 : 4) added, and the mixture allowed to remain for 18 hours. A further quantity of 10 grams of potassium dichromate and 50 c.c. of sulphuric acid mixed with an equal volume of water are now added and the contents of the flask heated to boiling for about 10 minutes. The carbon dioxide is swept out by a current of air and collected in weighed soda-lime tubes. When ethyl alcohol is present, a subtractive correction of 0·1 gram of carbon dioxide for each gram of ethyl alcohol must be made. This method is of great convenience in determining the adulteration of tinctures and other medicinal preparations by methylated spirits.

Other substances yielding carbon dioxide in these circumstances are allyl alcohol, methyl acetate, and acetone. Ether and pyridine do not affect the estimation.

Properties.—A colourless liquid with an odour like that of ethyl alcohol; miscible with water in all proportions, and with contraction and evolution of heat (*v.* table). It burns with a blue flame. It possesses, like ethyl alcohol, remarkable solvent powers, dissolving most substances which are soluble in ethyl alcohol; consequently it may be used in many cases instead of that liquid.

Its vapour pressure at various temperatures is given in the following table (Dittmar and Fawsitt):—

Temperature	Vapour pressure	Temperature	Vapour pressure
°C	mm.	°C.	mm.
0°	29·7	40°	259·4
5°	40·2	45°	327·3
10°	53·8	50°	409·4
15°	71·4	55°	507·7
20°	94·0	60°	624·3
25°	122·7	65°	761·1
30°	158·9	64·96°	760·0
35°	203·9		

Anhydrous copper sulphate is slightly soluble in absolute methyl alcohol, yielding a bluish-green solution, hence it cannot be used as a test of the freedom of methyl alcohol from water (Kelpl, J. pr. Chem. [ii.] 25, 526). This blue solution deposits crystals of $CuSO_4,2CH_3OH$ (Forcrand, Compt. rend. 102, 551). Hydrated copper sulphate dissolves to the extent of 11·5 p.c. at 0° and the solution on standing deposits green rosettes of crystals having the composition $3CuSO_4{\cdot}CuO,4CH_3OH$ (Auger, *ibid.* 142, 1272). Methyl alcohol combines with many salts in a manner similar to water of crystallisation, *e.g.* $LiCl,3CH_3OH$; $MgCl_2,6CH_3OH$; $CaCl_2,4CH_3OH$, six-sided tables, decomposed by water, may be heated to 100° without decomposition (Kane, Phil. Mag. [iii.] 10, 45). A compound with barium oxide, $BaO,2CH_3OH,2H_2O$, is obtained in brilliant prisms, when BaO is dissolved in aqueous methyl alcohol, and the liquid evaporated at the ordinary temperature (Forcrand, Compt. rend. 102, 1557).

When passed over heated zinc, methyl alcohol yields carbon monoxide, hydrogen, and a small quantity of methane (Jahn, Ber. 13, 983). By the action of zinc chloride, hydrocarbons C_nH_{2n+2} are the chief products, also some hexamethyl benzene (Le Bel and Greene, J. 1878, 388). By electrolysis in presence of sulphuric acid, *methylal* $CH_2(OCH_3)_2$ is produced (Renard, Ann. Chim. Phys. [v.] 17, 290).

Methyl alcohol is not decomposed by *bacterium aceti.* Potassium or sodium liberates hydrogen and forms a methoxide; sodium methoxide $NaCH_3O$ combines at 160° with carbon monoxide to form sodium acetate.

Magnesium dissolves in methyl alcohol on gently heating, forming magnesium methoxide, which separates in pointed prisms from solutions containing about 6 grams in 40 of alcohol, or as an amorphous powder from more concentrated solutions. The crystals contain 3 molecules of methyl alcohol and effloresce rapidly. Bromine converts it into bromoform and magnesium bromide. Magnesium nitride reacts energetically with methyl alcohol forming trimethylamine, according to the equation:

$$Mg_3N_2+6CH_3OH =3Mg(OH)OCH_3+NH_3+N(CH_3)_3$$

(Szarvasy, Ber. 1897, 305, 806).

Chlorine acts on methyl alcohol readily if moist. In diffused daylight at 99·5° the chief product is formaldehyde, which probably results through the intermediate formation of chloromethyl alcohol CH_2ClOH, and dichloromethyl ether $(CH_2Cl)_2O$. The latter may actually be isolated. Carbon dioxide and carbon monoxide and also methyl chloride are continuously evolved during the reaction. If the alcohol is diluted with water the reaction proceeds with explosive violence. Bromine has but little action, but in sunlight at 130°–150° methyl bromide is formed, mixed with carbon monoxide and dioxide and formic acid if the bromine is not in excess.

Iodine is even more inert, but at 180°–200° hydrogen iodide, carbon dioxide, and methyl iodide are formed. The chief bulk of the alcohol is converted into methyl ether, which is also readily produced by heating the alcohol in sealed tubes with 5 p.c. of iodine (André Brochet, Compt. rend. 121, 130).

Cold methyl alcohol absorbs one molecular proportion of boron trifluoride forming *boron methoxy difluoride* $BF_2{\cdot}OCH_3$, crystallising in prisms melting at 41·5° and boiling at 87°. Sodium methoxide (1 mol.) readily converts this compound into *boron dimethoxy fluoride*

$$BF(OCH_3)_2$$

which is a colourless mobile liquid fuming in air, burning with a green flame, and boiling at 53°. It has a sp.gr. of 1·053 at 0°. Sodium methoxide changes this into *methyl borate* $B(OCH_3)_3$. Methyl borate boils at 55°–56° and has sp.gr. 0·919 at 0°. It burns with a green flame and is readily decomposed by moist air or water.

There is also formed by the action of boron trifluoride on methyl alcohol a molecular compound with methyl ether, $BF_3,O(CH_3)_2$. It boils at 126°–127° and dissociates at a slightly higher temperature. Sp.gr. at 0°=0·140. In addition an acid product of still higher boiling-point is produced to a small extent (V. Gasselin, Ann. Chim. Phys. [vii.] 3, 5).

The catalytic oxidation of methyl alcohol to formaldehyde is the subject of several papers by E. Orloff (J. Soc. Chem. Ind. 1908, 139, 419, 1176). Ozone oxidises methyl alcohol to formaldehyde very readily in 50 p.c. aqueous solution (Harries, Ber. 1903, 1933).

White phosphorus, when heated with methyl alcohol (1 mol.) for some hours at at least 250°, produces tetramethyl phosphonium hydroxide and, in addition, phosphines and phosphoric acid (J. Berthaud, Compt. rend. 143, 1166).

Methyl alcohol decomposes diazonium salts, forming, with benzene diazonium nitrate, anisole, *o*-nitrophenol, and 2 : 4-dinitrophenol. If water is present, *p*-nitrophenol is also formed. The alkoxy derivative only is produced from diazobenzenesulphate. Sodium methoxide in solution in methyl alcohol produces benzene and diphenyl (Beeson, Amer. Chem. J. 16, 235).

Impurities.—The impurities of commercial wood spirit are small quantities of aldehyde, dimethylacetal, allyl alcohol, acetone, methylethyl ketone, higher ketones, and chloroform.

Acetone is the most objectionable, especially when the alcohol is to be used in the preparation of aniline colours. In order to estimate the amount of acetone 1 c.c. of the wood spirit is mixed with 10 c.c. of a double normal solution of soda, and 10 c.c. of a double normal solution of iodine are added with constant shaking, and then 10 c.c. of absolute ether. The ethereal layer is then measured, an aliquot portion taken and evaporated on a watch-glass and the residual iodoform weighed. The weight of the iodoform (calculated to the total volume of ethereal solution) multiplied by 0·28 gives the amount of acetone in 1 c.c. of wood spirit (Kramer, Ber. 1880, 1002).

According to Messenger (Ber. 21, 3366), this method gives too high results if the quantity of acetone be small. The following method and details are due to Milan and Stritar (Zeitsch. anal. Chem. 1904, 387). *Crude wood spirit*: 5 c.c. are diluted to 500 c.c. and 5 c.c. of this mixture are submitted to Zeisel's process. The weight of silver iodide multiplied by 272·9 gives grams of methyl alcohol per 100 c.c. *Aqueous wood spirit* containing under 10 p.c. methyl alcohol: 10 c.c. are diluted to 50 c.c. and shaken for ¼ hour with 0·5 gram of charcoal, filtered, washed, and diluted to 100 c.c. and estimated as above. *Crude pyroligneous acid*: 50 c.c. are neutralised with sodium carbonate made up to 250 c.c. and filtered. 100 c.c. are then made strongly alkaline and distilled till 50 c.c. have collected. The distillate is treated with charcoal, &c., as above. The shaking with charcoal removes guaiacol and other phenol ethers, but the estimation is invalidated by the presence of acetal, methyl acetate, and allyl alcohol. A correction for these may be made by determining the iodine number and esterification number of the sample.

Methyl boride $B(CH_3)_3$, *bormethyl, trimethylborine*, V.D. 1·9108 (calc.=1·9314), a gas obtained from methyl borate by the action of zinc methyl (Frankland and Duppa, Annalen, 124, 129); has an intensely disagreeable smell, ignites spontaneously in the air; can be liquefied by a pressure of three atmospheres at 10°. Caustic potash absorbs the gas and yields, on evaporation, a viscid residue of $B(CH_3)_3{\cdot}KOH$. Ammonia forms a compound, $B(CH_3)_3{\cdot}NH_3$, which can be crystallised from ether in large crystals; m.p. 56°; b.p. 110°.

Methyl bromide CH_3Br, *bromomethane*; b.p. 4·5° (corr.) (Perkin, Chem. Soc. Trans. 1884, 454); sp.gr. 1·73306 at 0·8°/0·8°.

Preparation.—By heating the cacodyl compound, $As(CH_3)_2(OH)_2Br$ (Bunsen, Annalen, 46, 44); from methyl alcohol, bromine, and phosphorus (Pierre, Ann. Chim. Phys. [iii.] 15, 373). 133 grams red phosphorus, 800 grams methyl alcohol, are mixed in a retort, and 800 grams of bromine are gradually added; after some hours the mixture is distilled (Merrill, J. pr. Chem. [ii.] 18, 293).

Methyl bromide is a colourless mobile liquid with a smell resembling that of chloroform, unites with water to form a crystalline hydrate $CH_3Br,20H_2O$ (?) which is decomposed at 4° (Merrill).

For brominated compounds of methyl bromide, *v. Methylene bromide*, art. BROMOFORM; and *Carbon tetrabromide*, art. CARBON.

Methyl chloride CH_3Cl, *chloromethane*; b.p. −23·73° (Regnault); −21° (Berthelot); −23° (Vincent and Delachanal); sp.gr. 0·99145 at −23°; 0·95231 at 0° (Vincent and Delachanal, Bull. Soc. chim. [ii.] 31, 11). Vap. press. at 0°= 2·48 atmospheres, at 15°=4·11, at 30°=6·50 (Vincent and Delachanal).

Preparation.—From methyl alcohol, common salt and sulphuric acid (Dumas and Peligot, Annalen, 15, 17); from methane and chlorine (Berthelot, Ann. Chim. Phys. [iii.] 52, 97); by heating the cacodyl compounds

$$As(CH_3)_2(OH)_2Cl$$

or $As(CH_3)_2Cl$ (Bunsen, Annalen, 46, 44).

On the large scale by the dry distillation of 'vinasses' from beetroot. The methylamine is saturated with hydrochloric acid and concentrated, then heated to 260°–300°, when methyl chloride together with mono- and trimethylamine is evolved; the bases are removed by means of hydrochloric acid and the methyl chloride dried over calcium chloride and condensed by pressure in wrought-iron cylinders (Vincent and Delachanal, Bull. Soc. chim. [ii.] 31, 11; J. 1878, 1135). One part of melted zinc chloride is dissolved in two parts methyl alcohol and hydrogen chloride led into the mixture (Groves, Chem. Soc. Trans. 1874, 641).

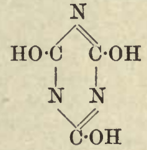
Properties.—Methyl chloride is a colourless gas with ethereal odour, and burns, when ignited in air, with a greenish flame. One part of water dissolves 4 volumes of methyl chloride; 1 of absolute alcohol, 35 volumes; and 1 of acetic acid, 40 volumes (Berthelot). The neutral solution is not precipitated by silver nitrate. With water at temperatures below 7·3° at 760 mm. it forms a solid hydrate $CH_3Cl,6H_2O$ (de Forcrand and Villard, Compt. rend. 106, 1402; Villard, Ann. Chim. Phys. [vii.] 11, 377). With chlorine in sunlight it yields methylene chloride (CH_2Cl_2), chloroform ($CHCl_3$), and finally carbon tetrachloride CCl_4 (*q.v.* art. CARBON); the chlorination can also be effected by leading a mixture of chlorine and methyl chloride over animal charcoal at 250°–350°.

Methylchloride forms with bromine methylene bromide, bromoform and carbon tetrabromide (Damoiseau, J. 1881, 376).

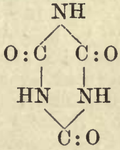
Methyl chloride is extensively used in the preparation of various coal-tar colours and also as a means of producing cold. By its evaporation a temperature of −23° is produced, or if the evaporation be accelerated by blowing in air −55° is easily reached, and since its vapour is non-poisonous, its superiority to liquid sulphur dioxide for this purpose is evident.

Methyl ***iso*****cyanate** $CH_3{\cdot}N:CO$, *methyl carbimide*; b.p. 43°–45° (Gautier, Annalen, 149, 313). Formed by the distillation of a mixture of 1 part of potassium cyanate with 2 parts of potassium methyl sulphate (Wurtz, Ann. Chim. Phys. [iii.] 42, 43); also by the action of diazomethane on nitro-urea (Degner and von Pechmann, Ber. 1897, 649). A liquid with intensely suffocating smell, converted by dry ammonia into methyl-urea $NH(CH_3)CO{\cdot}NH_2$ which forms prisms soluble in water. Water converts it into dimethyl-urea $NH(CH_3)CO{\cdot}NHCH_3$ with evolution of carbon dioxide.

Methyl cyanurates. Monomethyl, dimethyl, and trimethyl derivatives of both normal (I.) and *iso*cyanuric (II.) acids are known.



I.



II.

Normal trimethyl cyanurate $(NCOCH_3)_3$ is prepared from sodium methoxide and cyanogen chloride (Hofmann and Olshausen, Ber. 1870, 271). From dry sodium methoxide and cyanogen bromide (Ponomarew, *ibid.* 1885, 3264; Klason, J. pr. Chem. [ii.] 33, 131). Soluble in ether and water and crystallises in trimetric prisms melting at 135° and boiling at 265°. On long boiling it changes into the isomeride, melting at 175° (trimethyl *iso*cyanurate).

Normal dimethyl cyanurate $C_3N_3(OH)(OC_3H)_2$ results by heating 2 grams sodium in 15 grams absolute methyl alcohol and 15 grams normal trimethyl cyanurate to 100° for 1½ hours and decomposing the sodium salt with acetic acid (Hofmann, Ber. 1886, 2067). It forms small six-sided leaves soluble in alcohol and water but not ether. It softens at 165°–170° and decomposes on further heating into dimethyl *iso*cyanurate, m.p. 222° and also trimethyl *iso*cyanurate, m.p. 175°.

Trimethyl isocyanurate $C_3O_3N_3(CH)_3$ is produced together with the normal trimethyl ester from silver cyanurate and methyl iodide (Ponomarew, Ber. 1885, 3271); also from the silver salt of the dimethyl derivative and methyl iodide (Hofmann, *ibid.* 1886, 2096); also by the interaction of cyanuric acid and diazomethane (Palazzo and Scelsi, Gazz. chim, ital. 1908, 38, i. 659). Monoclinic prisms melting at 175°–176° and boiling at 274°. Soluble in alcohol but not in water.

Dimethyl isocyanurate $(CH_3)_2H(CNO)_3$ is obtained by the dry distillation of methyl acetyl urea (Hofmann, Ber. 1881, 2069); also from the normal dimethyl derivative (*v. supra*). Monoclinic, thin leaves from water melting at 222°.

Monomethyl isocyanurate

$(CH_3)H_2N_3C_3O_3,H_2O$

is prepared by heating nitrosocarbonyldimethylurea with water (Fischer and Frank, Ber. 1897, 2615). It forms thin leaves, readily dehydrated at 100°, melting at 296°–297°, and has an unpleasant odour. On methylation the trimethyl derivative is produced.

Mixed derivatives have been prepared by Hantzsch and Bauer (Ber. 1905, 38, 1005). The di-O-mono-N-derivative, m.p. 105°, is prepared by the interaction of silver cyanate and methyl iodide below 0°. The mono-O-di-N-derivative, m.p. 118°, is prepared from silver cyanurate and methyl iodide at low temperatures.

Methyl cyanide $CH_3{\cdot}CN$, *acetonitrile*; b.p. 81·6°; sp.gr. 0·8052 at 0°, 0·7891 at 15° (Vincent and Delachanal, Bull. Soc. chim. [ii.] 33, 405). H.C. at 18°=312·14 (Thomsen, Th. 4, 128) =291·6 (Berthelot and Petit, Compt. rend. 108, 1217).

From ammonium acetate and phosphorus pentoxide (Dumas, Compt. rend. 25, 383); from acetamide and phosphorus pentoxide; by distillation of potassium methyl sulphate with potassium cyanide (Dumas, Malaguti, and Leblanc, Annalen, 64, 333); in heating cyanacetic acid at 165° (Van 't Hoff, Ber. 1874, 1382); also by heating dimethyl sulphate with potassium cyanide (Walden, Ber. 40, 3214). It is also formed by the action of prussic acid on diazomethane (von Pechmann, *ibid.* 1895, 857); and by pouring acetic acid over magnesium nitride (Emmerling, *ibid.* 1896, 1635).

Preparation.—A mixture of 5 molecules of acetamide and 1 molecule of phosphorus pentasulphide is distilled, the product washed with caustic soda and digested with lead oxide (Henry, Annalen, 152, 149). By long heating of a mixture of acetamide and glacial acetic acid under a reflux condenser (Demarçay, Bull. Soc. chim. [ii.] 33, 456).

Acetonitrile is a colourless liquid with a pleasant ethereal smell, miscible with water, from which it separates on the addition of common salt. It burns in air with a peach-blossom flame; with acetic acid at 200° it produces diacetamide. It is miscible with methyl alcohol or with ethyl alcohol, and its b.p. is lowered by such admixture—a liquid containing 80 p.c. wood spirit and 20 p.c. acetonitrile has the lowest b.p. (63·7°), whilst, in the case of ethyl alcohol, a mixture of 56 p.c. spirits of wine and 44 p.c. acetonitrile boils at 72·6° (Vincent and Delachanal, Bull. Soc. chim. [ii.] 33, 405). It combines easily with dry hydrobromic or hydriodic acids, more difficultly with hydrochloric acid (Gautier, Annalen, 142, 291); by passing hydrogen chloride into a cooled mixture of acetonitrile and acetic acid, acetyl chloride and acetamide result (Colson, Bull. Soc. chim. [iii.] 17, 57). $CH_3CN{\cdot}2HBr$ forms crystals melting at 47°–50° (Engler, Annalen, 149, 306). Bromine combines with acetonitrile at 100° to form a compound—$CH_2Br{\cdot}CN{\cdot}HBr$—crystallising in prisms which melt at 65°, and are decomposed by moist air, forming ammonium bromide, acetic acid, and dibromodiacetamide (Engler, Annalen, 133, 137; 142, 69). Sulphur trioxide produces the compound $(CH_3CN)_2 2SO_3$, which crystallises and dissolves in water, but not in organic solvents. By precipitating its aqueous solution with alcohol and ether crystals of the composition $(CH_3CN)_3(SO_3)_2,H_2O$ are obtained (Eitner, Ber. 1893, 2834).

By the action of sodium upon methyl cyanide, methane and an oily substance $C_4H_6N_2$ soluble in ether (Holtzwart, J. pr. Chem. [ii.] 38, 343), sodium cyanide, and *cyanmethine* $C_6H_9N_3$ are obtained (Baeyer, Ber. 1869, 319). This is best obtained by heating 6 parts methyl cyanide with 1 part of sodium under a pressure of 100 mm., distilling off the excess of methyl cyanide and crystallising the residue from alcohol (Meyer, J. pr. Chem. [ii.] 27, 153). It forms monoclinic crystals (m.p. 180°–181°, which dissolve in 0·64 parts of water or 5·25 parts of alcohol at 18°. Cyanmethine unites with many acids, *e.g.* $C_6H_9N_3{\cdot}HCl$, needles soluble in water; b.p. 200°–250° $(C_6H_9N_3)_2H_2SO_4$, crystallises with difficulty. It also forms chlorine and bromine derivatives (Baeyer, Ber. 4, 176).

Substitution products of acetonitrile.

Chloracetonitrile $CH_2Cl{\cdot}CN$, from chloracetamide and phosphorus pentoxide (Bisschopinck, Ber. 6, 732); the reaction is better carried out in a vacuum (Scholl, *ibid.* 1896, 2417). A liquid; b.p. 123°–124°, sp.gr. 1·204 at 11·2°, 1·193 at 20° (Engler, *ibid.* 1873, 1003).

Dichloracetonitrile $CHCl_2{\cdot}CN$; b.p. 112°–113°; sp.gr. 1·374 at 11·4 (Bisschopinck, Ber. 6, 732).

Trichloracetonitrile $CCl_3{\cdot}CN$; b.p. 83°–84°, sp.gr. 1·439 at 12·2°. From trichloracetamide and phosphorus pentoxide (Bisschopinck, Ber. 6, 732). By action of chlorine upon acetonitrile in presence of iodine (Beckurts, *ibid.* 1876, 1594).

Bromacetonitrile $CH_2Br{\cdot}CN$, and *dibromacetonitrile* $CHBr_2{\cdot}CN$, m.p. 142°, are also known (*v.* Engler, Annalen, 142, 69, and Van 't Hoff, Ber. 1874, 1571; also Henry, Compt. rend. 103, 413).

Iodacetonitrile $CH_2I{\cdot}CN$; b.p. 186°–187°; sp.gr. 2·3065 at 12°; from chloracetonitrile and sodium iodide in alcoholic solution (Henry, Compt. rend. 103, 413).

Nitroacetonitrile $CH_2(NO_2)CN$ *v.* FULMINIC ACID.

Dinitroacetonitrile $CH(NO_2)_2CN$, a syrupy liquid obtained by the action of sulphuric acid upon the ammonia compound $CH(NO_2)_2CN{\cdot}NH_3$. This compound is obtained by the reduction of an ethereal solution of trinitroacetonitrile by means of dry sulphuretted hydrogen:

$$C(NO_2)_3CN+4H_2S$$
$$=CH(NO_2)_2CN{\cdot}NH_3+2H_2O+4S$$

(Schischkoff, Annalen, 101, 215; 119, 249; 104, 250).

Trinitroacetonitrile $C(NO_2)_3CN$, a solid, m.p. 41·5°; explodes when heated to 220°. Formed by the action of a mixture of fuming nitric and sulphuric acids upon sodium fulminate (Schischkoff, Ann. Chim. Phys. [iii.] 49, 310). Soluble in ether, but decomposed by alcohol, water, or alkalis.

Methyl *iso*cyanide $CH_3{\cdot}NC$, *iso-acetonitrile, methyl carbylamine*; b.p. 59·6°; sp.gr. 0·7557 at 14° (Gautier, Annalen, 152, 222). From methyl iodide and 2 molecules of silver cyanide at 130° (Gautier, Compt. rend. 65, 468); also from chloroform, methylamine, and alcoholic potash (Hofmann). It is also formed in small quantity when potassium methyl sulphate is distilled with potassium cyanide.

Methyl *iso*cyanide is a liquid with a very unpleasant smell; soluble in 10 parts of water at 15°; forms crystalline salts with acids.

Methyl fluoride CH_3F. A gas, sp.gr. $(H=1)$ 17·38, calc. = 17·05 (Collie, Chem. Soc. Trans. 1889, 110). Obtained from potassium methyl sulphate and potassium fluoride (Dumas and Péligot, Annalen, 15, 59); by the action of heat upon tetramethyl ammonium fluoride (Collie); from a mixture of methyl iodide and silver fluoride (Moissan and Meslans, Compt. rend. 107, 1153; Chem. Soc. Trans. 1889, 364). Liquefied by a pressure of 30 atmospheres at ordinary temperatures; slightly soluble in water, more so in methyl alcohol. It is very stable; critical temp. 44·9°; pressure 47123 mm. (Collie). Chlorine in sunlight displaces hydrogen and forms CH_2ClF, a gas soluble in water and of sp.gr. 34·18 (calc. = 34·25).

Methyl formamide $H{\cdot}CO{\cdot}NH(CH_3)$; b.p. 180°–185° (Gautier, J. 1869, 618); 190° (Linnemann, J. 1869, 601); sp.gr. 1·011 at 19°. A thick oily liquid soluble in water and alcohol, insoluble in ether, formed by the distillation of methylamine formate.

Methyl formate $H{\cdot}CO{\cdot}OCH_3$; b.p. 32°–32·5° (corr.) (Perkin, Chem. Soc. Trans. 1884, 491); Volhard, Annalen, 176, 133). Sp.gr. 0·98239 at 15°/15°

Preparation.—130 parts of methyl alcohol saturated with hydrogen chloride are gradually poured upon 100 parts of calcium formate; the mixture is then digested for some time, and finally distilled (Volhard, Annalen, 176, 133). A mixture of equivalent proportions of sodium formate, hydrochloric acid, and wood spirit may be used (Bardy and Bordet, Ann. Chim. Phys. [v.] 16, 561). Wood spirit is digested with formic acid, sp.gr. 1·22, and distilled; the distillate is then dehydrated by means of phosphorus pentoxide.

Methyl formate is a colourless liquid with a characteristic smell; its vapour is decomposed at a red heat, forming carbon monoxide and methyl alcohol. Chlorine in presence of sunlight yields *trichloro-methyl chloroformate* $Cl{\cdot}CO{\cdot}OCCl_3$, b.p. 127·5°–128°, sp.gr. 1·6525 at 14°, which, when heated at 340°–350°, yields the isomeric carbonyl chloride $COCl_2$ (Hentschel, J. pr. Chem. [ii.] 36, 99). If the action be stopped at an earlier stage, a compound $C_4H_3Cl_5O_4$, b.p. 108°–109°, sp.gr. 1·4741 at 27°/27°, is formed. In the absence of sunlight, chloroformic ester $Cl{\cdot}COOCH_3$ is produced immediately (Hentschel, J. pr. Chem. [ii.] 36, 213).

Methyl hydrate *v. Methyl alcohol.*

Methyl hydride, Methane, *marsh gas*, CH_4; sp.gr. 0·559 (air = 1); b.p. = −164·0° at 736·6 mm. (Olszewski, Ann. Chim. Phys. [ii.] 31, 58); sp.gr. of liquid = 0·415 (O.). H.F.p. = 21,750 cals.; H.F.v. = 21,170 cals.; H.C.p. 2 = 11,930 cals. (Thomsen, Th. 4, 50); H.C.p. = 213,500 cals. (Berthelot, Ann. Chim. Phys. [v.] 23, 179). 1 vol. of water at $t°$ absorbs $0{\cdot}05449-0{\cdot}001807t+0{\cdot}00001028t^2$ vols. of marsh gas, 1 vol. of alcohol at $t°$, $0{\cdot}522586-0{\cdot}0028655t+0000142t^2$ vols. (Bunsen).

Marsh gas is emitted from the surface of the ground in many parts of the world, notably in Italy, North America, and in the vicinity of the Caspian Sea. It is formed by the putrefaction of vegetable matter under water, and hence occurs in marshy places. It is evolved in large quantities from the mud volcanoes of Sicily, Italy, and the Crimea. It also occurs in the coal measures, and, in small quantities, in the gases of the human intestines (Ruge, J. 1862, 528), and in the breath of calves and sheep (Reiset, J. 1863, 638).

It is formed by the putrefaction of cellulose. According to Hoppe-Seyler, this is due to the action of a fungus (*Amylobacterium*, Van Tieghem, Compt. rend. 88, 205), and cellulose (sterilised filter-paper was used) is converted into a non-reducing sugar $C_6H_{12}O_6$, which splits up into $3CO_2$ and $3CH_4$; this action is stopped by a temperature above 60°.

Marsh gas is also produced by the destructive distillation of carbonaceous matter—*e.g.* wood or coal—and hence occurs, to the extent of about 40 p.c. by volume, in coal gas.

It can be obtained from chloroform or carbon tetrachloride by passing the vapour, mixed with hydrogen, through a hot tube, or by heating with copper, potassium iodide, and water (Berthelot, J. 1857, 267). Also by passing a mixture of the vapour of carbon disulphide and sulphuretted hydrogen over heated copper or iron (Berthelot, Ann. Chim. Phys. [iii.] 53, 69). Also by the action of the silent electrical discharge upon a mixture of hydrogen and carbon monoxide (Brodie, Proc. Roy. Soc. 21, 245), and by the direct combination of carbon and hydrogen at 1200° (Bone and Jerdan, Chem. Soc. Trans. 1897 42), and also by the action of water on aluminium carbide (Moissan, Bull. Soc. chim. [iii.] 11, 1012; 15, 1285).

Preparation.—By heating potassium acetate with caustic potash

$$KC_2H_3O_2+KOH=K_2CO_3+CH_4.$$

Sodium acetate and a mixture of equal volumes of calcined soda and powdered lime are heated in an iron or copper vessel (Schorlemmer, Chem. News, 29, 7), hydrogen and ethylene are also produced in this reaction (Kolbe); the latter may be removed by means of sulphuric acid.

It can also be obtained by the action of the copper-zinc couple upon a mixture of equal volumes of alcohol and methyl iodide (Gladstone and Tribe, Chem. Soc. Trans. 1884, 154). Pure methane is obtained by the decomposition of zinc methyl with alcohol or water.

Properties.—Methane is colourless and odourless, and forms an explosive mixture with air ('firedamp'). It is very stable, and is not affected by phosphorus pentoxide or antimony pentachloride, or even by strong nitric acid. Dry chlorine has no action in the dark, but in sunlight the mixture explodes; in diffused daylight chloro substitution derivatives are formed. When passed through a hot tube, a very small portion is converted into naphthalene, but the greater portion remains unaltered. It is very gradually absorbed by cold fuming sulphuric acid (Worstall, J. Amer. Chem. Soc. 1899, 246). It may be oxidised to methyl alcohol and formaldehyde (*see Methyl alcohol*).

It forms a hydrate with water at −2° or −3° under a pressure of 30 atmospheres. Tension of dissociation at 0° = 27·5 atmospheres; crit. temp. = 21·5° (Villard, Compt. rend. 107, 395).

Methyl iodide CH_3I; b.p. 42·3° corr. (Perkin, Chem. Soc. Trans. 1884, 459); 44·3° (Pierre, Annalen, 56, 147), sp.gr. 2·28517 at 15°/15° (P.); 2·2677 at 15° (Bardy and Bordet, Ann. Chim. Phys. [v.] 16, 569). Formed by the action of phosphorus and iodine upon methyl alcohol (Dumas and Péligot, Annalen, 15, 30).

Preparation.—In a similar manner to that of ethyl iodide (*q.v.*). 35 parts methyl alcohol, 100 parts iodine, and 10 parts of phosphorus are the proportions usually employed. These substances are allowed to remain in contact for some hours; the methyl iodide is then distilled off, washed with dilute caustic soda solution, and dried by means of calcium chloride. The preparation from an iodide of an alkali or alkaline earth by the action of methyl sulphate is patented by Weinland and Schmidt (D. R. P. 175209, 1905). A yield of 94 p.c. is obtained by dissolving yellow phosphorus in methyl iodide, and adding iodine to the liquid, and slowly dropping methyl alcohol into the cooled mixture (Walker and Johnson, Chem. Soc. Trans. 1905, 1595).

It forms a colourless liquid which turns brown on exposure to light owing to the liberation of iodine. It is extensively used in the preparation of various aniline colours owing to the ease with which it undergoes decomposition; it thus affords a ready means of introducing the methyl group into other compounds.

Methyl nitrate CH_3NO_3; b.p. 65°; sp.gr. 1·2167 at 15°/15° (Perkin, Chem. Soc. Trans. 1884, 682).

Preparation.—200 c.c. pure wood spirit are distilled with 40 grams urea nitrate and 150 c.c. pure nitric acid (sp.gr. 1·31) until two-thirds have distilled off; to the residue 170 c.c. of methyl alcohol and 130 c.c. nitric acid are added, again distilled, and then 150 c.c. methyl alcohol, 110 c.c. nitric acid, and 10 grams urea nitrate are added to the residue, and distillation again continued (C. Lea, J. 1862, 387).

Can also be prepared by mixing methyl alcohol and sulphuric acid, and adding 2 parts of this liquid to a mixture of 1 part nitric acid and 2 parts sulphuric acid. The distillate is washed with potassium carbonate solution. Delépine recommends the following. A mixture of 50 c.c. strong sulphuric acid and 150 c.c. methyl alcohol cooled to 12° are carefully added to a mixture of 100 c.c. strong sulphuric acid and 150 c.c. nitric acid (36°), cooled to 12°, so that the temperature does not rise above 15°. Afterwards the whole is shaken with 100 c.c. strong sulphuric acid. After a few minutes' standing the ester is separated off (Bull. Soc. chim. [iii.] 13, 1044).

Methyl nitrate is a colourless liquid with a pleasant smell; explodes when heated to 150°, or by percussion.

Methyl nitrite CH_3NO_2; b.p. −12°; sp.gr. of liquid 0·991 at 15°/. A gas, prepared by treating 1 molecule methyl alcohol with 1 molecule *iso*amyl nitrite (Bertoni, Gazz. chim. ital. 12, 438). Also by the action of nitric acid upon copper (or arsenious acid) and methyl alcohol, or by the action of nitric acid upon brucine (Strecker, Annalen, 91, 76).

Methyl oxalate $(CH_3)_2C_2O_4$; m.p. 54°; b.p. 163·3° corr. (Weger, Annalen, 221, 86). Oxalic acid (dried at 100°) is mixed with boiling methyl alcohol, and on cooling the crystals separate out (Erlenmeyer, J. 1874, 572).

Forms monoclinic plates, which, by action of chlorine yield, first, an oily liquid of the composition $C_2O_4(CHCl_2)_2$ (Malaguti, Annalen, 32, 49), and by prolonged action in sunlight, a body $C_2O_4(CCl_3)_2$, which crystallises in leaflets (Cahours, *ibid.* 64, 313).

Methyl hydrogen oxalate $H(CH_3)C_2O_4$. When oxalic ethyl ester is treated in methyl alcoholic solution with potassium methoxide, potassium methyl oxalate is thrown out in the form of fine leaves (Salomon, Ber. 8, 1509). Methyl hydrogen oxalate is a solid of low melting-point which boils at 108°–109°/ 12 mm. (Anschütz and Schönfeld, Ber. 19, 1442).

Methyl oxide, Dimethyl ether $(CH_3)_2O$,; b.p. −23·65° (Regnault, J. 1863, 70); −21° (Berthelot); sp.gr. (air=1) 1·617.

Formed by heating methyl alcohol with sulphuric acid (Dumas and Péligot, Ann. Chim. Phys. [ii.] 58, 19), or with boron trioxide (Ebelmen, *ibid.* [iii.] 16, 138; Annalen, 57, 328).

1·3 parts of wood alcohol are mixed with 2 parts of sulphuric acid, and heated to 140°. The gas evolved is passed into strong sulphuric acid, which absorbs 600 times its volume; the gas is then set free by diluting the acid with an equal volume of water (Erlenmeyer and Kriechbaumer, Ber. 1874, 699).

Methyl ether is a colourless gas with a pleasant odour; 1 vol. of water at 18° absorbs 37 volumes of the gas (Dumas and Péligot). It unites with hydrochloric acid to form a compound $(CH_3)_2O{\cdot}HCl$, which boils at 2° (Friedel, Bull. Soc. chim. [ii.] 24, 160, 241).

Chlorine Substitution Products.

Chlormethyl ether $CH_2Cl{\cdot}O{\cdot}CH_3$; b.p. 59·5° at 759 mm.; formed by bringing together, in diffused daylight, chlorine and excess of methyl oxide (Friedel, Bull. Soc. chim. [ii.] 28, 171). It is decomposed by water into hydrochloric acid, trioxymethylene $(CH_2O)_3$ and methyl alcohol.

Dichlormethyl ether $(CH_2{\cdot}Cl)_2O$; b.p. 105°; sp.gr. 1·315 at 20°; formed by the action of chlorine upon methyl oxide (Regnault, Annalen, 34, 31).

Tetrachlormethyl ether $(CHCl_2)_2O$; b.p. 130°; sp.gr. 1·606 at 20° (Regnault).

Perchlormethyl ether $(CCl_3)_2O$; b.p. 100° (with decomposition); sp.gr.=1·597; by the action of chlorine upon methyl oxide in sunlight (Regnault). Decomposed by heat, yielding carbon tetrachloride and carbonyl chloride. (*See also* de Sonay, Ber. 1894, Ref. 337.)

Methyl phosphates.

1. *Normal methyl phosphate* $(CH_3)_3PO_4$; b.p. 197·2° (corr.); sp.gr. 1·2378 at 0° (Weger, Annalen, 221, 89). From methyl iodide and silver phosphate (Hall, Chem. Soc. Trans. 51, 754).

2. *Dimethyl phosphoric acid* $(CH_3)_2HPO_4$; a syrupy liquid, produced when phosphoryl chloride $POCl_3$ is dropped into methyl alcohol (Schiff, Annalen, 102, 234). The salts are very soluble in water.

3. *Monomethyl phosphoric acid* $CH_3H_2PO_4$ is produced when methyl alcohol is dropped into phosphoryl chloride (Schiff, Annalen, 102, 337).

Methyl phosphites.

Monomethyl phosphite $CH_3H_2PO_3$, a syrupy liquid formed by the action of phosphorus trichloride upon methyl alcohol (Schiff, Annalen, 103, 164). It is miscible with ether, and forms salts which are amorphous, and decomposed by water into methyl alcohol and phosphites.

Trimethyl phosphite $P(OCH_3)_3$ is a liquid boiling with partial decomposition at 185°. It is prepared by the action of phosphorus trichloride on sodium methoxide. Sp.gr. 1·1785 at 15° (Jaehne, Annalen, 256, 281).

Methyl sulphates.

1. *Hydrogen methyl sulphate, methyl sulphuric acid* CH_3HSO_4. The free acid is an oily body, which remains liquid at $-30°$. Obtained from methyl alcohol and sulphuric acid (Dumas and Péligot, Annalen, 15, 40), or from methyl alcohol and chlorsulphonic acid in the cold (Claesson, J. pr. Chem. [ii.] 19, 240).

Preparation.—One part of methyl alcohol is mixed with two parts of concentrated sulphuric acid, allowed to stand in a warm place for some hours, diluted with water and neutralised with barium carbonate, filtered and the barium precipitated by the proper quantity of sulphuric acid. Methyl sulphuric acid forms salts with the metals, which are soluble and readily crystallise. On distillation it decomposes into dimethyl sulphate and sulphuric acid (Claesson).

Chloride of methyl sulphuric acid CH_3SO_3Cl. *Methyl chlorosulphonate* is obtained by dropping methyl alcohol into sulphuryl chloride in molecular proportions (Behrend, J. pr. Chem. [ii.] 15, 32), or by passing sulphur dioxide into methyl hypochlorite (Sandmeyer, Ber. 1886, 861). It is an oily liquid with pungent smell; decomposed by water into methyl sulphuric and hydrochloric acids.

2. *Dimethyl sulphate* $(CH_3)_2SO_4$; b.p. 188°; sp.gr. 1·33344 at 15° (Perkin, Chem. Soc. Trans. 1886, 785). By distilling wood spirit with 8 or 10 parts of sulphuric acid (Dumas and Péligot, Ann. Chim. Phys. [iii.] 58, 54) or by distilling anhydrous methyl sulphuric acid, best *in vacuô* (Claesson, J. pr. Chem. [ii.] 19, 244). Methyl sulphate is best prepared by bringing together methyl alcohol (27 grams) and chlorsulphonic acid (100 grams) at $-10°$ and then distilling the mixture under 20 mm. pressure at 140°. The yield is 80–83 p.c. theoretical. Nordhausen sulphuric acid gives a yield of only 42 p.c. (D. R. P. 113239). The Société Anonyme des Produits Chimiques de Fontaines in Lyon-Monplaisir uses practically the same process with carbon tetrachloride as a diluent (D. R. P. 193830). It is extensively used as a methylating agent for aromatic amines, the reaction being:

$$Me_2SO_4+2R{\cdot}NH_2=RNH_2{\cdot}MeHSO_4+R{\cdot}NHMe$$

(Ullmann, Annalen, 327, 103), *cf.* however, Claesson and Lundvall (Ber. 13, 1699). Quinoline and quinaldine are both quantitatively converted into their ammonium bases by treatment with methyl sulphate in benzene solution (Ullmann, *l.c.*). It is also a very convenient reagent for esterifying acids (Carl Graebe, *ibid.* 344, 244). On distillation under reduced pressure of the products obtained by the action of methyl sulphate on alcoholic solutions of sodium penta-, tetra-, or tri-sulphide *methyl trisulphide*, Me_2S_3, has been obtained by Strecker (Ber. 1908, 1105. *Cp.* also Klason, Chem. Soc. Abstr. 1888, 356). A colourless liquid with odour like that of peppermint.

Methyl sulphides.

1. *Hydrogen methyl sulphide, methyl mercaptan, methyl sulphydrate,* CH_3SH (Gregory, Annalen, 15, 239); b.p. 5·8° at 752 mm. (Klason, Ber. 20, 3407). By heating potassium hydrogen sulphide with potassium methyl sulphate (Dumas and Péligot). It is a colourless liquid with a disagreeable odour and forms a crystalline hydrate with water. By the action of chlorine upon carbon disulphide containing a little iodine, *Perchlormethyl mercaptan* CCl_3ClS, a liquid (b.p. 146°–148° corr.; sp.gr. 0°1·712 at 12·8°) is obtained (Rathke, Annalen, 167, 195). This substance is decomposed by heating to 200° into carbon tetrachloride and sulphur chloride.

2. *Dimethyl sulphide* $(CH_3)_2S$; b.p. 37·1°–37·3° at 754·7 mm. (Beckmann, J. pr. Chem. [ii.] 17, 453); b.p. 37·2° at 758 mm. (Klason, Ber. 20, 3407). Sp.gr. 0·845 at 21° (Regnault, Annalen, 34, 26). From potassium sulphide and methyl chloride (Regnault, Ann. Chim. Phys. [ii.] 71, 391).

Preparation.—500 c.c. methyl alcohol are treated with 750 c.c. sulphuric acid, and a solution of 2·75 kilos. sodium carbonate (crystals) is added, and the solution concentrated until the sodium sulphate crystallises out. To the solution of sodium methyl sulphate 500 grams of potash dissolved in water and half saturated with sulphuretted hydrogen are added. The yield is about 150 grams (Klason, Ber. 1887, 3407; Chem. Soc. Trans. 1888, 356). Methyl sulphide is a colourless liquid with an unpleasant smell. It combines directly with chlorine to form oily substitution products $(CH_2Cl)_2S$, $(CHCl_2)_2S$, and $(CCl_3)_2S$ (Riche, Ann. Chim. Phys. [iii.] 43, 283). Bromine unites with it to form a crystalline bromide $(CH_3)_2SBr_2$ (Cahours, Annalen, 135, 355). It also forms many crystalline compounds with various salts, *e.g.*

$$(CH_3)_2S{\cdot}HgCl_2;$$

$2(CH_3)_2S{\cdot}PtCl_4)$, &c. (Loir, Ann. Chim. Phys. [iii.] 39, 448; 54, 42). It combines at ordinary temperatures with methyl iodide to form *trimethyl sulphine iodide* $(CH_3)_3SI$, which crystallises in prisms.

By the action of moist silver oxide upon this compound there is formed *trimethyl sulphine hydroxide* $(CH_3)_3S{\cdot}OH$, an oily liquid which possesses strongly basic properties and forms characteristic salts with the acids. Sulphuretted hydrogen reacts with the base, yielding the *hydrosulphide* $[(CH_3)_3S]SH$, which on treating with one molecular proportion of the hydroxide yields the *normal sulphide* $[(CH_3)_3S]_2S$, which resembles in its reactions the sulphides of the alkalis (Brown and Blackie, Chem. News, 37, 130; 39, 51).

Methyl trisulphide $(CH_3)_2S_3$ has been prepared by Strecker (*see* above *Dimethyl sulphate*).

Methyl sulphite $(CH_3)_2SO_3$ or $SO(OCH_3)_2$; b.p. 121·5°; sp.gr. 1·0456 at 16·2°/4°. Obtained from methyl alcohol and sulphur chloride S_2Cl_2 (Carius, Annalen, 110, 209; 111, 96). Is isomeric with ethyl sulphurous acid $OH{\cdot}SO{\cdot}OC_2H_5$, and ethyl sulphonic acid $C_2H_5SO_2{\cdot}OH$.

Methyl sulphonic acid $CH_3SO_2{\cdot}OH$, a syrupy liquid decomposed at about 130°. By the action of nitric acid upon methyl thiocyanate or disulphide (Muspratt, Annalen, 65, 261). Also by heating methyl iodide with sodium sulphite solution to 120° (Collmann, *ibid.* 148, 105), and by the reduction of trichloromethane sulphonic acid (Kolbe, *ibid.* 54, 174), and also by the action of chloride of lime on methyl thiocyanate (de Coninck, Compt. rend. 126, 828). It forms stable crystalline salts which are very soluble in cold water but almost insoluble in alcohol. The potassium compound $CH_3\cdot SO_2\cdot OK$, is decomposed by heating with caustic potash—

$$CH_3\cdot SO_2OK+3KOH=3H_2+K_2CO_3+K_2SO_3$$

(Berthelot, J. 1869, 336).

Methyl sulphonic chloride $CH_3\cdot SO_2Cl$; b.p. 150°–153° (Carius); 160° (Nithack); sp.gr. 1·51 (Gowan, J. pr. Chem. [ii.] 30, 281). By the action of phosphorus pentachloride upon methyl sulphonic acid (Carius, Annalen, 114, 142). It is not acted upon by sulphuretted hydrogen or potassium cyanide in alcoholic solution. Ammonia forms an amide

$$CH_3\cdot SO_2\cdot NH_2$$

which crystallises in long prisms (Gowan, *l.c.*, also Chem. Soc. Trans. 48, 367).

Chlormethyl sulphonic acid $CH_2Cl\cdot SO_2\cdot OH$, an acid syrup obtained by the action of nascent hydrogen upon trichlormethyl sulphonic acid (Kolbe, Annalen, 54, 168).

Dichlormethyl sulphonic acid $CHCl_2\cdot SO_2\cdot OH$, an unstable body formed by the action of zinc upon trichlormethyl sulphonic acid (Kolbe, Annalen, 54, 164); also by heating chloroform with a solution of potassium sulphite to 180° (Strecker, *ibid.* 148, 92). The *chloride*

$$CHCl_2\cdot SO_2Cl$$

(b.p. 170°–180°, sp.gr. 1·71) is formed by the action of phosphorus pentachloride upon the acid (Gowan, J. pr. Chem. [ii.] 30, 399), or by reducing, by means of sulphur dioxide or stannous chloride, trichlormethyl sulphonic chloride (Kolbe).

Trichlormethyl sulphonic acid

$$CCl_3\cdot SO_2\cdot OH,H_2O;$$

m.p. 130°. The free acid is obtained from the chloride by treatment with baryta, and precipitation of the dissolved barium by means of sulphuric acid, the excess of sulphuric acid is then removed by means of lead carbonate and excess of lead by means of sulphuretted hydrogen (Gowan, J. pr. Chem. [ii.] 30, 284).

It forms small prisms which are very stable and insoluble in water, but soluble in alcohol or ether. It has strong acid properties and is not affected by nitric acid, aqua regia, or chromic trioxide.

Trichlormethyl sulphonic chloride $CCl_3\cdot SO_2Cl$ (m.p. 135°, b.p. 170°) forms camphorlike crystals, and is obtained by the action of moist chlorine upon carbon disulphide (Berzelius and Marcet, Gilbert's Annalen, 48, 161). Bassett (Chem. News, 54, 79) recommends the following process: 100 grams of powdered potassium chlorate, 200 c.c. hydrochloric acid, 400 c.c. water and 50 c.c. carbon disulphide are mixed together and allowed to stand for some days until the carbon disulphide becomes solid; the white solid is then removed by filtration and washed; the yield is 63 grams. It is very stable and reacts with difficulty or not at all with aromatic amines. With secondary and tertiary organic bases it yields colouring matters. It also oxidises leuco bases and their sulphonic acids to colouring matters (Espenschied, D. R. P. 14621).

Methyl thiocyanate $CH_3\cdot S\cdot CN$; b.p. 132·9° at 757·2 mm.; sp.gr. 1·088 at 0° (Pierre, J. 1851, 51). H.C.=398·95 cals. (Thomsen, Th. 4, 196). By heating methyl sulphide with cyanogen bromide to 100° (Cahours, J. 1875, 257). By distilling a concentrated solution of equal parts of potassium thiocyanate and calcium methyl sulphate (Cahours, Annalen, 61, 95). Calcium methyl sulphate may be replaced with advantage by methyl sulphate in theoretical proportions.

If heated to 180°–185° it is partially converted into the *iso*thiocyanate. By the action of chlorine in daylight cyanuric chloride $Cl_3(CN)_3$, thiocarbonyl chloride $CSCl_2$ and thiocarbonyl tetrachloride $CSCl_4$ are obtained (James, Chem. Soc. Trans. 51, 272). By heating with methyl iodide to 100° trimethyl sulphine iodide $(CH_3)_3SI$ is produced (Cahours, J. 1875, 257).

Methyl *iso*thiocyanate $CH_3\cdot NCS$, *methyl mustard oil*; m.p. 34°; b.p. 119° (Hofmann, Ber. 1, 172). By heating the silver salt of methyl thiocarbamic acid $CS(NH\cdot CH_3)SH$ with water. This acid is formed by the action of carbon disulphide upon methylamine. Methyl mustard oil forms white crystals which have a smell resembling that of horseradish.

Methyl selenide $(CH_3)_2Se$; b.p. 58·2°. Obtained by distilling a solution of sodium selenide (prepared from phosphorus pentaselenide and caustic soda), with potassium methyl sulphate (Jackson, Annalen, 179, 1). A disagreeably smelling liquid; with platinum tetrachloride forms a yellow compound $2(CH_3)_2Se\cdot PtCl_4$, soluble in alcohol. It also unites with chlorine and bromine $(CH_3)_2SeCl_2$, m.p. 59·5°; $(CH_3)_2SeBr_2$, m.p. 82°.

Methyl diselenide $(CH_3)_2Se_2$, a heavy, reddish yellow liquid with very unpleasant odour, formed when potassium diselenide is heated with potassium methyl sulphate (Wöhler and Dean, Annalen, 97, 5; Rathke, *ibid.* 152, 211).

METHYLAMINES.

These are compounds with strongly marked basic properties, derived from ammonia by the replacement of one, two, or three atoms of hydrogen by an equal number of methyl groups.

Methylamine $(CH_3)NH_2$, *monomethylamine*; b.p. −6° to −5·5° at 768·35 mm., sp.gr. 0·699 at −10·8° (Hofmann, Ber. 22, 699).

Occurrence.—In the oil yielded by the dry distillation of bone (Anderson, Annalen, 88, 44). In the plants *Mercurialis annua* (Linn.) and *M. perennis* (Linn.) (Reichardt, J. 1865, 457). In herring brine (Tollens, Zeitsch. Chem. 1866, 516) and in the products of the putrefaction of fish. In crude wood spirit (Commaille, J. 1873, 686; Vincent, Ann. Chim. Phys. [v.] 1, 444). In the products of the dry distillation of the residues from beet-sugar 'vinasses' (Duvillier and Buisine, Ann. Chim. Phys. [v.] 23, 317).

In the products of distillation of bran with lye (Laycock, Chem. News, 1898, 78, 210, 223). In the products yielded by the decomposition of fibrin by *streptococci* (Emmerling, Ber. 1897, 30, 1863).

Formation.—By the action of caustic potash upon methyl *iso*cyanate or *iso*cyanurate (Wurtz, Ann. Chim. Phys. [iii.] 30, 443). From ammonia and methyl iodide (Hofmann, Phil. Trans. 1851, 381) or methyl nitrate (C. Lea, Chem. News, 6, 46; Juncadella, Compt. rend. 48, 342). By heating wood spirit with sal ammoniac to 300° (Berthelot, Ann. Chim. Phys. [iii.] 38, 69).

By heating caustic potash with certain alkaloids—*e.g.* morphine, codeïne, creatine, &c. (Wertheim, Annalen, 73, 210; Dessaignes, J. 1855, 331). By the action of chlorine upon caffeïne or theobromine (Rochleder, J. 1850, 435). By the action of nascent hydrogen, from zinc and sulphuric acid, upon hydrocyanic acid (Mendius, Annalen, 121, 139). By passing a stream of hydrogen and hydrocyanic acid gas over platinum black, heated to 110° (Debus, Chem. Soc. Trans. 16, 249).

By the reduction of hexamethylene tetramine with zinc dust and hydrochloric acid (D. R. P. 73812); of formamide with sodium in amyl alcohol solution (Guerbet, Bull. Soc. chim. [iii.] 21, 780); or of nitromethane electrolytically in sulphuric acid solution at 70°–75° (Pierron, *ibid.* 783).

Preparation.—Equal molecules of methyl nitrate and ammonia dissolved in methyl alcohol are heated to 100°. The product is decomposed by caustic soda, and the base combined with hydrochloric acid, the dried chloride is then heated with caustic soda, and the liberated methylamine passed into sulphuric acid, the sulphate is dried at 110° and treated with absolute alcohol in which the di- and tri-methylamine salts are soluble; the insoluble monomethylamine sulphate is then decomposed by potash, and the free methylamine passed into a cooled solution of ethyl oxalate. The resulting di-methyl oxamide is dissolved in hot water, filtered and recrystallised, then decomposed by caustic potash, and the gas passed into absolute alcohol (Duvillier and Buisine, Ann. Chim. Phys. [v.] 23, 324; *v.* also Muller, Bull. Soc. chim. [ii.] 42, 202; Chem. Soc. Trans. 48, 501).

It can also be prepared by the interaction of acetamide and bromine in caustic potash solution (Hofmann, Ber. 1882, 15, 765; 1885, 18, 2741; François, Compt. rend. 1908, 147, 680). By heating phosphorus with excess of methyl alcohol solution under pressure at 225° (D. R. P. 64346), or by heating formaldehyde with ammonium chloride at 40°–95°.

Methylamine can be prepared electrolytically, cheaply and conveniently, according to the following process: An electrolytic cell, provided with a diaphragm separating the cathode and anode, is filled with a solution of sodium sulphate, and 140 grams hexamethylene tetramine is added. The electrolysis is carried out by means of lead electrodes and a current of 3 amperes per square decimetre. The alkali formed at the cathode is neutralised by the careful addition, drop by drop, of dilute sulphuric acid. The temperature must be kept at about 20°. Methylamine and trimethylamine are thus formed, and can be separated in the ordinary way. Ammonium sulphate can replace the sodium sulphate (D. R. P. 148054; Frdl. 1902–04, 26; *see* also D. R. P. 143197; Frdl. 1902–04, 25).

Commercial methyl sulphate is added in small portions at a time to excess of a 10 p.c. aqueous solution of ammonia at −5°. The product is then added to an excess of a 30 p.c. aqueous solution of sodium hydroxide, and the mixture is distilled, the issuing gas being collected in 20 p.c. hydrochloric acid. The methylamine hydrochloride is separated from the ammonium chloride by fractional crystallisation, and is finally purified by recrystallisation from alcohol (Burmann, Bull. Soc. chim. 1906, [iii.] 35, 801).

According to Bertheaume (*ibid.* 1908, 146, 1215) this method of separation is of very little use (Fleck, J. Amer. chem. Soc. 1896, 18, 670).

A better method of separating the three amines than the one given above, is to treat the concentrated solution of their hydrochlorides with caustic soda and collect the gas evolved in formaldehyde. The liquid is now treated with an equal weight of caustic potash, whereby the greater part of the trimethylamine is evolved, whilst the methylene derivatives of mono- and di-methylamine remain in solution, and can be fractionated by distillation. The amines are regenerated by boiling the condensation products with alcoholic hydrochloric acid (Delépine, Compt. rend. 1896, 122, 1064; Ann. Chim. Phys. 1896, [vii.] 8, 439).

Methylamine may be separated from ammonia by shaking the aqueous mixture of the two substances with yellow mercuric oxide during an hour. The liquor is then decanted and distilled when pure methylamine is obtained, providing no other nitrogenous bases are present in the impure liquor (François, J. Pharm. Chim. 1907, 25, 517, 523; Compt. rend. 1907, 144, 567; *ibid.* 1908, 147, 428).

To distinguish the three amines from ammonia the solution is neutralised with hydrochloric acid and evaporated to dryness. The residue is dissolved in 95 p.c. alcohol, and 5 c.c. of the solution is heated at 70°–75° with a few grammes of tetrachlorobenzoquinone. If any of the amines are present a violet colouration is produced, whereas ammonia gives no colouration (Tsalapatini, Chem. Zentr. 1908, i. 299). For the detection and estimation of ammonia in the methylamines, *see* François (Compt. rend. 1907, 144, 857). Methylamine can be distinguished from the di- and tri-amines by treatment with Nessler's reagent, with which it gives a yellow precipitate insoluble in excess of water and reagent. The other two amines form a white precipitate, which disappears on addition of water (Delépine, Compt. rend. 1896, 122, 1272).

Properties.—Methylamine is a colourless gas with a strong ammoniacal smell. It is very inflammable and burns with a yellow flame; it is decomposed at a red heat into ammonia hydrocyanic acid, hydrogen, and marsh gas. It is very soluble in water, 1 volume of water at 12·5° dissolving 1150 volumes and 959 volumes at 25°. The solution behaves like *liquor ammoniæ* and yields crystallisable salts on neutralisation with acids.

Heat of neutralisation with hydrochloric acid =25·9 cals. (Muller, Ann. Chim. Phys. 1888, [vi.] 15, 517). For salts of methylamine, which, as a rule, resemble those of ammonia, *v.* Wurtz, *ibid.* [iii.] 30, 443; Topsoë, J. 1883, 618; Bailey, Chem. Soc. Trans. 45, 692; Petit and Polonowsky, Bull. Soc. chim. [iii.] 9, 1013; Brochet and Cambier, *ibid.* 13, 536; Jarry, Compt. rend. 1897, 124, 964; Cook, Amer. Chem. J. 1899, 22, 437; Ragland, *ibid.* 417; Lenher, J. Amer. Chem. Soc. 1898, 20, 572; Dunstan and Goulding, Chem. Soc. Trans. 1897, 579; Ladenburg, Ber. 1896, 29, 2711; Wende, *ibid.* 2719; Ristenpart, *ibid.* 2530; Partheil and Broich, *ibid.* 1897, 30, 618; Fenner and Tafel, *ibid.* 32, 3228; Delépine, Ann. Chim. Phys. [vii.] 8, 461; Compt. rend. 1896, 122, 1272; Hofmann and Marburg, Annalen, 1899, 305, 191; Lang, Chem. Soc. Trans. 1903, 724; Rengade, Compt. rend. 1905, 140, 246; François, *ibid.* 1906, 142, 1199; Litterschild, Arch. Pharm. 1904, 242, 37; Guareschi, Chem. Zentr. 1891, ii. 620; Christensen, J. pr. Chem. [ii.] 45, 356; Gutbier and Woernle, Ber. 1906, 39, 4134.

Methylamine, like ammonia, in aqueous solution precipitates metallic hydroxides from solutions of many salts; but, unlike ammonia, dissolves, when in excess, the hydroxide of aluminium, whereas it fails to dissolve the hydroxides of cadmium, nickel, and cobalt.

When methylamine is oxidised with monopersulphuric acid (Caro's acid), according to Bamberger and Seligman, it undergoes the following changes

$$CH_3NH_2 \rightarrow CH_3{\cdot}NH{\cdot}OH \rightarrow CH_2{:}NOH \rightarrow \text{either}$$
$$OH{\cdot}CH{:}NOH \text{ or } CH_2NH{\cdot}OH \rightarrow CH_3NO_2,$$

hydrogen cyanide also being formed (Ber. 1902, 35, 4299). Unlike the di- and tri-amines, it is readily decomposed by chromic acid with evolution of nitrogen (Coninck and Combe, Compt. rend. 1898, 127, 1221; 128, 682).

Methylamine interacts with cyanogen chloride in cold ethereal solution forming principally *s*-dimethylguanidine hydrochloride and also methylcyanamide (Kaess and Gruszkiewicz, Ber. 1902, 35, 3598).

It also reacts slowly with sodium phosphate and magnesium sulphate in dilute aqueous solution, forming methylamine magnesium phosphate (François, J. Pharm. Chim. 1908, 28, 86). Neither di- nor tri-methylamines react thus.

Liquid methylamine is a very good solvent for organic compounds, and combines readily with both organic and inorganic compounds, forming addition products (Gibbs, J. Amer. Chem. Soc. 1906, 28, 1395; Hochstetter and Kohn, Monatsh. 1903, 24, 773). For a number of addition products with inorganic substances, *see* Bonnefoi, Compt. rend. 1897, 124, 773; 127, 516; Jarry, *l.c.*; and Ann. Chim. Phys. [vii.] 27, 376; Matthews, J. Amer. Chem. Soc. 1898, 20, 826; Lenher, *ibid.* 1900, 23, 486; Moissan, Compt. rend. 128, 26; Lang and Jolliffe, Chem. Soc. Proc. 1903, 147; Ephraim and Weinberg, Ber. 1909, 42, 4447; Ekeley, J. Amer. Chem. Soc. 1909, 31, 664.

In the presence of soil, calcium carbonate and oxygen, methylamine is converted into ammonia, and finally into nitrites and nitrates (Demoussy, Compt. rend. 1898, 126, 253).

Under the influence of the silent electric discharge methylamine evolves nitrogen (Berthelot, *ibid.* 775; *see* also Mixter, Amer. J. Sci. 1898, [iv.] 6, 217).

Methyl chloramine Me·NHCl is obtained by distilling methylamine hydrochloride with sodium hypochlorite (Berg. Compt. rend. 1893, 116, 887). It is a colourless volatile oil with a piquant irritating odour.

Methyl dichloramine $MeNCl_2$ is obtained by leading chlorine into aqueous methylamine (Köhler, Ber. 1878, 12, 771) or by the distillation of methylamine hydrochloride with bleaching powder (Bamberger and Renauld, Ber. 1895, 28, 1683). It is a golden-yellow liquid, b.p. 59°–60°. Similar bromo and iodo compounds are also known (Dehn, J. Amer. Chem. Soc. 1909, 31, 123).

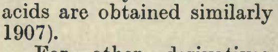
Methyl nitramine MeN_2O_2H is obtained by treating δ-dimethyl dinitro-oxamide with barium hydroxide (Franchimont, Rec. trav. chim. 1894, 13, 313; 321, 331; also v. Pechmann, Ber. 1897, 30, 647). It forms long needles, m.p. 38°, readily soluble in water and in alcohol. On reduction with aluminium amalgam and aqueous alcohol it yields diazomethane, whilst with zinc and hydrochloric acid it is reduced to methylamine, hydrazine and methylhydrazine (Thiele and Meyer, Ber. 1896, 29, 962). When heated with β-naphthol, β-naphthol methyl ether is formed with evolution of nitrogen (Franchimont and Umbgrove, Rec. trav. chim. 1897, 15, 215). It forms a number of metallic salts (Franchimont, *l.c.*; Ley and Kissel, Ber. 1899, 32, 1364). The *potassium* salt $KMeO_2N_2$, m.p. 220°, explodes on heating or on being struck.

Thionylmethylamine MeN : SO is an oil which fumes in air, b.p. 58°–59° (Michaelis and Storbeck, Annalen, 1893, 274, 187). Methylamine derivatives of various aliphatic acids are described by Duden, Bock and Reid (Ber. 1905, 38, 2036); Fosse (Compt. rend. 1906, 143, 914); Tafel and Wassmuth (Ber. 1907, 40, 2831); Benary (Ber. 1909, 42, 3912); Gansser (Zeitsch. physiol. Chem. 1909, 61, 16); Fourneau (Bull. Soc. chim. 1909, [iv.] 5, 229); also D. R. PP. 198306, 1908; 202167, 1909.

Methylaminoanthraquinones are prepared by dissolving a mixture of the desired amino-derivative of anthraquinone and formaldehyde in concentrated sulphuric acid and warming to 55°–60° (D. R. P. 156056, 1905).

α-Methylaminoanthraquinone, m.p. 167°, is obtained by treating α-mononitroanthraquinone with methylamine solution (D. R. P. 144634; Frdl. 1902–04, 201).

1-Methylaminoanthraquinone-5-sulphonic acid



$$SO_3H{\cdot}C_6H_3{<}\begin{smallmatrix}CO\\CO\end{smallmatrix}{>}C_6H_3NHMe,$$

and also the diamino compound

$$NHMe{\cdot}C_6H_3(CO)_2C_6H_3NHMe,$$

are formed by treating potassium 1 : 5-anthraquinonedisulphonate with aqueous methylamine at 150°. The potassium salt of the former crystallises from water in violet brown needles. Other methylamine anthraquinone sulphonic acids are obtained similarly (D. R. P. 186722, 1907).

For other derivatives of methylamine anthraquinone which are used as dyes, *see* D. R. PP. 156759, 164791; Frdl. 1905–07, 293, 280; D. R. PP. 212470, 1909; 220314; Chem. Zentr. 1910, i. 1306).

Methylaminoacetocatechol

$$C_6H_3(OH)_2CO{\cdot}CH_2{\cdot}NHMe$$

is formed by warming gently chloroacetocatechol with an excess of methylamine. It is a white crystalline powder darkening at 200° and decomposing at about 230°. Ferric chloride gives an emerald-green colour (D. R. P. 152814; Dakin, Chem. Soc. Proc. 1905, 154). When reduced and then treated with ammonia, it yields methylamino-*o*-dihydroxyphenylethanol, m.p. 208°, which is an astringent, and has hæmostatic properties (J. Soc. Chem. Ind. 1909, 1005). The ethanol yields a hydrochloride, m.p. 157° (D. R. P. 202169).

Methylaminoquinones are described by Fichter (Annalen, 1908, 361, 363).

2-Methylamino-8-methoxyquinoline crystallises in silver prisms, m.p. 151°, and forms a crystalline nitrosamine, m.p. 180° (Fischer, Ber. 1902, 35, 3674).

Methylaminocamphene has b.p. 202°–203°/756 mm. $[\alpha]_D+28{\cdot}7°$ (Forster and Micklethwait, Chem. Soc. Trans. 1904, 334).

Methylaminocoumarins are described by v. Pechmann and Schaal (Ber. 1899, 32, 3690, 3696); and by Morgan and Micklethwait (Chem. Soc. Trans. 1904, 1238).

Methylaminothiazoles are described by Young and Crookes (Chem. Soc. Trans. 1906, 68). *Uracils* by Wheeler and Jamieson (Amer. Chem. J. 1904, 32, 342).

Dimethylamine $(CH_3)_2NH$; b.p. 7·2°–7·3° at 764·1 mm.; sp.gr. 0·6865 at −5·8° (Hofmann, Ber. 1889, 22, 699). From methyl iodide and ammonia (Hofmann, J. 1862, 329). In small quantity by distilling the compound of aldehyde ammonia and sulphurous acid with caustic lime (Petersen, Annalen, 1857, 102, 317). In the putrefaction of fishes; occurs in herring brine (Bocklisch, Ber. 18, 87, 1924). Is obtained together with methylamine in the action of methyl alcohol on phospham (*see Methylamine;* also Vidal, Chem. Zentr. 1897, ii. 517).

Preparation.—The product of the action of ammonia upon methyl iodide (consisting of the hydriodides of mono-, di- and tri-methylamine and tetramethylammonium iodide) is treated with alcohol in order to remove the last-mentioned compound. The residue on treatment with caustic potash yields the free bases which can be partially separated by condensation, the more volatile monomethylamine escaping condensation may be received in hydrochloric acid.

The mixture of the free bases is then treated with ethyl oxalate, the trimethylamine remains unacted upon, the dimethylamine is converted into the ethyl ester of dimethyl oxamic acid, whilst the mono- base is converted into dimethyl oxamide. The latter is difficultly soluble in cold water, and is thus separated from the dimethylamine compound which is then distilled with potash

$$(CH_3)_2N{\cdot}C_2O_2(OC_2H_5)+2KOH = (KO)_2C_2O_2+C_2H_5OH+(CH_3)_2NH.$$

The alcoholic solution is then neutralised with hydrochloric acid, evaporated to dryness, and decomposed by caustic potash. The hydrochloride of dimethylamine can be freed from admixed ammonium chloride by treatment with chloroform, in which the latter is insoluble (Behrend, Annalen, 1883, 222, 119).

By the reduction of a mixture of formaldehyde and methylamine with zinc-dust and hydrochloric acid (D. R. P. 73812).

Dimethylamine can be obtained by heating thiodimethylamine (185 grammes) with sulphuric acid chlorhydrin (130 grammes), the temperature being raised gradually and the mass finally heated for 2–3 hours at 130°–150°. On cooling the product is shaken with ether to remove benzenethiochloride, and the residue is treated with water, made alkaline, and the dimethylamine is separated by distillation in steam (D. R. P. 105870; Frdl. 1897–1900, 34).

An almost theoretical yield of dimethylamine hydrochloride is obtained by adding powdered nitrosodimethylaniline hydrochloride and a few zinc shavings to a nearly boiling, dilute aqueous solution of sodium hydroxide, the amine being absorbed in concentrated hydrochloric acid contained in a Péligot's U-tube (Menschutkin, J. Russ. Phys. Chem. Soc. 1898, 30, 243; Norris and Laws, Amer. Chem. J. 1898, 20, 54).

The free base can be liberated by treatment with caustic soda.

Properties.—Dimethylamine is a colourless, inflammable liquid with a strong ammoniacal smell. Bromine acts upon an aqueous solution forming dimethylamine hypobromite and bromide $N(CH_3)_2H{\cdot}HBrO$ and $NH(CH_3)_2{\cdot}HBr$; or, if the bromine be in excess, the unstable tribromide $N(CH_3)_2Br_3$, a yellow flocculent precipitate, is obtained (Raschig, Ber. 1885, 18, 2250).

At 0° it combines directly with two atoms of bromine (Remsen and Norris, Amer. Chem. J. 18, 94).

When oxidised with hydrogen peroxide it yields nitrous acid, formaldehyde and formic acid (Dunstan and Goulding, Chem. Soc. Trans. 1899, 1009). With Nessler's reagent, dimethylamine gives a white precipitate.

When heated with hydrogen at 820°–1120°, hydrocyanic acid, methane and ammonia are formed, the relative quantities of the products depending on the quantity of hydrogen present (Voerkelius, Chem. Zeit. 1909, 33, 1025, 1078, 1090).

Dimethylamine forms salts resembling those of ammonia (Topsoë, J. 1883, 618; Delépine, Ann. Chim. Phys. [vii.] 8, 459; Norris and Laws, *l.c.*; and 490; Ragland, *l.c.*; Cook, *l.c.*; Jörgensen, Zeitsch. anorg. Chem. 1906, 48, 374).

Dimethylamine dihydrochloride is a white crystalline substance formed by passing dry hydrogen chloride into the base or into the normal hydrochloride (Kaufler and Kunz, Ber. 1909, 42, 385).

Dimethylchloramine Me_2NCl, b.p. 46°/765 mm., is obtained in the same way as the monomethyl derivative, and has similar properties (Berg, *l.c.*). The corresponding bromo derivative has b.p. 64°–66° (Seliwanoff, Ber. 1893, 26, 423; Willstätter and Hottenroth, Ber. 1904, 37, 1775).

Other halogen derivatives are described by Cohn (J. pr. Chem. 1897, [ii.] 56, 345) and Knorr (Ber. 1904, 37, 3504).

Dithiodimethylamine $S_2(NMe_2)_2$ is a reddish-yellow liquid, b.p. 82°–83°/22 mm., 170°–180°/760 mm. (decomp). It is decomposed by acids into the amine, sulphur, and sulphur dioxide (Michaelis and Luxembourg, Ber. 1895, 28, 165).

Dimethylnitramine $Me_2O_2N_2$ forms bright colourless needles, whilst the *isonitramine* is a liquid, b.p. 112° (Franchimont and Umbgrove, *l.c.*; Lachman, Amer. Chem. J. 1899, 21, 483; Bamberger, Ber. 1895, 28, 402; Kirpal, *ibid.* 537).

Dimethylamine acetone $NMe_2{\cdot}CH_2{\cdot}COMe$ is prepared by adding chloracetone to an aqueous 30 p.c. solution of dimethylamine. It is a colourless oil, b.p. 123°, miscible with water, yielding a platinochloride, which forms beautiful crystals, m.p. 176° (decomp.). It also yields a hydrochloride; an aurichloride (m.p. 145°–146°); a methiodide (m.p. 168°); and an oxime, m.p. 99° (Stoermer and Dzimski, Ber. 1895, 28, 2220; 1896, 29, 866).

Methyl dimethylaminoacetate is a volatile oil, boiling at 135°. The corresponding ethyl compound boils at 149°–150°.

Methyl β-dimethylaminopropionate

$$NM_2{\cdot}CH_2{\cdot}CH_2{\cdot}CO_2Me,$$

b.p. 154·5°, yields a methiodide, m.p. 191°–192° (decomp.), which, when warmed with alkalis, gives acrylic acid and trimethylamine, whilst with silver oxide it gives β-trimethylpropiobetaine (Willstätter, Ber. 1902, 35, 584).

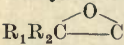
Methyl-γ-dimethylaminobutyrate has b.p. 171·5°–173°, and yields a crystalline aurichloride and picrate.

Dimethylaminodimethylacetal is a colourless mobile liquid, b.p. 137·5°, which has no reducing properties. Other dimethylamino derivatives of aliphatic acids have also been prepared (Willstätter, Ber. 1902, 35, 1378).

Dimethylamino derivatives of aliphatic hydrocarbons are described by Willstätter (Ber. 1901, 34, 129; Annalen, 1903, 326, 1); Duden and Lemme (Ber. 1902, 35, 1335); Hochstetter and Kohn (Monatsh. 1903, 24, 773); Bouveault (Bull. Soc. chim. 1904, [iii.] 31, 1306, 1322).

A number of methyl and dimethyl aminocarbinol derivatives of the type

$$R_1R_2C(OH)CH_2NR_3R_4$$

(where R_1,R_2=alkyl or aryl groups R_3= methyl or other alkyl and R_4=an alkyl group or hydrogen) are obtained by the action of methyl or dimethylamine on an ethylene oxide  $R_1R_2C\overset{O}{\text{——}}CH_2$ (D. R. P. 199148; Frdl. 1908–10, 975; also D. R. P. 173610; Knorr and Matthes, Ber. 1901, 34, 3482).

These substances, which have valuable anæsthetic properties, and are less toxic than cocaine or eucaine, can also be obtained by treating aminoacetones or esters of amino acids containing a tertiary amino group with magnesium organo compounds of the type $R{\cdot}Mg{\cdot}X$ (D. R. PP. 169819, 169746; Frdl. 1905–07, 1029, 1033).

Esters having pronounced saporific properties and a low toxicity are produced by condensing alkyl dimethylaminohydroxy*iso*butyrates with anhydrous chloral (D. R. PP. 203643, 198306, 202167; Frdl. 1908–10, 980, 984, 1000).

For other dimethylamino compounds used in medicine, *see* D. R. PP. 121051, 129967; Frdl. 1900–02, 1219, 1226; J. Soc. Chem. Ind. 1909, 491.

Dimethylaminoparaxanthine known in commerce as *paraxine*, is an energetic diuretic (D. R. P. 156901, 1905) and is decomposed into

2:6-Dioxy-8-dimethylamino-7-methylpurine, m.p. above 319°, a crystalline substance which can be separated from the urine and has also a strong diuretic action (Forschbach and Weber, Arch. exp. Path. Pharm. 1907, 56, 186).

Dimethylamine reacts in equimolecular proportion with polyhydroxyaromatic compounds forming addition products with an alkaline reaction which can be used for developing in photography without further addition of alkali (D. R. P. 141101; Frdl. 1900–02, 1217).

Dimethylamine is used in the production of a large number of valuable dyestuffs; thus violet to blue dyestuffs are obtained by heating gallocyanine with mono- di- or tri-methylamine (D. R. PP. 57459, 65000; Frdl. 1890–94, 367).

Blue dyes are also obtained by the action of dimethylamine on the dyes of the oxazine series. The substances so obtained differ from the parent dye in giving purer colours and in being stable towards alkalis (D. R. P. 54658; Frdl. 1890–94, 373).

See also Freund and Wirsing, Ber. 1907, 40, 204; D. R. PP. 172079, 161665; the article on AMINES and the various parent dyes.

When dimethylamine is heated with *p*-aminophenol-azo-β-naphthol and formaldehyde, a dark-brown powder is obtained, which is a good dye for tannined cotton (D. R. P. 95546; Frdl. 1897–1900, 555).

3-Dimethylaminoanthraquinone is obtained when dimethylaminobenzoylbenzoic acid (1 part) is heated with concentrated sulphuric acid (10 parts) at 175°–180°. It forms red needles, m.p. 181°. When 12 parts of sulphuric acid is used, and the temperature is kept at 80°, dimethyl-aminoanthranol is formed, but is readily oxidised to the anthraquinol, by ferric chloride (Haller and Guyot, Compt. rend. 1898, 126, 1544; D. R. P. 108837).

1-Dimethylamino-5-phenoxyanthraquinone m.p. 147°–149°, and similar compounds which form important materials for the manufacture of dye-stuffs, have been obtained by treating the corresponding anthraquinone derivative with the desired mono- or di-alkylamine in pyridine solution at 110°–115° (D. R. P. 165728; Frdl. 1905–7, 289).

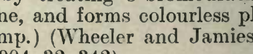
For other dimethylaminoanthraquinone derivatives, *see* Severin, Compt. rend. 1906, 142, 1274; D. R.PP. 136777, 136778; Frdl. 1900–02, 374; D. R. P. 146691; Frdl. 1902–04; D. R. PP. 146691, 1904; 205096, 1909).

Dimethylamine, when heated with fluorescein chloride or dichlorofluorescein chloride in presence of zinc chloride at 160°–170°, gives derivatives of chloroaminofluoran, whilst at higher temperatures rhodamines are produced (D. R. P. 139727, 1903).

Chloromethyl- and dimethyl-aminofluoran form pink crystals, melting at 168° and 218° respectively.

Dimethylaminocamphor is a colourless oil, b.p. 241°/758 mm. It does not reduce Fehling's solution, and is only slowly acted on by silver nitrate. It forms a picrate, m.p. 220° (decomp.); hydriodide, m.p. 251° (decomp.); a platinichloride, m.p. 211° (decomp.); and acetate, m.p. 251°, with evolution of gas (Forster, Chem. Soc. Trans. 1905, 240; Rabe and Schneider, Ber. 1908, 41, 872).

5-Dimethylaminouracil



$$NH\left\langle\begin{matrix}CO\text{——}NH\\CO{\cdot}C(NMe_2)\end{matrix}\right\rangle CH$$

is formed by treating 5-bromouracil with dimethylamine, and forms colourless plates, m.p. 297° (decomp.) (Wheeler and Jamieson, Amer. Chem. J. 1904, 32, 342).

Trimethylamine $N(CH_3)_3$; b.p. 3·2°–3·8° at 764·6 mm., sp.gr. 0·662 at −5·2° (Hofmann, Ber. 22, 699; sp.gr. 0·673 at 0° (Bleunard). Does not solidify at −75° under a pressure of 10 mm.; forms a crystalline hydrate with 7 molecules of water, melting at 4·3°. Occurs in certain plants, *e.g.* *Chenopodium Vulvaria* (Linn.), *Arnica montana* (Linn.), hawthorn blossom, pear and wild cherry blossom, in ergot (Dessaignes, J. 1857, 481; Walz, J. 1852, 552), in certain lichens such as the *Sticta fuliginosa*, in hops and in cod liver oil, in bone oil and guano (Zopf, Annalen, 1897, 297, 272). It also occurs in various animal fluids, *e.g.* in calves' blood (Dessaignes), and in human urine (Filippi, Zeitsch. physiol. Chem. 1906, 49, 433). Also in large quantities in herring brine, which owes to it its peculiar smell (Wertheim, J. 1851, 480).

It is also a product of the decomposition of fibrin by *streptococci* (Emmerling, Ber. 30, 1863).

It is obtained by treating methyl iodide with ammonia (Hofmann), by the distillation of tetramethylammonium hydroxide (Hofmann, Annalen, 93, 325); by distillation of narcotine (Wertheim, *ibid.* 73, 208), or codeïne (Anderson, *ibid.* 77, 367), with potash.

By the action of methyl alcohol on magnesium nitride (Szarvasy, Ber. 1897, 30, 305). By the reduction of trimethyloxamine with zinc-dust (Hantzsch and Hilland, Ber. 1898, 31, 2058; Dunstan and Goulding, *l.c.*). By the interaction of hexamethylenetetramine with formaldehyde (Eschweiler, Ber. 1905, 38, 880).

By the putrefaction of yeast or of wheat meal (Hesse, J. 1857, 403). Also by the dry distillation of 'vinasses' from the beetroot sugar manufacture (Vincent, Bull. Soc. chim. [ii.] 27, 150).

Preparation.—The crude methylamine from the distillation of the 'vinasse' is treated with sulphuric acid, the solution evaporated to a syrup and treated with absolute alcohol, the monomethylamine sulphate is thus precipitated. The filtrate is treated with the proper amount—1 molecule for every 2 molecules of primary amine present—of ethyl oxalate, and allowed to stand for 24 hours. The precipitate, consisting of a mixture of di-*iso*butyl oxamide and di-*iso*propyl oxamide, is filtered off and the filtrate distilled; the residue is then decomposed by potash, the free bases received in alcohol, and the alcoholic solution mixed at 0° with ethyl oxalate (1 molecule to each molecule of free base) and allowed to stand for a day. The mixture is then distilled, and the triethylamine obtained pure. The non-volatile residue is made slightly alkaline with milk of lime and evaporated, calcium *iso*propyl oxamate first crystallises out, and then calcium ethyl oxamate. The mother liquor, on addition of alcohol, gives a precipitate of calcium methyl oxamate, whilst calcium dimethyl oxamate remains in solution (Duvillier and Buisine, Ann. Chim. Phys. [v.] 23, 299).

A mixture of herring pickle and lime is subjected to distillation, the alkaline distillate is neutralised with hydrochloric acid, evaporated to dryness, and the residue treated with alcohol, which leaves the ammonium chloride undissolved. The solution is evaporated, the residue dissolved in a little water, and redistilled with lime, the vapours being led through an empty bottle to separate less volatile constituents, and then conducted into water or condensed with ice.

50 grammes of ammonium chloride are heated with 440 grams of 40 p.c. formaldehyde solution in an autoclave at 120°–160°.

Trimethylamine can more readily be obtained in a pure state by the distillation of tetramethylammonium hydroxide (Schmidt, Annalen, 1892, 267, 254).

Properties.—Trimethylamine is a volatile liquid with a strong, fish-like smell. It is very soluble in water, and possesses strong basic properties, although it can be displaced from its compounds by either mono- or di-methylamine.

When heated at 800°–1000° it decomposes almost quantitatively into hydrocyanic acid and methane, whilst at 600°, *tetramethyl hydrazine* is formed (Voerkelius, Chem. Zeit. 1909).

When passed through a hot tube with hydrogen it decomposes, forming dimethyl dimethylene diamine $(CH_2)_2(CH_3)_2N_2$, ammonia, cyanogen, and other products (Romeny, Ber. 11, 835). It forms salts with acids, of which the hydrochloride is of some importance; it has been suggested to employ it in the manufacture of potassium carbonate from potassium chloride by a process analogous to the Solvay ammonia soda process. Ammonia cannot be employed in this process, since ammonium chloride has only about the same solubility as potassium hydrogen carbonate, whilst trimethylamine hydrochloride is very much more soluble.

For a number of salts formed by trimethylamine with inorganic salts, *see* Guareschi, *l.c.*; Christensen, *l.c.*; Ragland, *l.c.*; Cook, *l.c.*; Hofmann and Marburg, *l.c.*; Mylius and Foerster, Ber. 24, 2424; Wiede, *ibid.* 31, 3140; Michael and Hibbert, Annalen, 1909, 364, 64.

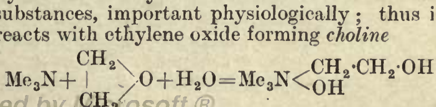
Trimethylamine dibromide NMe_3Br_2 is formed by passing dry trimethylamine into ice-cold bromine, or by heating trimethylamine hydrobromide (1 molecule) with a small quantity of hydrogen bromide and bromine (1 molecule). Similar iodine, chlorine, and mixed halogen derivatives have also been obtained (Remsen and Norris, Amer. Chem. J. 1896, 18, 90; *see* also Hantzsch and Graf, Ber. 1905, 38, 2154; Norris, *ibid.* 3904). They are crystalline unstable substances.

For other halogen and halogen acid compounds of trimethylamine, *see* Gabriel and Stelzner, Ber. 1895, 28, 2929; Delépine, Compt. rend. 1896, 122, 272; Ann. Chim. Phys. 1896, [vii.] 8, 439; Norris, Amer. Chem. J. 1898, 20, 51; Pictet and Krafft, Bull. Soc. chim. [iii.] 7, 72; Hantzsch, Ber. 1905, 38, 2161; Kaufler and Kunz, *ibid.* 1909, 42, 2482).

Trimethylamine combines with carbon disulphide to form a colourless crystalline compound $N(CH_3)_3{\cdot}CS_2$, m.p. 125°, which is somewhat unstable; it is soluble in chloroform, and combines with dilute acids, but is decomposed by strong acids into its constituents.

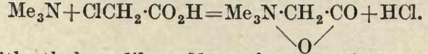
Trimethyloxamine (*Trimethylamine oxide*) $Me_3N{:}O,2H_2O$ forms needle-shaped crystals m.p. 96°, and is best obtained by the action of hydrogen peroxide on an aqueous solution of trimethylamine (Dunstan and Goulding, Chem. Soc. Trans. 1899, 794, 1005; Mamlock and Wolffenstein, Ber. 1901, 34, 2499).

Trimethylamine, like dimethylamine, enters into the constitution of a number of important dyes. It also yields derivatives which form substances, important physiologically; thus it reacts with ethylene oxide forming *choline*



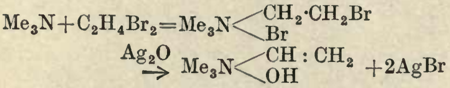
$$Me_3N + \begin{array}{l} CH_2 \\ | \\ CH_2 \end{array}\!\!\!>O + H_2O = Me_3N\!<\!\begin{array}{l} CH_2{\cdot}CH_2{\cdot}OH \\ OH \end{array}$$

With monochloracetic acid producing *betaine*



$$Me_3N+ClCH_2{\cdot}CO_2H=Me_3N{\cdot}CH_2{\cdot}CO+HCl.$$
$$\underbrace{\qquad\qquad\qquad}_{O}$$

With ethylene dibromide, to form *neurine*



$$Me_3N+C_2H_4Br_2=Me_3N\begin{cases}CH_2{\cdot}CH_2Br\\Br\end{cases}$$
$$\xrightarrow{Ag_2O} Me_3N\begin{cases}CH:CH_2\\OH\end{cases}+2AgBr$$

***iso*Crotyltrimethylammonium bromide**

$CMe_2:CH{\cdot}NMe_3Br$,

obtained by the interaction of *iso*butylene bromide and trimethylamine, is homologous with neurine bromide, and, like valeryltrimethyl ammonium bromide, closely resembles it in its physiological action. Dibrom*iso*butyl trimethyl ammonium bromide and dibrom*iso*butyltrimethyl ammonium dibromide and other similar compounds have also been prepared (Kleine, Chem. Zentr. 1894, i. 16).

Ethylene bromide reacts with trimethylamine in molecular proportion at 100°, yielding tetramethylammonium bromide, trimethylvinylammonium bromide (neurine bromide), dimethylamine bromide, and other compounds.

Propylene and amylene bromides also react with trimethylamine, yielding a number of methylammonium compounds (Kleine, *l.c.*).

Trimethylamine reacts with halogen ketones, forming ketonic bases (Schmidt, Arch. Pharm. 1898, 236, 334).

Trimethylacetonylammonium chloride (coprine chloride) $AcCH_2{\cdot}NMe_3Cl$ is a crystalline substance which gives a platinochloride, yellowish red needles, m.p. 238°–240°; an aurichloride, beautiful yellow needles, m.p. 139·5°; and an oxime, colourless plates, m.p. 212° (Furnée, Arch. Pharm. 1898, 236, 343).

Trimethylacetonylammonium bromide melts at 190°, and at 195° it gives rise to a yellow distillate, and tetramethylammonium bromide (Brendler and Tafel, Ber. 1898, 31, 2683).

For the interaction of trimethylamine with other aliphatic compounds, *see* Malbot, Bull. Soc. chim. [iii.] 6, 845, 709, 711; *ibid.* 7, 213; Duvillier, *ibid.* [iii.] 23, 507; Menozzi and Pantoli, Gazz. chim. ital. 23, ii. 209; Hartmann, Chem. Zentr. 1896, i. 999; André, Compt. rend. 1898, 126, 1107; Benary, Ber. 1908, 41, 2399; D. R. P. 195813; Frdl. 1908–10, 990.

In France and in Russia trimethylamine has been employed successfully in medicine, but English and American doctors have not obtained such good results. For the physiological effects of trimethylamine, *see* Combemale and Brunelle, Compt. rend. Soc. Biol. 1891, 175).

Methylammonium cobaltinitrite

$(MeNH_3)_3CO(NO_2)_6$

is prepared by adding to a nearly saturated solution of methylamine hydrochloride, a nearly saturated solution of pure sodium cobaltinitrite. It is a yellow powder, stable when dry, but slowly decomposing in the presence of moisture or on heating. When treated with strong mineral acids it decomposes violently (Cunningham and Perkin, Chem. Soc. Trans. 1909, 1564).

Monomethylammonium hexabromoplatinate $(NH_3Me)_2PtBr_6$ and the corresponding di- and tri-methyl compounds are all crystalline substances (Gutbier and Bauriedel, Ber. 1909, 42, 4243).

Magnesium methylammonium arsenate

$NH_3Me{\cdot}MgAsO_4,8H_2O$

and the trimethylammonium compound

$NHMe_3{\cdot}MgAsO_4,6H_2O$

are white crystalline powders (Brisac, Bull. Soc. chim. 1903, [iii.] 29, 591). Similar methylammonium phosphates have also been prepared (Porcher and Brisac, *ibid.* 587). For other methyl ammonium compounds, *see* Reynolds, Chem. Soc. Trans. 1891, 394; François, Compt. rend. 1905, 140, 1697; Gutbier, Zeitsch. physikal. Chem. 1909, 69, 304.

Tetramethylammonium $N(CH_3)_4$, *tetramethylium*, according to Palmaer (Zeitsch. Elektrochem. 1902, 8, 729) is produced when a solution of tetramethylammonium chloride or hydroxide in liquid ammonia is electrolysed between platinum electrodes, but it could only be observed as giving a transient blue colouration and could not be isolated.

The base, **Tetramethylammonium hydroxide** NMe_4OH is formed as the pentahydrate

$NMe_4OH,5H_2O$,

m.p. 62°–63°, by the action of a methyl alcohol solution of potassium hydroxide on a similar solution of tetramethyl ammonium chloride. When this hydrate is desiccated it forms a trihydrate, m.p. 59°–60°, and a monohydrate which decomposes at 130°–135° without melting (Walker and Johnson, Chem. Soc. Trans. 1905, 955). The hydroxides are hygroscopic, strongly alkaline, and readily absorb carbon dioxide when exposed to the air. When heated they decompose forming methyl alcohol and trimethylamine. The *iodide* $N(CH_3)_4I$ is the main product of the action of ammonia upon methyl iodide (Hofmann, Proc. Roy. Soc. 1851, 381), or by heating trimethylazonium iodide with methyl iodide at 125°–130° (Harries and Haga, Ber. 31, 59). It forms quadratic prisms soluble in hot water, but only slightly in cold water; sp.gr. 1·84 (Schröder, Ber. 12, 562). Similar chlorine and bromine compounds are also known.

Tetramethylammonium pentaiodide NMe_4I_5, m.p. 126°–127°, is obtained by the action of methyl iodide on nitrogen iodide (Silberrad and Smart, Chem. Soc. Trans. 1906, 173).

Tetramethylammonium forms many salts which have the power of producing crystalline double compounds with many metallic salts (*v.* Topsöe, J. 1883, 619; Risse, Annalen, 107, 223; Lossen, *ibid.* 181, 374; Ragland, *l.c.*; Prescott, J. Amer. Chem. Soc. 1898, 20, 96; Wiede, *l.c.*; Auld and Hantzsch, Ber. 1905, 38, 2685; Milbauer, Zeitsch, anorg. Chem. 1907, 53, 135; Schmidt, Chem. Zentr. 1907, ii. 1593; Braun, Ber. 1908, 41, 2123; Kaufler and Kunz, *l.c.*).

Tetramethylammonium formate (*Forgenine*) $H{\cdot}CO_2{\cdot}N(CH_3)_4$ is obtained by the action of tetramethylammonium iodide on silver formate. It is a white crystalline, odourless, hygroscopic substance, stable in dry air and in solution, decomposing above 200°, and giving the reactions of formates (Vanzetti, Chem. Zentr. 1906, ii. 1347).

Forgenine is employed in medicine, but in large doses it is toxic, and may even prove fatal (Piccinini, Chem. Zentr. 1907, i. 651).

α-Methyl hydroxylamine $MeO{\cdot}NH_2$ is formed by treating methyl ethyl benzhydroxamate with hydrochloric acid (Lossen and Zanni, Annalen, 1876, 182, 225). The hydrochloride forms prisms, m.p. 149°, and gives an orange-red crystalline platinochloride (Lossen, Ber. 1883, 16, 827; Petraczek, *ibid.* 827).

β-Methyl hydroxylamine MeNH·OH is formed by heating benz*syn*aldoxime methyl ether or its nitro derivative with hydrochloric acid (Dittrich, Ber. 1890, 23, 3598; Kjellin, *ibid.* 1893, 26, 2382), but is best prepared by the electrolytic reduction of nitromethane in alcoholic sulphuric acid solution at 15°–20° (Pierron, Bull. Soc. chim. [iii.] 21, 783; *see* also Bamberger, Ber. 1894, 27, 1350; Kirpal, *ibid.* 1892, 25, 1715). It forms long prisms, m.p. 42°, b.p. 62·5°/15 mm., sp.gr. 1·0003 at 20°/4°. It is readily soluble in water and alcohol, decomposes on standing, and is reduced to methylamine by hydriodic acid.

The *hydrochloride* has m.p. 88°–90°; the *picrate* m.p. 128°–130°.

α-Methyl β-ethyl hydroxylamine NHEtOMe is a colourless alkaline liquid, b.p. 60°–61°, readily soluble in water and does not reduce silver nitrate. It forms a hydrochloride and a platinichloride. *β-Methyl α-ethyl hydroxylamine* has b.p. 65°–65·5° and similar properties to the α-methyl β-ethyl compound (Jones, Amer. Chem. J. 1907, 38, 253).

αβ-Dimethylhydroxylamine hydrochloride
NHMe·OMe,HCl
forms long prismatic needles m.p. 115°–116°. It is volatile at 100°, does not reduce Fehling's solution or silver nitrate. The platinochloride forms red prismatic crystals which melt at 180° (decomp.). The free base is a colourless volatile liquid, b.p. 42·2°–42·6° (Jones, Amer. Chem. J. 1898, 20, 1).

Methyl hydrazine $CH_3HN{\cdot}NH_2$ is prepared by the reduction of diazomethane with sodium amalgam and alcohol or by agitating methyl iodide with excess of methylhydrazine in aqueous solution (Pechmann, Ber. 1895, 28, 859; Harries and Haga, *ibid.* 1898, 31, 56). A colourless liquid with ammoniacal smell. The sulphate $NHCH_3{\cdot}NH_2,H_2SO_4$, a crystalline compound, is obtained from methyl hydrazine carbamide which results from the action of nascent hydrogen upon nitroso-methyl carbamide $NH_2{\cdot}CO{\cdot}N(CH_3)NO$ (Brüning, Ber. 21, 1809). The oxalate has m.p. 166°. Methyl hydrazine gives benzoyl and other derivatives (Michaelis and Hadanck, Ber. 1908, 41, 3285).

as-**Dimethyl hydrazine** $(CH_3)_2N{\cdot}NH_2$; b.p. 62·5° at 717 mm.; sp.gr. 0·801 at 2·2°; b.p. 63·9° at 752·5 mm.; sp.gr. 0·7914 at 22·3°/0° (Brühl, Ber. 1897, 30, 160); from nitroso-dimethylamine and nascent hydrogen (zinc-dust and acetic acid) in alcoholic solution (Renouf, Ber. 1880, 13, 2171), or by the dry distillation of trimethylazonium hydroxide (Harries and Haga, *l.c.* 58). It has a strong ammoniacal smell, and is very soluble in water, alcohol, and ether. It is decomposed by nitrous acid into nitrous oxide and dimethylamine.

The *oxalate* has m.p. 142°–143°. The *cyanide* crystallises in beautiful needles and decomposes at 0°–10° (Peters, Ber. 1906, 39, 2784).

sym-**Dimethylhydrazine** MeNH·NHMe is obtained by the action of methyl iodide on potassium or lead diformyl hydrazine (Harries and Klamt, Ber. 1895, 28, 504; Harries and Haga, *l.c.* 63), or by boiling the methyl iodide salt of methyl pyrazole with strong potassium hydroxide (Knorr and Köhler, Ber. 1906, 39, 3257; Knorr, *ibid.* 3265). It is a mobile, colourless, fuming liquid, b.p. 81°/747 mm., with the characteristic odour of aliphatic hydrazines. It dissolves in water with evolution of heat, attacks cork, rubber, and the epidermis, and its vapour, when mixed with air, burns with a faintly luminous flame, depositing soot, and is liable to explosion. It is a fairly strong reducing agent, and forms salts with mineral and organic acids. It also forms a semicarbazide and a phenylthiosemicarbazide, m.p. 115°; a dibenzoyl derivative, m.p. 85°; a dimethyl picrazide, m.p. 141°, and other derivatives (Knorr and Köhler, *l.c.*).

Trimethylazonium iodide $NH_2{\cdot}NMe_3I$ is obtained by agitating an aqueous solution of hydrazine hydrate with methyl iodide and caustic potash. It resembles ammonium chloride in crystalline structure, and has m.p. 235° (decomp.). It is converted into hydrochloride when acted on by silver chloride, and into the hydroxide by its interaction with silver oxide (Harries and Haga, *l.c.*).

Tetramethyl tetrazone $(CH_3)_2N{\cdot}N{:}N{\cdot}N(CH_3)_2$, b.p. 130°; a yellow explosive oil, slightly soluble in water. It is a strong base, and its salts are very soluble in water; it reduces silver solution with formation of a mirror (Renouf).

Methylene Compounds.

Methylene CH_2, a dibasic radicle not known in the free state.

Methylene diacetate $CH_2(C_2H_3O_2)_2$. B.p. 170°; from methylene iodide and silver acetate (Butlerow, Annalen, 107, 111); from chlormethyl acetate $C_2H_3O_2{\cdot}CH_2Cl$ and potassium acetate (Henry, Ber. 1873, 739). A liquid decomposed by water at 100° into acetic acid and trioxymethylene.

Methylene bromide CH_2Br_2, *Dibromomethane.* B.p. 96·5°–97·5° corr.; sp.gr. 2·4985 at 15°/15°, 2·47745 at 25°/25°; Perkin, Chem. Soc. Trans. 1884, 520). Obtained by the action of bromine upon methylene iodide under water (Butlerow, Annalen, 111, 251); from methyl bromide and bromine at 250° (Steiner), or by the action aluminium bromide heated to 100° on trioxy methylene (Gustavson).

A liquid which, by the action of water and excess of lead oxide at 150° gives ethylene glycol (Eltekoff, Ber. 6, 558).

Methylene chloride CH_2Cl_2, *Dichlormethane.* B.p. 41·6° corr.; sp.gr. 1·37777 at 0°/4° (Thorpe, Chem. Soc. Trans. 1880, 195); b.p. 40°; sp.gr. 1·33771 at 15°/15°, 1·32197 at 25°/25° (Perkin, *ibid.* 1884, 527). From methane and chlorine after preliminary formation of methyl chloride (Regnault, Annalen, 33, 328); from methylene iodide and chlorine (Butlerow, Annalen, 111, 251).

Preparation.—A mixture of chloroform (1 vol.), zinc, and alcohol (3 vols.) is gradually treated with hydrochloric acid and distilled; the distillate, consisting of chloroform and methylene chloride, is rectified, and the residue boiling above 53° is again treated with zinc (Greene, Chem. News, 50, 75). It may also be prepared by treating methylene iodide under water with chlorine.

Properties.—A colourless liquid with a pleasant smell, resembling that of chloroform.

When heated with water to 200°, hydrochloric and formic acids and methyl chloride are produced; the latter, on further heating, forming methyl alcohol and hydrochloric acid. With aqueous ammonia at 140° it forms ammonium chloride, methylamine hydrochloride, and formic acid (André, Compt. rend. 102, 1474). When treated with ammonia, dissolved in methyl alcohol, hexamethylene tetramine is obtained.

Methylene chlorobromide CH_2ClBr, *Chlorobromomethane.* B.p. 68°–69° at 765 mm.; sp.gr. 1·9907 at 19°/19°; V.D.=4·43 (Henry, Compt. rend. 101, 599). Obtained by the action of bromine upon chloriodomethane. A mobile colourless liquid, with agreeable smell. It gives rise when treated with 2 mols. of ammonia in saturated methyl alcohol solution for 2 hours at 60°–70° to hexamethylene tetramine hydrobromide, ammonium chloride and ammonium bromide.

Methylene chlorofluoride CH_2ClF, *Chlorfluormethane.* A gas, sp.gr. 34·18 (calc. 34·25). From methyl fluoride and chlorine in sunlight. Is colourless, and slightly soluble in, and slowly decomposed by, water; burns with difficulty in oxygen (Collie, Chem. Soc. Trans. 1889, 112).

Methylene chloroiodide CH_2ClI, *Chloriodomethane.* B.p. 109°–109·5° at 760·4 mm.; sp.gr. 2·444 at 14·5°/14·5°; V.D. 88·14. An oily liquid obtained by the action of iodine monochloride upon methylene iodide (Sakurai, Chem. Soc. Trans. 1885, 198); also by action of iodine in potassium iodide solution upon monomercuric methylene chloriodide (*ibid.* 1882, 362).

Methylene iodide CH_2I_2, *Diiodomethane.* M.p. 4°; b.p. 180°, with partial decomposition; sp.gr. 3·3326 at 15°/15° (Perkin, Chem. Soc. Trans. 1896, 1173); M.M. at 15°=18·827 (Perkin, *ibid.* 45, 464). From iodoform and sodium ethoxide (Butlerow, Ann. Chim. Phys. [iii.] 53, 313); by heating iodoform either alone or with iodine (Hofmann, Annalen, 115, 267; Dunn, Chem. Soc. Proc. 1910, 116); from chloroform or iodoform and hydriodic acid (Leben, Zeitsch. Chem. 1868, 712). By the action of iodine on diazomethane dissolved in ether (*v.* Pechmann, Ber. 1894, 1889). A yellow liquid which, when heated with water and copper to 100°, yields ethylene (Butlerow, Annalen, 120, 356). With zinc ethyl it forms butane. With silver acetate yields methylene acetate; combines with mercury to form mercuric methylene iodide CH_2I,HgI. It dissolves phosphorus very readily at ordinary temperatures (more than 1 : 1). An attempt to prepare the radicle methylene (CH_2), by heating with silver powder produces carbon methane and ethane and other products (Sudborough, Chem. Zentr. 1897, ii. 180). It is considerably used in the construction of sp.gr. columns for rock analysis by the density method, the usual diluents being benzene or ether.

Methylene oxide CH_2O *v.* FORMALDEHYDE.

Methylene sulphides.

Trimethylene sulphide $(CH_2S)_3$, *Parathioformaldehyde.* B.p. 216°; sublimes without decomposition. Formed by the action of sulphuretted hydrogen upon a solution of formaldehyde. Also by reducing, by means of zinc and hydrochloric acid, carbon disulphide (Girard, Annalen, 100, 306), potassium thiocyanate, or allyl mustard oil (Hofmann, Ber. 1, 176). It also results from the action of potassium sulphide on methylene iodide (Husemann, Annalen, 126, 294; Mansfeld, Ber. 1886, 698). It crystallises from benzene, carbon disulphide, or chloroform in quadratic prisms which are insoluble in water and possess a penetrating odour. It forms crystalline compounds with many salts, *e.g.* $C_3H_6S_3{\cdot}HgCl_2$, needles, insoluble in water; $2C_3H_6S_3{\cdot}PtCl_4$, golden-yellow needles.

Metathioformaldehyde $(CH_2S)x$ is formed by leading sulphuretted hydrogen for 10 hours into a boiling solution of hexamethylenetetramine saturated with ammonia (Wohl, Ber. 1886, 2345). The precipitate is purified by washing with water and hydrochloric acid, and by boiling with alcohol and glacial acetic acid. It has a characteristic odour, melts at 175°–176°, is not volatile without decomposition, and does not form salts with mercuric or platinic chlorides.

Methylene hydrogen sulphide $CH_2(HS)_2$, *thiomethylene glycol*, is not known in the free state. The diethyl ether, $CH_2(SC_2H_5)_2$, b.p. 184°, sp.gr. 0·987 at 20°, is obtained by the treatment of sodium mercaptide with methylene iodide (Claesson, J. pr. Chem. [ii.] 15, 176).

Methylene sulphonic acid $CH_2(SO_3H)_2$, *Methane disulphonic acid*, forms very unstable needle-like crystals. Produced in small quantity by the action of sulphur trioxide upon ether (Liebig, Annalen, 13, 35; Strecker, *ibid.* 100, 199); by the oxidation of methylene thiocarbonate (Husemann, *ibid.* 126, 293); from chloroform and potassium sulphite solution at 180° or from iodoform and potassium sulphite at 150° (Strecker, *ibid.* 148, 92).

Preparation.—Lactic acid or calcium lactate is heated with fuming sulphuric acid until sulphur dioxide begins to be evolved; the mixture is then neutralised with barium carbonate. It can also be prepared by heating 2 volumes of acetamide with 1 volume of fuming sulphuric acid (Buckton and Hofmann, Annalen, 100, 133). For salts *v.* Hofmann, Strecker, *l.c.*, also Monari (Ber. 1885, 1343).

Hexamethylenetetramine, *hexamethyleneamine, formamine, ammonio-formaldehyde, ammonaldehyde, cystamin, cystogen, formin, metramine, urisol, uritone, urotropine, vesalvine* $(CH_2)_6N_4$, is prepared by the action of ammonia on trioxymethylene (Butlerow, Annalen, 115. 322); from alcoholic ammonia and methylene chloride at 125° (Höland, *ibid.* 240, 225); or by passing formaldehyde vapour into a concentrated solution of ammonia, evaporating to a syrupy consistency and pouring into alcohol (Wohl, Ber. 1886, 1842). It forms rhombohedral crystals from alcohol, is insoluble in ether, but readily in water and chloroform. It can be sublimed *in vacuô.* Thioformaldehyde is produced by treating it with H_2S in the warm. It is precipitated from its aqueous solution by bromine as an orange-red tetrabromide

$$C_6H_{12}N_4Br_4,$$

which, when kept over potash, loses two atoms of bromine; the resulting dibromide melts at 198°–200°. This dibromide when boiled with water is decomposed into formaldehyde, water, ammonia, and hexamethylenetetramine. Hexamethylenetetramine is also precipitated from its solutions by mercuric chloride quantitatively. In the presence of ammonium salts it may be estimated by expelling the ammonia by heating with strong potash, by which it is unaffected, until all ammonia is expelled, then making acid and boiling to decompose the hexamethylene tetramine and subsequently making alkaline and estimating the ammonia in the usual way (Puckner and Hilpert, J. Amer. Chem. Soc. 1908, 1471). The purity of a specimen is readily examined qualitatively by means of Nessler's solution, which shows the presence of ammonia and ammonium salts by the usual yellow colour or brown precipitate, and of formaldehyde by a precipitate of mercury (Wöhlk, Zeitsch. anal. Chem. 1905, 765). Many compounds and derivatives of hexamethylene tetramine have been prepared and patented. The compounds with halogen pyrroles and aromatic sulphuric acids by Stange (Eng. Pat. 4804, 1899); with phenol and phenol mono- and poly- sulphuric acids and their halogen derivatives by the Chemische Fabriken vonn Weiler-ter-Meer (D. R. P. 124231); basic compounds by Karl Hock (D. R. P. 139394); cystopurin, a compound of 1 mol. hexamethylenetetramine and 2 mols. sodium acetate by Bergell and Wülfing (Eng. Pat. 29093, 1906; U.S. Pat. 852993, 1907; Chem. Zentr. 1907, i. 487); the chloral, bromal, and butyl chloral derivatives by Lederer (Eng. Pat. 17693, 1897); the quinate by Wichmann and Gabler (U.S. Pat. 690804, 1902; Zimmermann, Eng. Pat. 14834, 1899); the salicylic acid compound by O. Imray (Eng. Pat. 22481, 1895); a powerfully astringent compound resulting from the condensation with tannin by H. E. Newton (Eng. Pat. 10790, 1898); 'ammonium compounds' by Farbenfabriken von Baeyer & Co. (D. R. P. 164510); the borate by Aktien Gesellschaft für Anilinfabriken (Fr. Pat. 363764, 1906; U.S. Pat. 869636; Eng. Pat. 5039, 1906). In addition the following derivatives have been prepared: salts of inorganic acids and compounds with metallic salts by B. Grützner (Chem. Zentr. 1898, ii. 663); halogen derivatives by Horton (Ber. 1888, 1999), and Höhnel (Chem. Zentr. 1900, i. 409); bromoiodides and chloroiodides by Mouneyrat (Compt. rend. 136, 1472); the chromate by K. A. Hofmann (Ber. 1906, 3181). The products of decomposition have been studied by Ischidzu and Inouye (Chem. Zentr. 1906, i. 1087), Grassi-Cristaldi; and Di Franco by the catalytic hydrogenation with reduced nickel has obtained trimethylamine, ammonia, and methane (*ibid.* 1907, i. 237).

Methylene tetramethyl diamine

$CH_2[N(CH_3)_2]_2$

is prepared from formaldehyde and dimethylamine (Henry). It boils at 85°, and has sp.gr. 0·7491 at 18·7°.

Methylene tetraethyl diamine $CH_2[N(C_2H_5)_2]_2$, b.p. 166°–169° (168° Henry). Formed by the action of trioxymethylene, 6·5 parts, upon diethylamine, 29·2 parts (Kolotoff, J. Russ. Phys. Chem. Soc. 17, 244). It is an unpleasant-smelling liquid, insoluble in water, but very soluble in alcohol; sp.gr. 0·8105 at 18·7° (Henry, Ber. 1893 (Ref.) 934).

Methylene tetrapropyl diamine

$CH_2[N(C_3H_7)_2]_2$,

boils at 225°–230° with decomposition; sp.gr. 0·8014 at 18° (Henry).

Methylene thiocarbonate CH_2CS_3. A yellowish-white, amorphous powder insoluble in water, almost insoluble in alcohol, ether, or carbon disulphide, obtained by the action of methylene iodide upon sodium thiocarbonate in alcoholic solution (Husemann, Annalen, 126, 292). Is decomposed by ammonia into ammonium thiocyanate and methylene sulphide $(CH_2S)_3$.

Methylene thiocyanate $CH_2(CSN)_2$, m.p. 102°. From methylene iodide and potassium thiocyanate in alcoholic solution (Lermontoff, Ber. 1874, 1282). It forms needles or prisms which are almost insoluble in cold, moderately soluble in warm water, and easily soluble in alcohol or ether. By oxidation, *e.g.* by nitric acid, it yields methylene disulphonic acid.

Dimethylene dimethyl diamine

$(CH_2)_2N_2(CH_3)_2$.

A crystalline non-volatile body obtained by passing trimethylamine and hydrogen through a heated tube (Romeny, Ber. 1878, 835).

Dimethylene diethyl diamine

$(CH_2)_2N_2(C_2H_5)_2$,

b.p. 205°–208°. Obtained by heating in a sealed tube a mixture of trioxymethylene with ethylamine (Kolotoff, J. Russ. Phys. Chem. Soc. 17, 231). An oily liquid with an unpleasant odour, soluble in cold water or in alcohol. Is decomposed by hydrochloric acid into trioxymethylene and ethylamine.

β-METHYLADIPIC ACID *v.* PIMELIC ACID.

METHYLAL *v.* SYNTHETIC DRUGS.

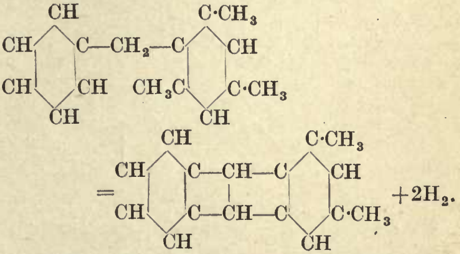
METHYLALLOXAN *v.* ALLOXAN.

METHYL-ANTHRACENE AND OTHER ALKYL DERIVATIVES OF ANTHRACENE. In order to obtain the higher homologues of anthracene, it has been found necessary in most cases to resort to synthetical methods, as very few of these substances have been met with in coal tar.

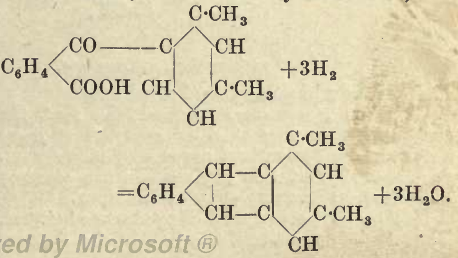
The methods usually employed are the following:—

(1) Elimination of hydrogen from the hydrocarbons of the C_nH_{2n-14}, or C_nH_{2n-16} series, by passing them through red hot tubes.

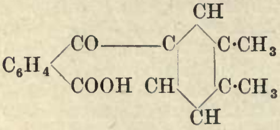
Benzyl mesitylene is thus converted into dimethylanthracene.



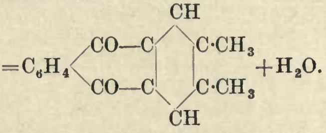
(2) By distilling *o*-ketonic acids with zinc-dust (Gresly, Annalen, 234–238); *m*-xyloyl-*o*-benzoic acid yields *m*-dimethylanthracene,



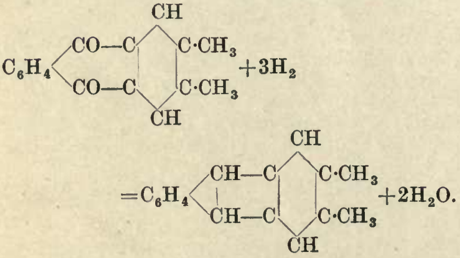
(3) By the action of sulphuric acid on *o*-ketonic acids (at about 125°), and subsequent reduction with zinc-dust and ammonia (Elbs, J. pr. Chem. 1890, 41, 1, &c.).



o-Xyloyl-*o*-benzoic acid.



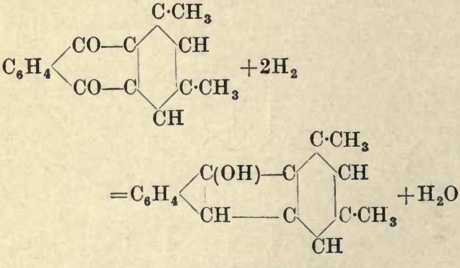
o-Dimethylanthraquinone.



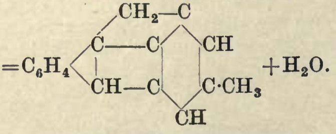
o-Dimethylanthracene.

This reaction cannot be successfully employed in a number of cases where one of the methyl groups is attached to the carbon atom next to the carbonyl group, as under these conditions anthracylene derivatives frequently result (*v.* Elbs, *l.c.* pp. 15–18).

Thus *m*-dimethylanthraquinone, on reduction with zinc-dust and ammonia, yields *m*-dimethylanthracylene and not *m*-dimethylanthracene.



m-Dimethylanthranol.

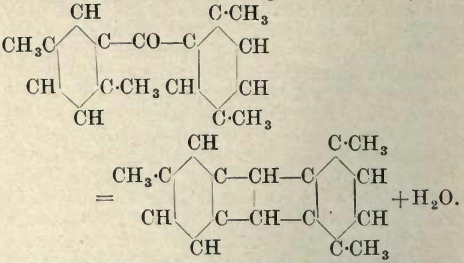


m-Dimethylanthracylene.

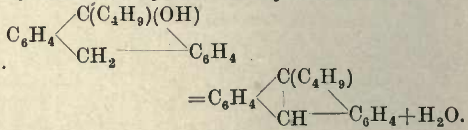
And similarly in a number of other cases.

It should, however, be remarked that the results of a number of Elbs' analyses of these anthracylene derivatives agree only so very approximately that this explanation can scarcely be looked on as completely satisfactory.

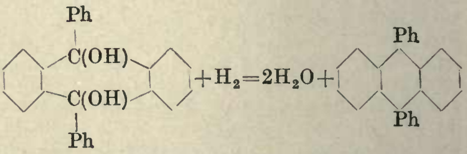
(4) By the prolonged boiling of some ketones. Thus di-*p*-xylyl ketone, when boiled for 6 hours on a reversed condenser yields (1,4,7) trimethylanthracene (Elbs and Olberg, Ber. 19, 409).



(5) The homologues of anthracene of the formula $C_6H_4(C_2HC_nH_{2n+1})C_6H_4$ are produced by boiling the alkylhydroanthranol with alcohol, hydrochloric acid, or picric acid. Thus *iso*butyl hydranthranol yields *iso*butylanthracene.

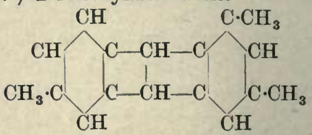


(6) Homologous arylanthracenes substituted in the γ position arise when the carbinols resulting from the action of magnesium aryl halogen compounds on anthraquinone and its derivatives are reduced. Thus diphenyl anthracene results when the corresponding carbinol is treated with zinc and acetic acid.

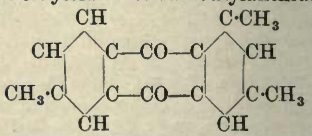


In their properties and reactions the homologues of anthracene behave very similarly to anthracene itself. On oxidation with chromic acid they yield corresponding anthraquinone derivatives, but in most cases the oxidation goes further and converts a portion of the anthraquinone into mono-, di-, or tricarboxylic acid, according to the number of side chains present, thus

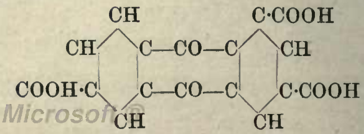
(1,3,6¹) Trimethylanthracene



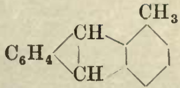
on oxidation yields first trimethylanthraquinone



and ultimately (1,3,6¹) anthraquinone tricarboxylic acid



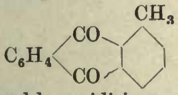
α-Methyl anthracene



According to Birukoff (Ber. 20, 2069), α-methyl anthracene may be prepared by the distillation of methyl erythroxy anthraquinone with zinc-dust. O. Fischer and Sapper (J. pr. Chem. 1911, [ii.] 83, 201), obtained only a small yield of the substance in this manner, the main product was anthracene. The best method of preparation, according to these authors, consists in heating 4-chloro-1-methylanthraquinone with zinc-dust at a very low red heat. α-methylanthracene crystallises in long, colourless needles, has m.p. 85°–86°, and is much more soluble in most solvents than anthracene or β-methylanthracene. Its solution in alcohol exhibits blue fluorescence. With picric acid, α-methylanthracene forms a compound crystallising in red needles, having m.p. 113°–115°.

4-Chloro-1-methyl anthracene is obtained on boiling 4-chloro-1-methylanthraquinone with zinc-dust and aqueous ammonia. It melts at 112° and, unlike the corresponding quinone, does not part with halogen on distillation with zinc-dust.

α-Methyl anthraquinone

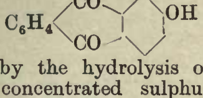


is readily prepared by oxidising α-methylanthracene with chromic acid in acetic acid solution, only small quantities of anthraquinone carboxylic acid being produced.

α-Methylanthraquinone crystallises from dilute acetic acid in small white needles, which, when exposed to light, become reddish-coloured. It melts at 170°–171°, is very readily soluble in alcohol or benzene, but difficultly soluble in glacial acetic acid.

It differs from its 4-hydroxy derivative in that it does not lose its methyl group on distillation with zinc dust. Since α- and β-methylanthracene are obtained on submitting many natural products to zinc-dust distillation, it is of importance to be able to distinguish between them. α-Methylanthraquinone differs from the corresponding β- compound in turning red on exposure to light. Moreover it is oxidised by dilute nitric acid at 160° to anthraquinone-1-carboxylic acid, which develops a rose coloration when heated with soda lime. Under these conditions anthraquinone-2-carboxylic acid gives a blue colour.

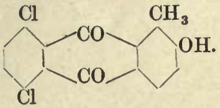
2-Hydroxy-1-methylanthraquinone



is obtained by the hydrolysis of its methyl ether with concentrated sulphuric acid. It crystallises from acetic acid in yellow needles which melt above 300°. Its red violet potassium salt is sparingly soluble in water.

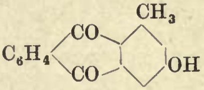
Methyl ether. This is the product of the action of sulphuric acid at 155° on 4′-methoxy-5′-methyl-2-benzoylbenzoic acid. It crystallises in canary yellow needles from methyl alcohol and melts at 184°. The substance is soluble in acetic acid or ethyl alcohol and may be sublimed. It forms a monobrom derivative, melting at 228°, and when dissolved in fuming nitric acid, yields a nitro-methoxy-methylanthraquinone which forms canary yellow needles, melting at 179°. The latter on reduction with stannous chloride in alkaline solution is converted into the corresponding amino compound. This amino-methoxy-methyl anthraquinone separates from methyl alcohol in bright red needles of m.p. 187°. Acetamino-methoxy-methyl anthraquinone crystallises from acetic acid in brown needles, melting at 204°. On energetic nitration, 2-methoxy-1-methylanthraquinone yields a trinitro derivative (Bentley, Gardner and Weizmann, Chem. Soc. Trans. 91, 1626).

5:8-dichlor-2-hydroxy-1-methylanthraquinone

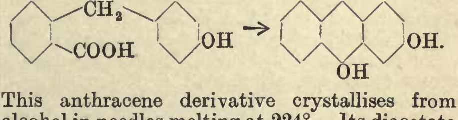


3 : 6 : dichlorphthalic anhydride condenses with *o*-tolyl methyl ether in presence of aluminium chloride and the product is probably 3 : 6-dichlor-3′-hydroxy-2-*o*-toluoyl benzoic acid. This acid on heating with fuming sulphuric acid and boric acid, is converted to the quinone which separates from acetic acid as a yellow flocculent powder, decomposing at 249°. It should be remarked that in the above methyl hydroxy compounds, the methyl group may have the position 3 (Walsh and Weizmann, Chem. Soc. Trans. 97, 691).

3-Hydroxy-1-methylanthraquinone



This quinone has been synthesised by the following series of operations (Bistrzycki and Yssel de Schepper, Ber. 31, 2795). The condensation of phthalic anhydride and *m*-cresol yields a benzoyl benzoic acid which, on reduction, furnishes 4-hydroxy-2′-methyl diphenyl methane carboxylic acid. This compound, on treatment with sulphuric acid, is changed with loss of the elements of water into 1-methyl-3 : 10-dihydroxy anthracene thus :—



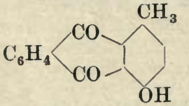
This anthracene derivative crystallises from alcohol in needles melting at 224°. Its diacetate forms microprisms from benzene and melts at 171°–173°. On oxidation with chromic acid in acetic acid solution, this diacetate yields the acetyl derivative of 3-hydroxy-1-methyl anthraquinone. The derivative crystallises from alcohol in yellow needles, melting at 130°–135°. and on hydrolysis with alcoholic potash the parent quinone is produced.

3-hydroxy-1-methylanthraquinone occurs in needles, sublimes at 200° and melts at 299°–300°. It dissolves in ammonia to an orange solution.

5 : 8 - dichlor - 3 - methoxy - 1 - methylanthraquinone (Walsh and Weizmann, *l.c.*) is obtained

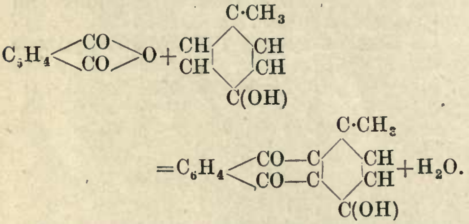
in small yield by treatment of the benzoyl benzoic acid from dichlorphthalic anhydride and *m*-tolyl methyl ether with sulphuric acid. The yellow compound crystallises from acetic acid and decomposes at 236°.

4-Hydroxy-1-methylanthraquinone



(Methyl erythroxyanthraquinone)

is produced when a mixture of phthalic anhydride and *p*-cresol is heated with concentrated sulphuric acid (Birukoff, *l.c.*).



Preparation.—5 parts of phthalic anhydride, 2 parts of *p*-cresol, and 15 parts of concentrated sulphuric acid are heated to 160° for ten minutes, the product poured into water, the precipitate well washed with boiling water, and extracted with boiling dilute caustic potash solution. 4-Hydroxy-1-methylanthraquinone is obtained from the alkaline solution by the addition of hydrochloric acid in yellow flocks, which are readily purified by recrystallisation from glacial acetic acid. The pure substance is thus obtained in beautiful dark-brown needles, melting at 175°.

This quinone may also be obtained by the hydrolysis of its methyl ether, either by means of acetic acid and hydrochloric acid at 100° under pressure or with concentrated sulphuric acid. Further, the condensation of phthalic anhydride and *p*-cresol is well effected by fusion with boric acid. A benzoyl benzoic acid results, and this, by further treatment with sulphuric acid, yields the quinone (Bentley, Gardner and Weizmann, *l.c.*).

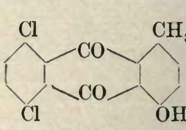
4-Hydroxy-1-methylanthraquinone is almost insoluble in ammonia and sodium carbonate solution, readily soluble in caustic potash solution with a red coloration; with baryta or lime-water insoluble brick-red lakes are produced. It dissolves in sulphuric acid with an orange-yellow colour, sublimes very easily, and in all its reactions, and also in its absorption spectrum, shows great similarity with erythroxyanthraquinone.

Fusion with potash converts it with difficulty into a colouring matter which is probably α-methylalizarin.

The *acetate* crystallises from acetic acid in yellow needles, which melt at 179°–180°.

Methyl ether. O Fischer and Sapper (J. pr. Chem. 1911, [ii.], 83, 201) obtained this substance by the action of methyl alcoholic potassium hydroxide at 100° under pressure on 1-methyl-4-chloroanthraquinone. They described it as consisting of yellow needles of m.p. 128° and reddening under the action of light. Bentley, Gardner and Weizmann (*l.c.*) condensed phthalic anhydride with *p*-tolylmethylether and so obtained 2′-methoxy-5′-methyl-2-benzoyl benzoic acid. The action of sulphuric acid at 150° on this compound led to the formation of the methyl ether of 4-hydroxy-1-methyl-anthraquinone described as orange-yellow needles from methyl alcohol, melting at 171°.

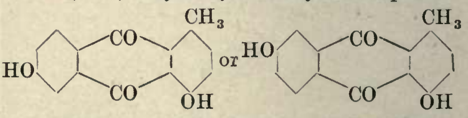
5 : 8-dichlor-4-hydroxy-1-methylanthraquinone



3 : 6 : dichlorphthalic anhydride was condensed by means of aluminium chloride with *p*-tolyl methyl ether. The resulting 3 : 6 : dichloro-5′-hydroxy-2-toluoyl-benzoic acid was heated with fuming sulphuric acid (10 p.c. SO_3) in presence of boric acid for a few minutes at 130°. The quinone separates from acetic acid in micro-needles of m.p. 259°. Its brilliant red solution in concentrated sulphuric acid exhibits purple fluorescence. Its acetyl derivative forms lemon-yellow needles, melting at 181°.

When heated with sodium phenoxide and copper powder, one chlorine atom is replaced by phenoxyl.

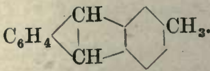
4:6-(or 7) dihydroxy-1-methylanthraquinone



4-Hydroxyphthalic acid or its anhydride, when fused with boric acid and *p*-cresol, yields a benzoyl benzoic acid from which, by the further action of sulphuric acid, this quinone is obtained. The substance crystallises as a yellow powder from alcohol, and melts at 244°–246°.

A methyl dimethoxy anthraquinone, which is probably, although not necessarily, the dimethyl ether of the above quinone, is obtained by condensing 4-methoxy phthalic anhydride with *p*-tolylmethyl ether by means of aluminium chloride and subsequently treating the benzoyl benzoic acid so produced with sulphuric acid (containing 60 p.c. SO_3) in presence of boric acid below 40°. The substance crystallises from acetic acid and melts at 141°. One methoxyl group is hydrolysed by the action of sulphuric acid at 110°.

β-Methylanthracene



This hydrocarbon is found in varying quantities, together with anthracene and phenanthrene, in the fraction of coal tar which distils above 340°.

It may be synthetically prepared by the following reactions.

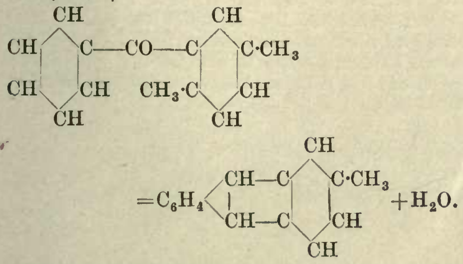
1. By passing the vapours of ditolylmethane (Weiler, Ber. 7, 1185) $CH_2(C_6H_4CH_3)_2$, ditolylethane (Fischer, *ibid.* 7, 1195),

$$CH_3\text{-}CH(C_6H_4CH_3)_2,$$

or of oil of turpentine (Schultz, *ibid.* 10, 117) through a red-hot tube.

It is best in this reaction to employ ditolylethane since the hydrocarbon from ditolylmethane is mixed with anthracene.

2. By boiling *p*-xylylphenylketone for several days on a reflux apparatus (Elbs, J. pr. Chem. 1890, 41, 3).

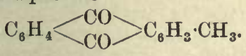


3. By the distillation of chrysophanic acid $C_{15}H_{10}O_4$, emodin $C_{15}H_{10}O_5$ (Liebermann, Annalen, 183, 163), colophonium, benzoe resin (Ciamician, Ber. 11, 273), chrysarobin $C_{30}H_{26}O_7$ (Liebermann and Seidler, Annalen, 212, 34) and methylquinizarine $C_{15}H_{10}O_4$ (Nietzki, Ber. 10, 2013) with zinc-dust.

Preparation (Japp and Schultz, Ber. 10, 1049). The high boiling distillate of coal tar, known as crude phenanthrene, is freed from the greater part of the anthracene it contains by oxidation with potassium dichromate and sulphuric acid. The dark-brown mass is extracted with hot alcohol, the well-cooled solution allowed to deposit as much anthracene and phenanthrene as possible, the mother-liquors which contain the methylanthracene evaporated and the residue repeatedly recrystallised from alcohol.

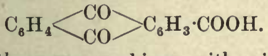
β-Methylanthracene crystallises from alcohol in pale yellow needles and melts at 202°–203°. It sublimes readily when heated continuously at 100°. It is difficultly soluble in ether, alcohol, glacial acetic acid, acetone, and light petroleum, readily soluble in benzene, chloroform, and carbon disulphide.

Oxidation with nitric acid converts it into methylanthraquinone



$$C_6H_4\!<\!\begin{matrix}CO\\CO\end{matrix}\!>\!C_6H_3\cdot CH_3.$$

Chromic acid oxidises it for the most part direct to anthraquinone-2-carboxylic acid

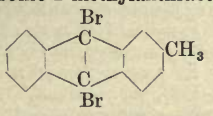


$$C_6H_4\!<\!\begin{matrix}CO\\CO\end{matrix}\!>\!C_6H_3\cdot COOH.$$

Methylanthracene combines with picric acid, forming a compound which crystallises in large red needles; alcohol and water decompose this compound.

When sunlight acts on a benzene solution of the hydrocarbon, a dimeride, bisβ-methylanthracene, is formed (Orndorff and Megraw, Amer. Chem. J. 22, 152). It crystallises in rhombic crystals from toluene and melts at 228°. The substance is sparingly soluble and is converted on melting or solution in xylene into β-methylanthracene.

9 : 10-**Dibromo-2-methylanthracene**

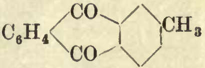


is produced by treating methylanthracene in CS_2 with bromine; it crystallises from glacial acetic acid in yellow needles, m.p. 142°–143°.

The position of the halogen atoms is proved by the oxidation of the substance to 2-methylanthraquinone.

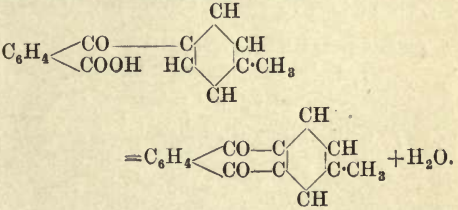
Tetrabromomethylanthracene $C_{15}H_8Br_4$ is formed when dibromomethylanthracene is treated with bromine. It crystallises from toluene in yellow needles. Oxidation with nitric acid converts this compound into dibromomethylanthraquinone $C_{15}H_8Br_2O_2$.

β-Methylanthraquinone



(O. Fischer, Ber. 8, 675) is obtained by boiling methylanthracene in alcoholic solution with nitric acid, or by carefully oxidising the hydrocarbon with CrO_3, in which latter case, however, considerable quantities of anthraquinone and anthraquinone carboxylic acid are also formed.

It has also been isolated from the by-products which accumulate in the manufacture of anthraquinone (Wachendorff and Zincke, Ber. 10, 1485; Börnstein, *ibid.* 15, 1820). This substance is identical with the methylanthraquinone which is obtained synthetically by heating *p*-methyl benzoylbenzoic acid with concentrated sulphuric acid (Gresly, Annalen, 234, 239).



This latter preparation is carried out in the following manner:—

The powdered acid is slowly added to 7 or 8 times its weight of concentrated sulphuric acid, and the mixture gradually heated until at the end of half an hour the temperature has risen to 120°–125°.

The clear dark brownish-red coloured solution is kept at this temperature for about an hour, allowed to cool and poured into much water. Steam is passed through the liquid for some time, the precipitate collected, washed well first with water, and lastly with dilute ammonia, dried, and the greenish-yellow mass purified by recrystallisation from a mixture of xylene and alcohol. Yield 70–75 p.c. of theory.

β-Methylanthraquinone sublimes in yellow needles, m.p. 176°–177°; moderately soluble in ether, acetone, chloroform, or hot alcohol; difficultly soluble in glacial acetic acid and benzene.

Dibromomethylanthraquinone is obtained by the action of bromine at 130°–140° on β-methylanthraquinone. It is colourless and melts at 219°–220° (O. Fischer, J. pr. Chem. 1909, [ii.] 79, 555).

ω-Dichloro-β-methylanthraquinone is obtained by chlorination of methyl anthraquinone. The substance melts at 200° and is converted by the action of sulphuric acid (66° Baumè) at 130° into β-anthraquinone aldehyde (Badische Anilin und Soda Fabrik, D. R. P. 174984).

Methylanthraquinone disulphonic acid (O. Fischer, *l.c.*) $C_{15}H_8(HSO_3)_2O_2$.

Preparation. — Methylanthraquinone is heated with 5–6 parts of fuming sulphuric acid for several hours at 250°–270°. The alkali salts and the barium and calcium salts of this acid are soluble in water. Fusion with potash converts the acid into methylalizarin.

Nitromethylanthraquinone

$C_{15}H_9NO_4$ or $CH_3{\cdot}C_{14}H_6(NO_2)O_2$.

Preparation.—Methylanthraquinone (2 parts) is dissolved in concentrated H_2SO_4 (12–14 parts), and to the resulting solution KNO_3 (1 part) is slowly added. The product after standing 24 hours is carefully mixed with water, the precipitate collected, and extracted repeatedly with alcohol until the filtrate is only slightly yellowish-coloured. The resulting nitromethylanthraquinone is purified by recrystallisation from acetic acid (Römer and Link, Ber. 16, 695), from which solvent it is obtained in yellow needles melting at 269°–270°. It is difficultly soluble in alcohol, ether, benzene, chloroform, glacial acetic acid, and ethyl acetate, readily soluble in nitrobenzene. It dissolves in sulphuric acid, producing a yellow solution which on warming turns brown. Water precipitates from this solution a purple precipitate, which dissolves in alkalis with a violet-blue colour. Nitromethylanthraquinone sublimes in small almost colourless needles. It is not decomposed by boiling caustic potash solution.

Aminomethylanthraquinone

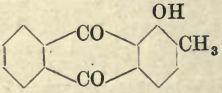
$C_{15}H_{11}NO_2$ or $CH_3{\cdot}C_{14}H_6(NH_2)O_2$

is readily produced by the reduction of nitromethylanthraquinone with $SnCl_2$ (Römer and Link, *l.c.*). The freshly precipitated nitro compound is added in small quantities at a time to a dilute solution of $SnCl_2$ in KOH, and the product heated nearly to boiling. The resulting precipitate, which must dissolve completely in excess of cold HCl, is purified by recrystallisation from dilute HCl.

Aminomethylanthraquinone crystallises in glittering red needles which melt at 202°, and sublime on heating in long dark-red needles. It is almost insoluble in water, readily soluble in alcohol, ether, chloroform, benzene, and glacial acetic acid. Boiling with hydriodic acid and phosphorus converts it into aminomethylanthranol; at 150°, however, aminomethylanthracenedihydride $CH_3{\cdot}C_{14}H_{10}NH_2$ results.

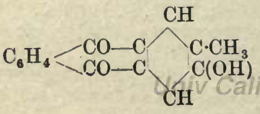
The *acetyl-derivative* $CH_3{\cdot}C_{14}H_6O_2NH(C_2H_3O)$ crystallises from glacial acetic acid in yellow needles, m.p. 176°–177°.

1-Hydroxy-2-methylanthraquinone (Weizmann, Bentley and Gardner, *l.c.*)

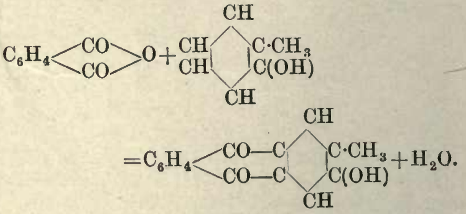


Phthalic anhydride condenses with orthocresol in presence of boric acid at 170° and yields 2′-hydroxy-3′-methyl-2-benzoylbenzoic acid. The yellow solution of this substance in concentrated sulphuric acid goes red on heating and yields on dilution this hydroxyanthraquinone. It forms yellow needles on crystallisation from acetic acid and melts at 184°–185°.

3-Hydroxy-2-methylanthraquinone

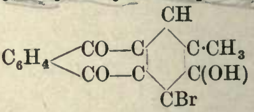


Preparation (Fraude, Annalen, 202, 613).—By heating 2 parts of *o*-cresol, 3 parts phthalic anhydride, and 100 parts of sulphuric acid at 160° for two days. The product is poured into water, extracted repeatedly with ether; the ether distilled off, the residue dissolved in dilute soda, acidified with HCl, and the precipitate purified by sublimation and recrystallisation from alcohol.



Hydroxymethylanthraquinone melts at 260°–262°, is readily soluble in alcohol, ether, and acetic acid; it dissolves in alkalis, also in lime and baryta water, forming a dark reddish-brown solution. When strongly heated it sublimes in golden-yellow leaflets.

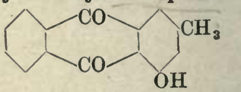
Bromohydroxymethylanthraquinone



is obtained by heating 4 parts of dibromo-*o*-cresol phthaleïne ($C_{22}H_{16}Br_2O_4$) with 1 part of phthalic anhydride and 200 parts of sulphuric acid at 150° for five hours.

Small yellow needles, m.p. 205°. Fusion with potash converts this substance into *α*-methylalizarin.

4-Hydroxy-2-methylanthraquinone



Bentley, Gardner and Weizmann (*l.c.*) obtained this quinone in a manner analogous to the preparation of 1-hydroxy-2-methylanthraquinone, by substituting *m*- for *o*-cresol. It melts at 178° and consists of yellow needles which are crystallised from acetic acid. A quinone probably identical was obtained by Römer and Link (Ber. 16, 700) from the aminomethylanthraquinone described above.

Preparation.—Aminomethylanthraquinone is dissolved in sulphuric acid, the solution mixed with small quantities of water until the resulting precipitate becomes reddish-coloured.

The well-cooled product is slowly mixed with a solution of KNO_2 until the precipitate becomes light yellow and free nitrous acid is evolved, then an equal volume of water is added and the whole heated to boiling.

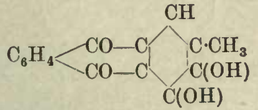
The precipitate is collected, dissolved in boiling dilute caustic potash solution, precipitated with HCl, and recrystallised from alcohol.

Hydroxymethylanthraquinone crystallises from alcohol in orange-yellow needles which melt at 177°–178°, and sublime in long thin yellow plates when carefully heated. It is almost insoluble in water, difficultly soluble in alcohol, readily soluble in ether, and benzene. Cold caustic potash solution dissolves it sparingly.

Fused with potash a small quantity of a colouring matter is produced which dissolves in alkalis with colorations similar to those produced by alizarin. Hydroxymethylanthraquinone, if freshly precipitated, dissolves in boiling lime or baryta water, but is insoluble in sodium carbonate or solution of alum. Its alcoholic solution is not precipitated by alcoholic lead acetate.

The *acetate* $C_{17}H_{12}O_4$ or $CH_3{\cdot}C_{14}H_6O_2(C_2H_3O_2)$ crystallises from alcohol in orange-yellow plates which melt at 177°.

Dihydroxymethylanthraquinone (*a*-methylalizarin)



is readily prepared by fusing methylanthraquinone disulphonic acid (O. Fischer, *l.c.*), hydroxymethylanthraquinone, or bromohydroxymethylanthraquinone (Fraude, Annalen, 202, 166) with potash. The mass is dissolved in water, acidified with HCl, and the precipitate purified by sublimation. Orange-yellow needles, m.p. 250°–252°, moderately soluble in alcohol, ether, and acetone. The calcium and barium salts are insoluble blue precipitates.

The absorption spectrum of a solution of this substance in concentrated sulphuric acid is represented in Fig. 1.

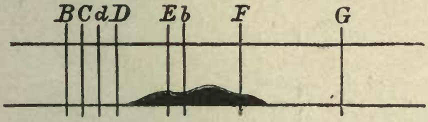
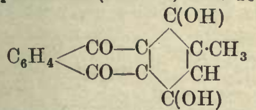


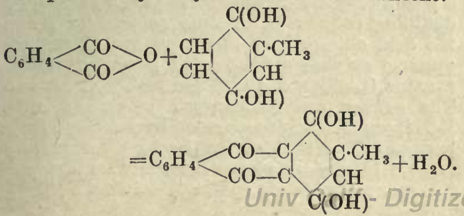
FIG. 1.

It corresponds very closely with that of alizarin itself (Liebermann and Kostanecki, Ber. 19, 2330). Methylalizarin dyes mordanted cloth similarly to alizarin, but according to some authorities the tinctorial power of methylalizarin is much inferior to that of alizarin, hence the introduction of this substance into artificial alizarin is avoided by the alizarin manufacturer as much as possible.

Methylquinizarin (Nietzki, Ber. 10, 2012)



This isomeride of methylalizarin is produced by heating a mixture of hydrotoluquinone and phthalic anhydride with 8–10 parts of sulphuric acid at 130°–150° for two to three hours. The product is treated with water, the precipitate repeatedly extracted with boiling water, and purified by recrystallisation from benzene.



Methylquinizarin crystallises in long fine bent needles which melt at 160° and sublime with slight decomposition. The solutions in ether and alcohol are fluorescent. Distilled with zinc-dust methylanthracene is formed.

The absorption spectrum of methylquinizarine dissolved in sulphuric acid is represented in Fig. 2—

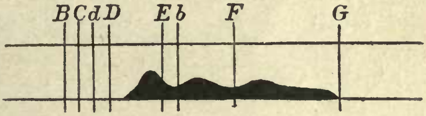
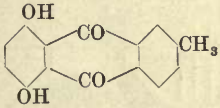


FIG. 2.

and is very closely allied to that of quinizarin itself.

Methylquinizarin when treated with acetic anhydride yields a *diacetate* $C_{15}H_8(C_2H_3O)_2O_4$, which crystallises in yellow needles, m.p. 185°.

5 : 8-Dihydroxy-2-methylanthraquinone (von Niementowski, Ber. 33, 1634).



This substance is prepared by heating together equimolecular quantities of 1-methyl-3 : 4-phthalic anhydride and hydroquinone with 6 parts of concentrated sulphuric acid for 5 to 10 hours at 140°–160°. It forms orange leaflets from alcohol mixed with benzene, or it may be crystallised from a large quantity of alcohol and obtained in beautiful ruby-red needles. It has the curious property of melting at 165°, resolidifying and melting again at 175°. The sublimed quinone melts at 175°. The solution in dilute caustic soda is violet red.

Diacetyl derivative.—This is readily produced by the action of sodium acetate and acetic anhydride. It crystallises from benzene, is intensely yellow, and melts at 204°.

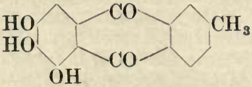
6 : 7-Dihydroxy-2-methylanthraquinone and **5 : 6- (or 7 : 8) dihydroxy-2-methylanthraquinone** (Niementowski, *l.c.*).

The 6 : 7-dihydroxy compound is the main product when catechol is substituted for hydroquinone in the above preparation. It crystallises from acetic acid in yellow micro-needles and melts with decomposition at 320°–340°. Its diacetate forms straw-yellow needles from alcohol, m.p. 208°. The 5 : 6- (or 7 : 8) dihydroxy compound is produced in small quantities in the same reaction. It crystallises from a little benzene in orange-red needles and melts and sublimes at 216°. Its diacetate crystallises from alcohol in groups of transparent yellow needles; m.p. 176°.

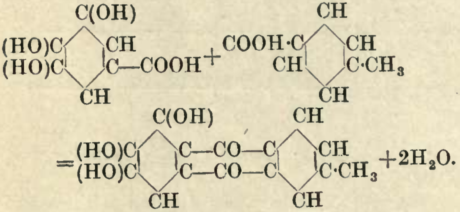
4 : 6- (or 7 :) **Dihydroxy-2-methylanthraquinone** (Bentley, Gardner, and Weizmann, *l.c.*).

4-Hydroxyphthalic anhydride and *m*-cresol, when fused with boric acid at 180°, yield a benzoyl benzoic acid in which the cresolic hydroxyl is in the ortho- position to carboxyl. With fuming sulphuric acid the substance condenses to the quinone, which separates from glacial acetic acid as a yellow crystalline powder of m.p. 284°.

β-Methylanthragallol, 5:6:7-trihydroxy-2-methylanthraquinone



Formation.—By heating a mixture of gallic acid and *p*-toluic acid to 130° (Cahn, Annalen, 240–284):



Sublimes in orange-red needles, m.p. 275°. Its other properties are very similar to those of anthragallol itself. The absorption spectrum of its solution in sulphuric acid is shown in Fig. 3.

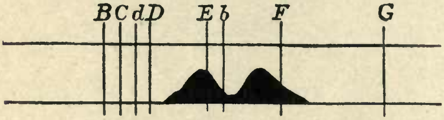
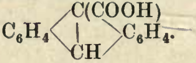


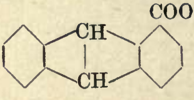
Fig. 3.

Considerable confusion exists in the literature with respect to the anthracene and anthraquinone carboxylic acids.

Anthracene-10-carboxylic acid (Liebermann, Graebe, Ber. 2, 678)  $C_6H_4\left\langle\begin{matrix}C(COOH)\\ |\\ CH\end{matrix}\right\rangle C_6H_4$. The chloride of this acid is produced by heating anthracene with $COCl_2$ to 180°–200°.

The acid crystallises from alcohol in long, silky, pale-yellow needles, which melt at 206° with decomposition. It is almost insoluble in cold water, readily soluble in alcohol. On distillation with soda lime it decomposes into CO_2 and anthracene. The salts are mostly soluble in water.

Anthracene-1-carboxylic acid

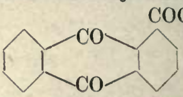


The nitrile of this acid is produced by distilling sodium anthracene α-monosulphonate with potassium cyanide (Liebermann and Pleus, Ber. 37, 646; see also Liebermann and Rath, *ibid.* 8, 246, and Dienel, *ibid.* 39, 926). The nitrile crystallises from alcohol in yellow leaflets, m.p. 126°, and is slowly hydrolysed by alcoholic potash with formation of the potassium salt of anthracene-1-carboxylic acid.

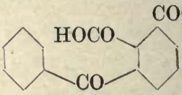
The acid may also be prepared by the reduction of anthraquinone-1-carboxylic acid with zinc-dust and ammonia (Graebe and Blumenfeld, *ibid.* 30, 1118). The acid forms yellow needles or prisms on crystallisation from alcohol and melts at 245°. It sublimes undecomposed in needles, is sparingly soluble in benzene and ether, readily soluble in alcohol and glacial acetic acid, insoluble in water. Distillation with soda lime decomposes it into CO_2 and anthracene. Chromic acid oxidises it to anthraquinone carboxylic acid $C_{15}H_8O_4$. The acid and its salts possess a blue fluorescence; the latter are mostly readily soluble in water. The Ba and Ca salts dried at 130° are yellow amorphous powders. The Pb salt is a flocky precipitate.

The amide of the acid is produced by the action of ammonia on the yellow oily chloride. It crystallises from alcohol and melts at 260° (Graebe, Blumenfeld), 256° (Dienel).

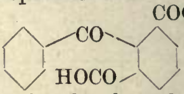
Anthraquinone-1-carboxylic acid



This acid is prepared by oxidising 1-methylanthracene with chromic acid (Liebermann and Bischoff, Ber. 13, 49), or by the hydrolysis of its nitrile (see below). A method which leaves no doubt as to its constitution has also been employed (Graebe and Leonhardt, Annalen, 290, 231; Graebe and Blumenfeld, Ber. 30, 1115). Hemimellitic anhydride and benzene in presence of aluminium chloride yield a mixture of 3-benzoylphthalic acid



and 2-benzoyl*iso*phthalic acid



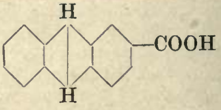
Each of these acids, when heated with sulphuric acid at 145°–150°, is changed to anthraquinone-1-carboxylic acid.

It crystallises from glacial acetic acid in long pale-yellow needles, which melt at 293°–294°. With caustic potash and zinc-dust, it develops a blood-red coloration. The barium salt is sparingly soluble. Its methyl ester is sparingly soluble in cold methyl alcohol and has m.p. 189°. The ethyl ester from the acid and alcoholic hydrochloric acid has m.p. 169°.

Nitrile (Dienel, Ber. 39, 926). This derivative is obtained by the distillation of sodium anthraquinone α-sulphonate with potassium cyanide, or by oxidising the nitrile of anthracene-1-carboxylic acid. It forms gold yellow leaflets of m.p. 216°–217°.

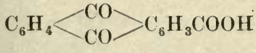
The amide has m.p. 280°.

Anthracene-2-carboxylic acid



The nitrile of this acid is obtained (together with a small quantity of the nitrile of the 1-acid) by distilling sodium anthracene sulphonate (from the acid obtained by the reduction of anthraquinone sulphonic acid) with potassium ferrocyanide (Liebermann and Bischoff, Ber. 13, 47). The nitriles are decomposed by boiling with KOH, and the acids separated by means of their barium salts; that of the 1-acid being readily soluble in water, whereas barium anthracene 2-carboxylate is very sparingly soluble.

The same acid is produced by the reduction of anthraquinone-2-carboxylic acid



$$C_6H_4<\begin{matrix}CO\\CO\end{matrix}>C_6H_3COOH$$

with zinc-dust and ammonia (Börnstein, Ber. 16, 2610).

Anthracene-2-carboxylic acid crystallises from alcohol in small yellow plates, which melt at about 280°, and sublime at a higher temperature in plates. It is sparingly soluble in $CHCl_3$, almost insoluble in CS_2 and benzene, less soluble in alcohol and glacial acetic acid than the β-acid. The alcoholic solution possesses an intense blue fluorescence. Reduction with sodium amalgam or hydriodic acid converts this acid into three acids, $C_{15}H_{12}O_2$, $C_{15}H_{14}O_2$, and $C_{15}H_{16}O_2$. Chlorine led into the solution in $CHCl_3$ produces first γ-chloranthracene carboxylic acid and then dichloranthracene (m.p. 209°). Bromine behaves similarly.

The *Sodium salt* is difficultly soluble in cold water, and crystallises in glittering flakes. The solutions fluoresce blue.

The *Barium salt* is almost insoluble in cold water, and only very sparingly soluble in hot.

Methyl ester (Behla, Ber. 20, 703)

$$C_{15}H_9O_2CH_3$$

crystallises in yellow prisms; m.p. 111°.

Ethyl ester (Liebermann, Bischoff, Ber. 13, 49) $C_{15}H_9O_2C_2H_5$ melts at 134°, and is readily soluble in alcohol. Both these salts distil without decomposition.

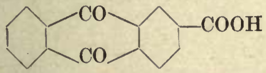
Chloride (Börnstein, *l.c.*) $C_{15}H_9OCl$ crystallises from benzene in yellow warts; m.p. not given. Readily soluble in alcohol, ether, $CHCl_3$ and CS_2. Decomposed only by boiling water.

Amide $C_{15}H_9ONH_2$ crystallises from glacial acetic acid in plates; m.p. 293°–295°. Insoluble in water, CS_2, $CHCl_3$, or benzene. Difficultly soluble in alcohol. The solutions fluoresce blue.

γ-Chloranthracene carboxylic acid (Behla, *l.c.*) (*v. supra*) crystallises from benzene in needles; m.p. 258°–259°, being at the same time decomposed into chloranthracene and CO_2.

γ-Bromanthracene carboxylic acid (Behla, *l.c.*) crystallises from alcohol in long, greenish-yellow needles; melts at 266°, being converted into CO_2 and bromoanthracene.

Anthraquinone-2-carboxylic acid



is produced by oxidising 2-methylanthracene or the corresponding quinone or carboxylic acid (Liebermann, Rath, Ber. 8, 248). It may also be obtained by the oxidation of anthranol β-carboxylic acid with potassium permanganate in alkaline solution (Limpricht, Annalen, 309, 122).

According to the Höchster Farbwerke (D. R. P. 80403), it is conveniently prepared by heating benzophenone-2 : 4′-dicarboxylic acid with sulphuric acid.

Preparation.—Methylanthraquinone (1 part) is dissolved in concentrated sulphuric acid (6 parts), mixed then with water (1 part), and $K_2Cr_2O_7$ ($2\frac{1}{2}$ parts) slowly added. The mass is warmed to 110°–120° for a short time, filtered, the precipitate washed with water, and boiled out with dilute ammonia. The excess of ammonia is evaporated off, the solution filtered, and precipitated with HCl (Börnstein, Ber. 16, 2609; *v.* also Liebermann and Glock, *ibid.* 17, 888).

Anthraquinone-2-carboxylic acid crystallises from alcohol in yellow prisms, which melt at 290°–292°, and sublime undecomposed when carefully heated. It is almost insoluble in ether, benzene, chloroform, and excess of caustic soda, difficultly soluble in glacial acetic acid and absolute alcohol, readily soluble in acetone. Gives with zinc-dust and KOH the anthraquinone reaction; reduction with zinc-dust and ammonia converts it into anthracene-2-carboxylic acid. Distillation over red-hot asbestos decomposes it into CO_2 and anthraquinone. It dissolves in sodium acetate and ammonium oxalate, and is not reprecipitated on the addition of acetic acid. Fusion with soda converts it into oxyanthraquinone carboxylic acid $C_{15}H_8O_5$.

The *Calcium salt* $Ca(C_{15}H_7O_4)_2$ and the *barium salt* $Ba(C_{15}H_7O_4)_2$ are sparingly soluble.

Ethyl ester (Liebermann and Glock, Ber. 17, 890) $C_{15}H_7O_4{\cdot}C_2H_5$ is formed by the action of alcohol on the chloride. It crystallises in needles, melts at 147°, and is readily soluble in alcohol.

Chloride $C_{15}H_7O_3Cl$ is produced by treating the acid with PCl_5. Crystallises from benzene in needles which melt at 147°.

Amide $C_{14}H_7O_2CONH_2$ is obtained by passing NH_3 into a benzene solution of the chloride. It crystallises from a mixture of glacial acetic acid and benzene in needles, which melt at 280°, and are difficultly soluble in alcohol and benzene.

Anilide crystallises from xylene in needles, m.p. 258°–260°.

Nitroanthraquinone carboxylic acid

$$C_{14}H_6(NO_2)O_2{\cdot}COOH$$

is produced by mixing the solution of the acid in concentrated sulphuric acid with nitric acid. Crystallises from glacial acetic acid in small needles, which melt above 300°. Gives with sulphuric acid a violet colouring matter.

Dinitroanthraquinone-2-carboxylic acid (Limpricht, Annalen, 309, 122) is obtained by the oxidation of the corresponding anthranol with chromic acid in acetic acid solution. It forms yellow needles from alcohol and melts at 315°.

Under the heading methylanthracene, besides *o*- and *m*-methylanthracene two other substances are to be found in chemical literature.

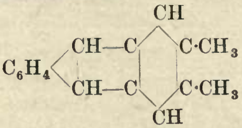
*iso***Methylanthracene** (Börnstein, Ber. 15, 1821) obtained by digesting *iso*methylanthraquinone with zinc-dust and ammonia, and by distilling *p*-toluene phthaloylic acid (Gresly, Annalen, 234, 238), with zinc-dust, is evidently identical with *m*-methylanthracene.

Methanthrene $C_{15}H_{12}$ (Oudemans, J. pr. Chem. [ii.] 9, 416), obtained by distilling podocarpinic acid $C_{17}H_{22}O_3$ with zinc-dust, is probably not an anthracene derivative at all. It melts at 117°, and gives on oxidation with CrO_3 and acetic acid, methanthraquinone $C_{15}H_{10}O_2$ which crystallises from 70 p.c. alcohol in orange-red needles melting at 187°.

It therefore possesses more the properties of a phenanthrene than of an anthracene derivative.

Dimethylanthracenes.

o-Dimethylanthracene

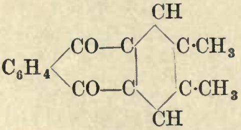


(Elbs, J. pr. Chem. 1890, 41, 5) is readily prepared by the reduction of the corresponding (2, 3) dimethylanthraquinone with zinc-dust and ammonia.

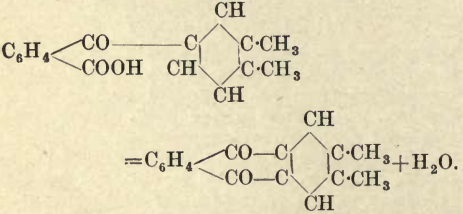
5 grams of the quinone, 30 grams zinc-dust, and 500 c.c. aqueous ammonia (equal parts of concentrated ammonia solution and water), are heated to boiling until the red liquid which is produced at first has become colourless. The mass is then filtered, the residue washed with hot water, dried in a water oven, and repeatedly extracted with boiling alcohol. The clear alcoholic extract deposits on cooling yellowish plates of dimethylanthracene. o-Dimethylanthracene melts at 246°, and sublimes in colourless plates which possess a bluish-green fluorescence. It is readily soluble in benzene and hot alcohol, but difficultly soluble in cold alcohol.

The picric acid compound crystallises in long garnet-red needles; it is readily decomposed by alcohol.

o- or (2, 3) **Dimethylanthraquinone**

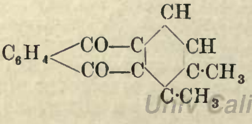


is obtained synthetically by heating o-xyloyl-o-benzoic acid with H_2SO_4.



1 part of o-xyloyl-o-benzoic acid is dissolved in 6 parts of warm concentrated H_2SO_4, and the mixture heated at 128° for a quarter to half an hour, the dark-coloured solution poured into a dish, and placed next to a dish of water. As the solution becomes dilute the quinone crystallises out, the operation being complete in 3–4 days.

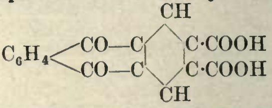
The precipitate is collected, washed with water and dilute ammonia, and purified either by sublimation or recrystallisation from xylene; o-dimethylanthraquinone is thus obtained in long yellow needles which melt at 183°. It is readily soluble in hot xylene, benzene, and alcohol, and is readily reduced by zinc-dust and ammonia to o-dimethylanthracene, hence its constitution is probably that given above, and not



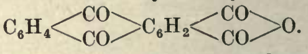
(Compare action of zinc-dust and ammonia on dimethylanthraquinones with a CH_3 group in the 1 or 4 position.)

A dimethyl anthraquinone, which is probably identical with this, is obtained by oxidising dimethyl anthranol with chromic acid in acetic acid solution (Limpricht and Martens, Annalen, 312, 103). It forms yellow needles from alcohol and melts at 200°.

Anthraquinone-2 : 3-dicarboxylic acid



is produced by heating o-dimethylanthraquinone (3 grams) with 20–25 c.c. of nitric acid (sp.gr. 1·1) in a sealed tube at 210°–220° for five hours. It crystallises in yellow needles, melts at 340°, and when strongly heated sublimes in yellow plates, which melt at 290°, and consist now of anthraquinone dicarboxylic anhydride.



$$C_6H_4{<}\begin{matrix}CO\\CO\end{matrix}{>}C_6H_2{<}\begin{matrix}CO\\CO\end{matrix}{>}O.$$

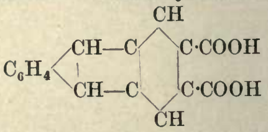
Ammonium salt. Red amorphous mass, easily soluble in water.

Calcium salt. Light red precipitate, almost insoluble in water.

Lead salt. Light red precipitate, almost insoluble in water.

Silver salt. Light red precipitate; is decomposed on heating into CO_2, Ag, and anthraquinone.

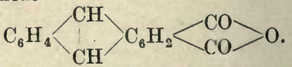
Anthracene-2 : 3-dicarboxylic acid



is readily prepared by treating the solution of the ammonium salt of anthraquinone dicarboxylic acid with zinc-dust and ammonia until the red solution becomes yellowish-green coloured; and then precipitating the clear solution with HCl.

Anthracene-o-dicarboxylic acid crystallises from alcohol in small yellowish-green crystals, which melt at 345°. It is insoluble in water, readily soluble in alcohol. The solution in dilute ammonia fluoresces blue-green, that in dilute NaOH blue.

The acid, if carefully heated, gives a yellowish-red sublimate of anthracene-o-dicarboxylic anhydride



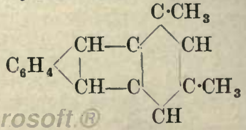
$$C_6H_4{<}\begin{matrix}CH\\CH\end{matrix}{>}C_6H_2{<}\begin{matrix}CO\\CO\end{matrix}{>}O.$$

Calcium salt. Brownish-green precipitate, almost insoluble in water.

Lead salt. Yellowish precipitate, insoluble in water.

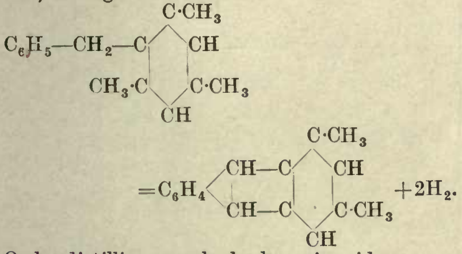
Silver salt. Yellowish-brown precipitate, insoluble in water; decomposes on distillation into CO_2, Ag, and anthracene.

m-**Dimethylanthracene**

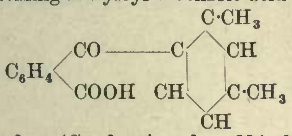


(Elbs, J. pr. Chem. 1890, 41, 13). This hydrocarbon cannot be produced by the reduction of *m*-methylanthraquinone with zinc-dust and ammonia.

It is obtained by passing mesitylphenyl methane (Louise, Ann. Chim. Phys. [vi.] 6, 187, 193) through a red-hot tube



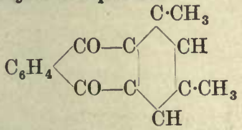
Or by distilling *m*-xyloyl-*o*-benzoic acid



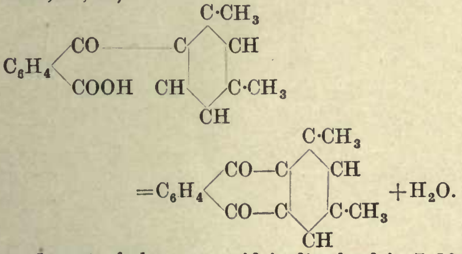
with zinc-dust (Gresly, Annalen, 234, 238).

m-Dimethylanthracene crystallises from alcohol in colourless plates, which melt at 202°–203°. Gives with bromine γ-brom-*m*-dimethyl anthracene tetrabromide (m.p. 175°–180°).

m-Dimethylanthraquinone

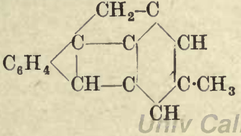


is prepared by the action of sulphuric acid on *m*-xyloyl-*o*-benzoic acid (Elbs, J. pr. Chem. 1890, 41, 13).



1 part of the pure acid is dissolved in 7–10 parts of concentrated sulphuric acid, the clear solution heated at 110°–125° for half an hour, the product poured in a thin stream into water, and the precipitate treated as described under *m*-methylanthraquinone. Yield 60–70 p.c. of theory. *m*-Dimethylanthraquinone crystallises in small needles which melt at 162°. It dissolves with difficulty in alcohol and benzene. Zinc-dust and ammonia reduces it to *m*-dimethylanthracylene $C_{16}H_{12}$, and not to dimethylanthracene.

m-Dimethylanthracylene

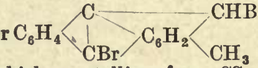
$C_{16}H_{12}$ or  (?)

Preparation.—*m*-Dimethylanthraquinone (5 grams), finely powdered, is mixed with zinc-dust (30 grams) and concentrated aqueous ammonia (200 c.c.), and a solution (5 c.c.) of basic copper carbonate in ammonia added. The product is well agitated, and gently warmed until it has assumed a light green colour, then boiled for six hours with the addition from time to time of small quantities of copper carbonate dissolved in ammonia. The mass is filtered, the precipitate washed with water, dried at the ordinary temperature, and extracted with boiling alcohol. The alcoholic solution on cooling deposits a small quantity of crystals, which are filtered off. The mother liquor is partially evaporated, again allowed to stand, filtered from the crystals which form, and this operation repeated until oily drops appear. The remainder of the hydrocarbon present in the mother liquor is purified by conversion into the picric acid compound and decomposing this with ammonia or sodium hydroxide solution (Elbs, *l.c.*).

m-Dimethylanthracylene crystallises from alcohol in groups of colourless plates which melt at 85°. It is readily soluble in hot alcohol and glacial acetic acid, difficultly soluble in cold alcohol.

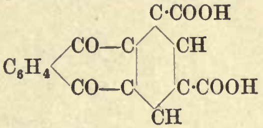
With picric acid it forms a deep garnet-red compound $C_{16}H_{12}$-$C_2H_2(NO_2)_3OH$, which is not decomposed by alcohol. M.p. 135°.

Treated with bromine in CS_2 solution (4 at. Br. to 1 mol. $C_{16}H_{12}$) an unstable dibromo compound

$C_{16}H_{10}Br_2$ or  (?)

is produced, which crystallises from CS_2 in sulphur-yellow prisms, which melt at 175° with decomposition.

Anthraquinone-*m*-dicarboxylic acid



This acid is produced quantitatively by the oxidation of *m*-dimethylanthraquinone with dilute nitric acid (for details, *v.* the *o-dicarboxylic acid*). It crystallises in fine yellow needles, which sublime above 330° without melting. It is almost insoluble in water, and difficultly soluble in the ordinary organic solvents.

Ammonium salt. Reddish warty masses, easily soluble in water.

Potassium salt. Reddish gelatinous mass, which becomes crystalline on standing, and contains then 2 mol. of water of crystallisation.

Sodium salt. Reddish crystalline crusts, contains 9 mol. of water of crystallisation.

Calcium salt. Light-red powder, insoluble in water and alcohol.

Barium salt. Light-violet powder, contains 1 mol. of water of crystallisation.

Lead salt. Red powdery precipitate, insoluble in water and alcohol.

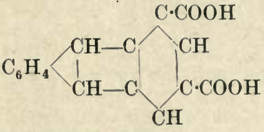
Copper salt. Dark-green crystalline powder, contains 1 mol. of water of crystallisation, insoluble in water and alcohol.

Silver salt. Pinkish precipitate, almost insoluble in water and alcohol. Decomposes on heating into CO_2, Ag, and anthraquinone.

Anthraquinone-*m*-dicarboxyl chloride is obtained by warming the acid (5 grams) with phosphorus pentachloride (7·5 grams), distilling off the phosphorus oxychloride at 140°, and shaking the residue with water and chloroform. The chloroform solution is dried over $CaCl_2$ and evaporated, when the acid chloride remains behind as a reddish mass, which showed little tendency to crystallise.

The *acid amide* prepared by treating the chloride with ammonia is also difficult to obtain in a crystalline condition.

Anthracene-*m*-dicarboxylic acid



is prepared by reducing anthraquinone-*m*-dicarboxylic acid with zinc-dust and ammonia (for details, *v.* the *o*-dicarboxylic acid). Crystallises in brownish-yellow masses, which do not melt at 330°. It is almost insoluble in water, difficultly soluble in most other solvents.

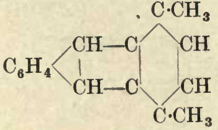
Ammonium salt. Greyish-green crystalline powder, readily soluble in water, difficultly soluble in dilute alcohol.

Copper salt. Dirty-green precipitate, almost insoluble in water and alcohol. Dissolves in ammonia, producing a yellow solution with a strong blue fluorescence (characteristic).

Silver salt. Light-brown powder. Dissolves in ammonia, producing a yellow solution with a blue fluorescence.

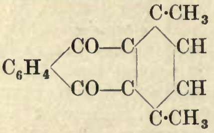
The chloride of the acid has the same properties and is produced in the same manner as the chloride of anthraquinone-*m*-dicarboxylic acid.

***p*-Dimethylanthracene**

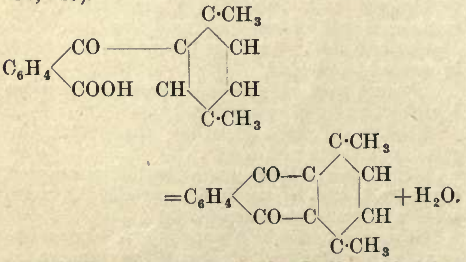


has not yet been prepared.

***p*-Dimethylanthraquinone**

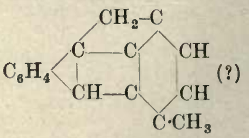


is produced by the action of H_2SO_4 on *p*-xyloyl-*o*-benzoic acid, at a temperature of 125° (Elbs, J. pr. Chem. 1890, 41, 27; Gresly, Annalen, 234, 240).



The details of the preparation and purification are the same as those of the ortho derivative. Yield 50–65 p.c. of the theoretical. *p*-Dimethylanthraquinone crystallises from xylene in yellow needles, which melt at 118°–119°. It is readily soluble in benzene and xylene, sparingly soluble in alcohol.

***p*-Dimethylanthracylene**

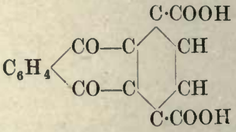


is produced when *p*-dimethylanthraquinone is reduced with zinc-dust and ammonia (*v.* *m*-dimethylanthracylene).

It crystallises from alcohol in plates which melt at 63°.

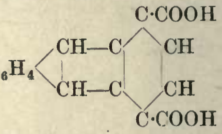
The picrate $C_{16}H_{12}{\cdot}C_6H_2(NO_2)_3OH$ crystallises from alcohol in dark-red needles, which melt at 129°.

Anthraquinone-*p*-dicarboxylic acid



is prepared by oxidising *p*-dimethylanthraquinone with dilute nitric acid (for details, *v.* the *o*- and *m*- derivatives). Yield nearly quantitative. It crystallises in small yellow crystals, which are difficultly soluble in water, but readily soluble in alcohol. The melting-point lies above 300°. The salts are similar to those of the *o*- and *m*- derivatives.

Anthracene-*p*-dicarboxylic acid

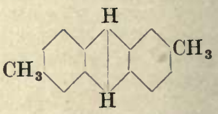


is obtained in the same way as its isomerides, by reducing anthraquinone *p*-dicarboxylic acid with zinc-dust and ammonia.

It crystallises from alcohol in the form of a light-brown crystalline powder which melts at about 320°. It is readily soluble in alcohol, but almost insoluble in water.

The salts are similar to those of the *o*-acid.

2 : 6-Dimethylanthracene



Friedel and Crafts (Ann. Chim. Phys. [vi.] 11, 265) obtained an unseparated mixture of dimethylanthracenes and other substances by each of two reactions, namely by the action of aluminium chloride on toluene and methylene chloride, or on toluene and acetylene tetrabromide.

Lavaux (Compt. rend. 139, 976) isolated from this product, benzene, xylene, dimetatolylmethane, diparatolylmethane, β-methylanthracene, and three isomeric dimethylanthracenes, having m.ps. 240°, 244·5°, and 86°

respectively. The substance of m.p. 244·5° is 2 : 6-dimethylanthracene and the constitution is proved by the following synthesis taken in conjunction with the other evidence:

m-Tolyl *m*-4 xylylketone (Seer, Monatsh. 32, 143), from *m*-toluoyl chloride and *m*-xylene, when boiled for five days is changed to 2 : 6-dimethylanthracene of m.p. 243°.

The hydrocarbon can also be prepared (Anschütz, Annalen, 235, 319) by distilling the tetrahydride of the tetramethylanthracene of Anschütz with zinc-dust. This preparation harmonises better with the constitution 2 : 4 : 6 : 8 for the latter hydrocarbon than for the 1 : 3 : 6 : 8 structure assigned by Dewar and Jones (*v. infra*).

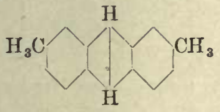
The substance crystallises from benzene in greenish yellow plates and is readily soluble in benzene, difficultly so in alcohol.

2 : 6-Dimethylanthraquinone is produced by the oxidation of the anthracene derivative by chromic acid in acetic acid solution. It is also obtained in 19 p.c. yield by heating *m*-toluoyl chloride and aluminium chloride at 130° for two hours and then at 130°–140° for 16 hours. It is very sparingly soluble and crystallises from acetic acid, nitrobenzene, or in the form of long silky needles, from alcohol. It melts at 236°.

Anthraquinone-2 : 6-dicarboxylic acid is obtained when the above quinone is boiled with chromic acid and acetic acid for 60 hours. It forms a chloride which has m.p. 197°–198°, and this with alcoholic ammonia yields an amide $C_{16}H_{10}O_4N_2$, infusible at 370°.

2 : 6-Di-α-naphthoylanthraquinone $C_{36}H_{20}O_4$, m.p. 183°–185°, is obtained from the chloride, naphthalene, and aluminium chloride in nitrobenzene at 75°–80° after 20 hours.

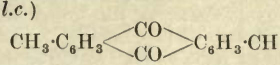
2 : 7-Dimethylanthracene (α and γ-dimethylanthracenes)



This hydrocarbon is produced (Elbs and Wittich, Ber. 18, 348) when a mixture of 3 parts toluene, 3 parts carbon disulphide, and 1 part chloroform is treated with 2 parts of aluminium chloride. It is formed further (1) together with ditolylmethane $C_{15}H_{16}$ and *m*- and *p*-xylene, by treating a mixture of toluene and methylene chloride with aluminium chloride (Friedel and Crafts, Bull. Soc. chim. [ii.] 41, 323); (2) by treating xylyl chloride $CH_3\cdot C_6H_4\cdot CH_2Cl$ with aluminium chloride (Friedel and Crafts, *ibid.* [ii.] 41, 326); (3) by treating toluene and acetylene tetrabromide with aluminium chloride (Anschütz and Immendorff, Ber. 17, 2816; Annalen, 235, 172); (4) by treating toluene with nickel carbonyl and aluminium chloride. In this reaction, *p*-tolualdehyde is a by-product (Dewar and Jones, Chem. Soc. Trans. 85, 212).

It is identical with the hydrocarbon isolated by Zincke and Wackendorff (Ber. 10, 1481) from the higher boiling fractions of coal tar. It crystallises from alcohol in glittering yellowish plates which melt at 215° (Elbs, *l.c.*; Dewar and Jones, *l.c.*); 224°–225° (Friedel and Crafts, *l.c.*). It sublimes readily, is moderately soluble, and yields the following oxidation products.

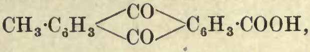
γ-Dimethylanthraquinone (Zincke and Wackendorff, *l.c.*)


$$CH_3\cdot C_6H_3\left<\begin{matrix}CO\\CO\end{matrix}\right>C_6H_3\cdot CH_3$$

is produced by the oxidation of the above hydrocarbon with CrO_3 and acetic acid; it crystallises from dilute alcohol in small straw-yellow needles, which melt at 155°.

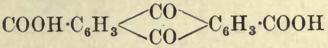
It sublimes in almost colourless flat needles, is moderately soluble in alcohol, ether, benzene, glacial acetic acid, and hot light petroleum.

Methylanthraquinone carboxylic acid,


$$CH_3\cdot C_3H_3\left<\begin{matrix}CO\\CO\end{matrix}\right>C_6H_3\cdot COOH,$$

is produced by the oxidation of γ-dimethylanthracene (m.p. 224°–225°) with CrO_3 and acetic acid. It crystallises in flocks, which melt at 244°–246°, and sublime, when strongly heated, in small needles.

Anthraquinone dicarboxylic acid


$$COOH\cdot C_6H_3\left<\begin{matrix}CO\\CO\end{matrix}\right>C_6H_3\cdot COOH$$

is formed, together with dimethylanthraquinone and methylanthraquinone carboxylic acid, by oxidising γ-dimethylanthracene with CrO_3. It crystallises in small warty masses (m.p. not given). It is readily separated from methylanthraquinone carboxylic acid by treatment with concentrated NaOH, in which the sodium salt of the dicarboxylic acid is readily soluble, but that of the monocarboxylic acid sparingly soluble. The solution of the acid in KOH becomes violet on exposure to the air. The Ba and Ca salts are gelatinous and insoluble.

DIMETHYL ANTHRACENE DERIVATIVES.

Nitro compounds. 4-nitro-1 : 3-dimethylanthraquinone of m.p. 234° is obtained by boiling 1 : 3-dimethylanthraquinone with nitric acid (sp.gr. 1·37) for 10 hours. It is reduced by alkaline hyposulphite to the amino compound which has practically the same m.p. 4-Iodo-1 : 3-dimethylanthraquinone, m.p. 118°, is produced when the diazotised amine is treated with potassium iodide (Scholl and Potschiwauscheg, Ber. 43, 346). 2 : 4-Dinitro-1 : 3-dimethylanthraquinone melts at 283°–285°, and is produced by agitating the quinone for many hours with fuming nitric acid (sp.gr. 1·52).

1 : 5-Dinitro-2 : 6-dimethylanthraquinone (?) (Seer, *l.c.*) is obtained by the nitration of 2 : 6-dimethylanthraquinone with sulphuric acid and potassium nitrate. It forms colourless needles and on reduction with alkaline hyposulphite yields the corresponding diamine, dark-red needles, melting at 255°–256°. The corresponding diiodo compound, obtained in the usual way, forms orange-yellow needles, m.p. 273°.

Chloro derivatives (Harrop, Norris, and Weizmann, Chem. Soc. Trans. 95, 1312).

3 : 6-Dichlorophthalic anhydride was condensed with the three xylenes by means of aluminium chloride in carbon disulphide solution.

The benzoyl benzoic acids were converted to the corresponding quinones by heating with sulphuric acid containing boric acid and 10 p.c. of sulphur trioxide for 10 minutes at 120°.

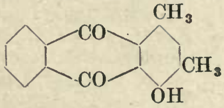
5 : 8 - Dichloro - 1 : 2 - dimethylanthraquinone from *o*-xylene crystallises from acetic acid in greenish-yellow needles and melts at 269°–270°. Its colour in sulphuric acid is orange red.

5 : 8 - **Dichloro - 1 : 3 - dimethylanthraquinone** is produced in poor yield. It crystallises from xylene in light yellow needles and melts at 208°.

5 : 8 - **Dichloro - 1 : 4 - dimethylanthraquinone** melts at 244°. When these chloro compounds are heated with aniline, sodium phenoxide, or phenyl mercaptan and caustic soda, the chlorine atoms are replaced by the groups —NHPh, —OPh, and —SPh respectively.

Hydroxy derivatives.

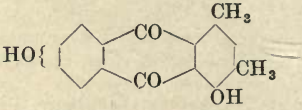
4-Hydroxy - 1 : 3 - dimethylanthraquinone (Bentley, Gardner and Weizmann, *l.c.*)



Phthalic anhydride and *m*-4-xylenol, when fused together with boric acid, yield a benzoyl benzoic acid which, on further treatment with sulphuric acid, changes to this quinone. It crystallises in needles from acetic acid and melts at 173°–175°.

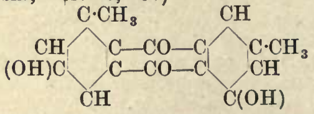
Methyl ether. Phthalic anhydride and *m*-4 : xylyl methyl ether in presence of aluminium chloride yield 2′-methoxy - 3′ : 5′-dimethyl - 2 - benzoyl benzoic acid. The latter, on treatment with sulphuric acid, yields 4 : methoxy : 1 : 3 : dimethylanthraquinone, yellow needles from acetic acid, m.p. 176°–177°.

4 : 6 - (or 7) **Dihydroxy-1 : 3-dimethylanthraquinone.**

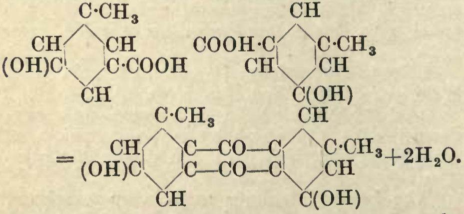


This quinone is obtained direct by the condensation of 4-hydroxyphthalic anhydride with *m*-4 - xylenol by means of boric acid. It crystallises in yellow needles from acetic acid and melts at 270°. Its solution in sulphuric acid is intensely bluish-red (Bentley, Gardner and Weizmann, *l.c.*).

Dimethylanthrarufin (Kostanecki and Niementowski, Ber. 18, 250)



is obtained, together with small quantities of two other isomers, by heating symmetrical *m*-hydroxytoluic acid with sulphuric acid.



The crude product is poured into water, the precipitate collected, washed with water, and treated with baryta water, which leaves the dimethylanthrarufin undissolved. The baryta extract is precipitated with HCl, the precipitate extracted with alcohol. Dimethylbenzdihydroxyanthraquinone dissolves, whereas dimethylanthraflavic acid is insoluble (*v. infra*).

Dimethylanthrarufin crystallises from benzene in yellow silky needles, which melt at 300° and sublime in orange-red needles. It does not dye mordanted cloth. The solution in sulphuric acid is cherry-red coloured, and similar to that of anthrarufin in H_2SO_4. The *diacetate*

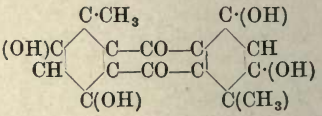
$$C_{16}H_{10}O_2(C_2H_3O_2)_2$$

crystallises in yellow plates, m.p. 236°–237°.

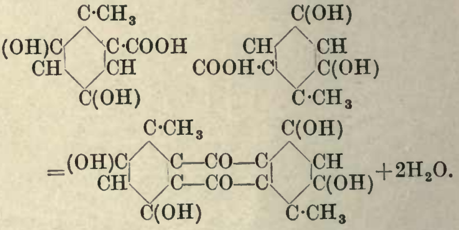
Dimethylanthraflavic acid (for preparation, *v. Dimethylanthrarufin*). It sublimes in yellow needles which do not melt at 360°. It is insoluble in benzene, difficultly soluble in alcohol and glacial acetic acid; it dissolves in alkalis and sulphuric acid with a yellow colour like anthraflavic acid. It does not dye mordanted cloth. The *diacetate* crystallises in needles which melt at 223°.

Dimethylbenzdihydroxyanthraquinone (for preparation, *v. Dimethylanthrarufin*). It crystallises from alcohol in yellow needles which melt at 213°. It dissolves in glacial acetic acid, but is sparingly soluble in alcohol and benzene. It does not dye mordanted cloth. The *diacetate* melts at 188°.

Dimethylanthrachrysone (Cahn, Annalen, 240, 280)



is prepared by heating cresorsellinic acid (1 part) with concentrated sulphuric acid (10 parts) to 100°.

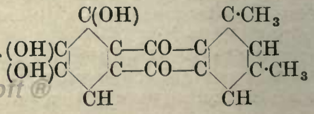


It crystallises from alcohol in bronze-coloured needles which do not melt when heated to 360°. It sublimes with difficulty, and then with considerable decomposition. It is insoluble in water, benzene, and light petroleum, sparingly soluble in alcohol and CS_2, readily soluble in $CHCl_3$, acetone, and glacial acetic acid. It is soluble in solutions of the alkalis and alkaline earths, with a yellowish-red colour. The solution in sulphuric acid is magenta-coloured, and shows two absorption bands in the green. It does not dye mordanted cloth.

The *tetraacetyl derivative* $C_{16}H_8O_2(C_2H_3O_2)_4$ crystallises in yellowish needles which melt at 234° and are readily soluble in hot alcohol, glacial acetic acid, and benzene.

Dimethylanthragallol (Birukoff, Annalen, 240, 287)

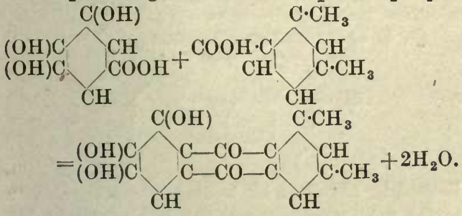
$C_{16}H_{12}O_5$ or



is obtained by heating a mixture of 5 parts xylylic acid

$C_6H_3(COOH)(CH_3)(CH_3),(COOH : CH_3 : CH_3=1, 2, 4)$

with 3 parts of gallic acid and 40 parts H_2SO_4.

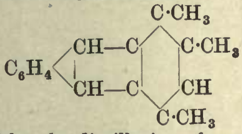


The product is mixed with water, the precipitate collected, washed with water, dissolved in absolute alcohol (in which small quantities of accompanying rufigallic acid are insoluble); evaporated and the residue extracted with benzene; again evaporated, and the product recrystallised from acetone. Glittering reddish-yellow needles (no m.p. given). Distilled with zinc-dust, dimethylanthracene (m.p. 224°) results. The absorption spectrum of a solution of dimethylanthragallol in concentrated sulphuric acid is almost identical with that of anthragallol itself.

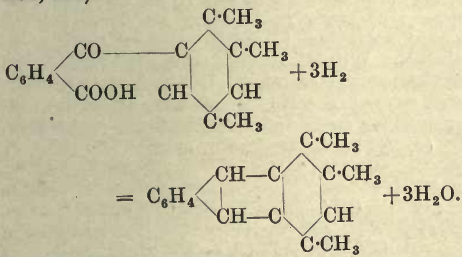
This substance should, from its method of preparation, be a derivative of *m*-dimethylanthracene, which, however, melts at 202°–203°, whereas the dimethylanthracene obtained from dimethylanthragallol melts at 224°, and is evidently identical with that obtained from coal tar by Zincke and Wackendorff. This point requires investigation.

Trimethylanthracenes (Elbs, J. pr. Chem. 1890, 41, 121).

(1, 2, 4) **Trimethylanthracene**



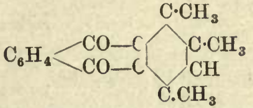
is produced by the distillation of pseudocumoyl-*o*-benzoic acid with zinc-dust (Gresly, Annalen, 234, 241).



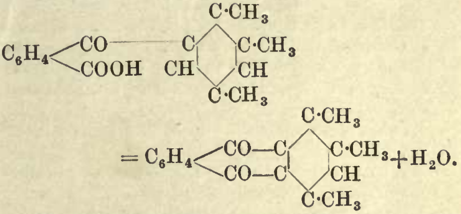
Preparation.—5 grams of the powdered acid are intimately mixed with 10 grams of zinc-dust, and distilled from a retort, the temperature being raised very gradually. The greenish-coloured oil which first passes over is separated from the reddish-coloured oil, which distils last and crystallises on cooling; the latter is dissolved in boiling light petroleum, and the crystals which separate out on cooling purified by recrystallisation.

Trimethylanthracene crystallises in white plates, possessing a blue fluorescence, and which melt at 244°. The picrate crystallises from benzene in brownish-red needles, which melt at 145° and are decomposed by alcohol.

(1, 2, 4) **Trimethylanthraquinone**



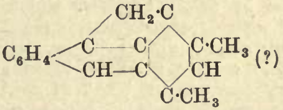
is obtained by the action of dehydrating agents on pseudocumoyl-*o*-benzoic acid.



In order to obtain a good yield of this substance, the following directions must be carefully observed.

10 grams of powdered *pseudo*cumoyl-*o*-benzoic acid are dissolved in 100 c.c. of concentrated sulphuric acid, and the product gently warmed. The solution, which becomes clear and cherry-reddish coloured at 60°, is heated at 115° for one hour, allowed to cool to 70°–80°, and then mixed with 10 grams of phosphorus pentoxide, the temperature being allowed to rise gradually to 115°–120° during the addition, at which temperature it is kept for further two hours. The well-cooled product is poured in a thin stream into water, the precipitate collected, washed with water, and then with cold carbonate of soda solution; dried at 100°, and recrystallised from a mixture of alcohol and xylene. Trimethylanthraquinone crystallises in long yellow needles which sublime readily and melt at 162°–163°. It is readily soluble in ether, benzene, and xylene; sparingly soluble in alcohol.

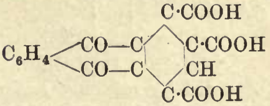
(1, 2, 4) **Trimethylanthracylene**



results from the action of zinc-dust and ammonia on trimethylanthraquinone (for details, *v.* dimethylanthracylene). It crystallises from alcohol in colourless plates which melt at 64° and resemble naphthalene in appearance. The picrate $C_{17}H_{14}{\cdot}C_6H_2(NO_2)_3OH$ melts at 134°, and is decomposed by alcohol.

Bromine converts the hydrocarbon into its unstable dibromo-trimethylanthracylene.

Anthraquinone-1 : 2 : 4-Tricarboxylic acid

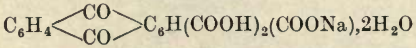


is produced by the oxidation of (1, 2, 4) trimethylanthraquinone with dilute nitric acid (*v. Anthraquinone dicarboxylic acids*). It crystallises from alcohol in yellowish-white warty masses, which do not melt at 320°. It is almost insoluble in water.

The *ammonium* salt separates from its

solution in reddish amorphous crusts, which dissolve in water with a deep-red colour.

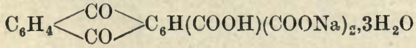
The *primary sodium salt*



$$C_6H_4\genfrac{}{}{0pt}{}{\diagup CO \diagdown}{\diagdown CO \diagup}C_6H(COOH)_2(COONa),2H_2O$$

crystallises in yellow plates, readily soluble in hot, but difficultly in cold water.

Secondary sodium salt



$$C_6H_4\genfrac{}{}{0pt}{}{\diagup CO \diagdown}{\diagdown CO \diagup}C_6H(COOH)(COONa)_2,3H_2O$$

crystallises in yellowish-red plates, more soluble in water than the primary salt.

Tertiary sodium salt is very readily soluble in water, and difficult to obtain in a crystalline form.

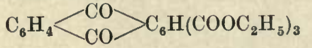
Neutral calcium salt. Rose-red plates from water.

Neutral copper salt. Light-green precipitate, very difficultly soluble in water.

Neutral lead salt. Yellow powdery precipitate insoluble in water.

Neutral silver salt. Reddish powdery precipitate which, when heated to a high temperature, decomposes into CO_2, Ag, and anthraquinone.

The *triethyl ester*



$$C_6H_4\genfrac{}{}{0pt}{}{\diagup CO \diagdown}{\diagdown CO \diagup}C_6H(COOC_2H_5)_3$$

crystallises from alcohol in glittering white plates, which melt at 125°.

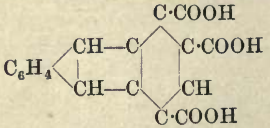
When treated with nitric acid and sulphuric acid trimethyl anthraquinone yields three nitro-derivatives which, on oxidation, yield two mononitro- and one dinitro-anthraquinone tricarboxylic acids.

I. *Mononitro-anthraquinone* (1, 2, 4) *tricarboxylic acid*, $C_{12}H_4(CO)_2(COOH)_3(NO_2)$, crystallises in small yellow crystals which melt at 308°–310°. It is soluble in alcohol, ether, acetone, glacial acetic acid, and benzene, insoluble in water.

II. *Mononitroanthraquinone tricarboxylic acid* crystallises in small crystals, which melt at 360°–370° with decomposition, is readily soluble in alcohol, ether, and benzene, insoluble in water. The copper salts of these two acids differ very distinctly. That of acid I. crystallises in green needles, which dissolve in ammonia with a green colour; that of acid II. crystallises in red needles which dissolve in ammonia, forming a red solution.

Dinitro anthraquinone (1, 2, 4) *tricarboxylic acid*, $C_{12}H_3(NO_2)_2(CO)_2(COOH)_3$, melts at 340°–360° with decomposition.

Anthracene-1 : 2 : 4-tricarboxylic acid

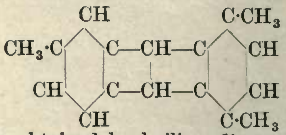


is readily obtained by reducing anthraquinone (1, 2, 4) tricarboxylic acid with zinc-dust and ammonia (for details, see the corresponding dicarboxylic acids). It is readily soluble in benzene and light petroleum, still more readily in alcohol, with a yellowish-green colour, insoluble in water. No sharp m.p. was observed, as the acid sublimed above 260°, being converted probably into the anhydride.

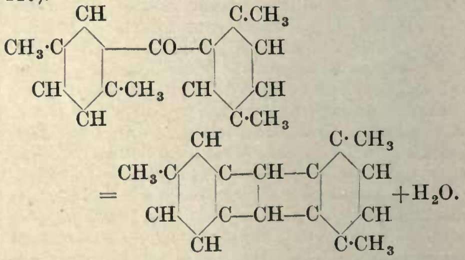
The *alkali salts* are very readily soluble in water, and do not crystallise readily.

The *silver salt* is a yellowish-green precipitate which, on heating, is decomposed, yielding a sublimate of anthracene.

(1, 4, 7) Trimethylanthracene



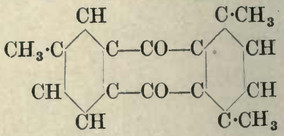
is readily obtained by boiling di-*p*-xylylketone under a reflux apparatus for 6 hours (Elbs, *l.c.* 140).



The yield is about 20–25 p.c. of the theoretical.

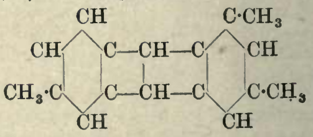
It crystallises in thin colourless plates, which fluoresce bluish-green, melt at 227°, and sublime with great readiness, even at 100°. It is difficultly soluble in cold alcohol, more readily soluble in hot alcohol, benzene, and ether.

(1, 4, 7) Trimethylanthraquinone

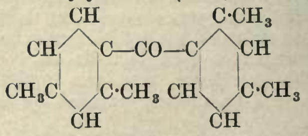


is obtained by oxidising (1, 4, 7) trimethylanthracene with the theoretical quantity of CrO_3 in glacial acetic acid solution. The yield is almost quantitative. It crystallises in yellow needles, which melt at 184°, and sublime with great readiness. It dissolves readily in glacial acetic acid, but is only sparingly soluble in alcohol. With zinc-dust and KOH it gives the anthraquinone reaction. On further oxidation this substance yields a mixture of carboxylic acids which could not be satisfactorily separated.

(1, 3, 6) Trimethylanthracene



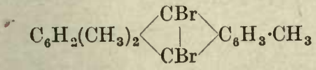
is synthetically prepared by the action of heat on di-*m*-xylylketone (Elbs, *l.c.* 142).



(*v. supra*).

The yield is 20–25 p.c. of the theoretical. It crystallises from a mixture of alcohol and acetone in plates which melt at 222°, is difficultly soluble in alcohol and light petroleum, more readily in ether and glacial acetic acid, very readily in CS_2, acetone, and benzene.

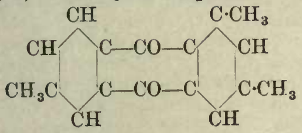
γ-*Dibromo* (1, 3, 6) *trimethylanthracene*



$$C_6H_2(CH_3)_2 \Big< \begin{matrix} CBr \\ | \\ CBr \end{matrix} \Big> C_6H_3{\cdot}CH_3$$

results when trimethylanthracene (1 mol.) dissolved in CS_2 is treated with bromine (2 mol.). On evaporation a brownish-yellow crystalline mass is obtained, which crystallises from acetone in rosettes of yellow plates which melt at 142°.

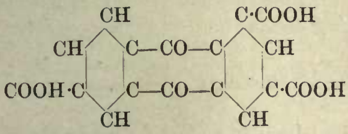
(1, 3, 6) **Trimethylanthraquinone**



is produced by oxidising (1, 3, 6) trimethylanthracene with the calculated quantity of chromic acid in acetic acid solution.

It crystallises in yellow needles which melt at 190°, are readily soluble in glacial acetic acid, difficultly soluble in alcohol. It sublimes readily and gives with zinc-dust and potash a deep-red solution.

Anthraquinone (1, 3, 6) **tricarboxylic acid**



To prepare this substance 0·5 gram (1, 3, 6) trimethylanthracene is heated with 15 grams HNO_3 (sp.gr. 1·1) in a sealed tube 10 hours to 180°, then 10 hours to 210°–220°. The tricarboxylic acid crystallises out in yellow plates. It is scarcely soluble in water, and very difficultly soluble in other solvents; it does not melt when heated to 300°.

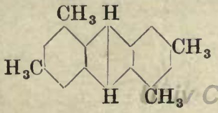
The *ammonium salt* is readily soluble in water, and crystallises in flesh-coloured plates.

The *barium salt* is a cherry-red crystalline precipitate, very sparingly soluble in water.

Tetramethylanthracene (Anschütz, Annalen, 235, 174) $C_{14}H_6(CH_3)_4$ is formed in small quantity, together with toluene and trimethylbenzene, by the action of aluminium chloride on a mixture of acetylenetetrabromide and *m*-xylene; m.p. 280°. If *o*-xylene be used in the place of *m*-xylene in the above reaction, a tetramethylanthracene, which melts above 280°, is obtained; in the case of *p*-xylene being used the tetramethylanthracene obtained melts at about 280°.

Since there are only two isomeric tetramethylanthracenes derivable from *m*-xylene, namely 1 : 3 : 6 : 8 and 2 : 4 : 6 : 8, and the former is chosen for the quinone described below, the hydrocarbon of Anschütz is probably 2 : 4 : 6 : 8-tetramethylanthracene.

1 : 3 : 6 : 8-**Tetramethylanthracene**

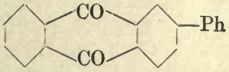


Dewar and Jones (Chem. Soc. Trans. 1904, 85, 212) obtained this hydrocarbon by the action of nickel carbonyl on *m*-xylene in presence of aluminium chloride.

The hydrocarbon is purified by successive crystallisation from hot benzene and acetic acid. It forms beautiful lustrous plates, melts at 280°, is very pale yellow, and exhibits green fluorescence.

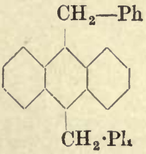
1 : 3 : 6 : 8-**Tetramethylanthraquinone** is obtained from the hydrocarbon in the usual manner. It crystallises in pale yellow prisms of m.p. 228°–230°.

2-**Phenylanthraquinone** (Scholl and Neovius, Ber. 44, 1075).



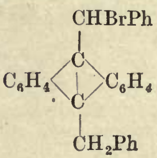
Phthalic anhydride condenses with diphenyl in presence of aluminium chloride in carbon disulphide solution, and the product is exclusively diphenyl-4-phthaloylic acid. When heated with zinc chloride at 280°, 2-phenylanthraquinone is obtained. The product is purified by reduction with alkaline hyposulphite, filtering the alkaline solution and oxidising by a current of air. The substance crystallises in yellow needles and melts at 160°–161°. The quinone may also be obtained by reducing diphenyl-4-phthaloylic acid to the corresponding diphenyl methane carboxylic acid, and this with zinc chloride at 185° is changed to 2-phenyl-9-anthrone which, on oxidation with chromic acid, yields 2-phenylanthraquinone.

9 : 10-**Dibenzylanthracene** (Lippmann and Fritsch, Monatsh. 25, 793).



This interesting hydrocarbon is prepared by heating anthracene (100 grams), benzyl chloride (145 grams), and zinc-dust (10 grams) with carbon disulphide (1 litre) on the water bath, and with continual passage of carbon dioxide, until the evolution of hydrogen chloride ceases. The substance forms blue fluorescent needles, crystallises from acetic acid and melts at 241°. It has a peculiar odour resembling carbylamine.

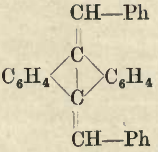
Monobromodibenzylanthracene

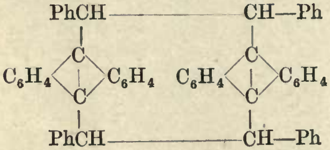


$$C_6H_4 \Big< \begin{matrix} CHBrPh \\ | \\ C \\ | \\ C \\ | \\ CH_2Ph \end{matrix} \Big> C_6H_4$$

This derivative is obtained by the action of bromine on dibenzylanthracene in carbon disulphide solution. The bromine is carried into the liquid mixed with carbon dioxide. The product crystallises from carbon disulphide or benzene in yellow prisms, melting, when quickly heated, at 187°.

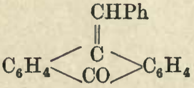
Uni- and bi-molecular **dibenzylidenedihydroanthracene**



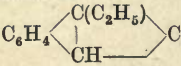


Unimolecular. Monobromodibenzylanthracene is boiled in benzene solution with aqueous potassium acetate, or the bromide is heated with a small excess of acetic anhydride. The substance melts at 234°–236°, and is soluble in chloroform with blue fluorescence.

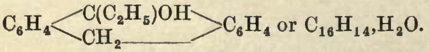
Bimolecular $C_{56}H_{40}$. Monobromodibenzylanthracene is boiled with quinoline in benzene solution for 20 hours. It forms yellow crystals of m.p. 184° and is soluble in hot benzene or chloroform with red fluorescence. It is easily distinguished from the monomolecular compound in that its solution in sulphuric acid is green.



Benzylidene anthrone $C_6H_4<\begin{array}{c}\overset{\overset{CHPh}{\|}}{C}\\CO\end{array}>C_6H_4$ (Haller and Padova, Compt. rend. 141, 857) is closely related to the above benzal dihydroanthracenes. It is obtained by the condensation of anthranol with benzaldehyde in pyridine solution containing piperidine. The yield is 36 p.c. of that demanded by theory. The substance crystallises in yellow needles, and is readily soluble in chloroform, benzene, and acetone, sparingly so in ligroin. It melts at 126°–127°. The corresponding anisylidene and *m*-nitrobenzylidene derivatives melt at 141° and 166° respectively. The benzylidene anthrone is also easily obtained on passing hydrochloric acid into the acetic acid solution of *benzyl oxanthranol*. The latter is prepared by the action of magnesium benzyl chloride on anthraquinone. It forms colourless crystals from alcohol and melts at 146°.



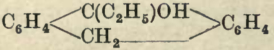
Ethylanthracene (Liebermann, Annalen, 212, 109) $C_6H_4<\begin{array}{c}C(C_2H_5)\\|\\CH\end{array}>C_6H_4$ is formed by boiling ethyl hydranthranol with alcohol and hydrochloric or picric acid.



$$C_6H_4<\begin{array}{c}C(C_2H_5)OH\\CH_2\end{array}>C_6H_4 \text{ or } C_{16}H_{14},H_2O.$$

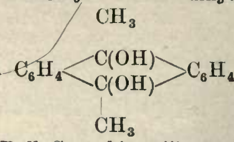
It crystallises from alcohol in large concentrically grouped plates which melt at 60°–61°. The picrate melts at 120°.

Ethylhydranthranol

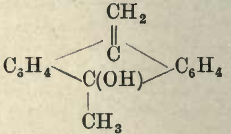


$$C_6H_4<\begin{array}{c}C(C_2H_5)OH\\CH_2\end{array}>C_6H_4$$

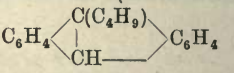
is produced by heating anthraquinone (3 parts) with zinc-dust (10 parts), caustic soda solution (10 p.c.), and ethyl bromide (2–4 parts).



9 : 10 - Dimethyl - 9 : 10 - dihydroxydihydroanthracene $C_6H_4<\begin{array}{c}\overset{CH_3}{C}(OH)\\\underset{CH_3}{C}(OH)\end{array}>C_6H_4$ (Guyot and Staehling, Bull. Soc. chim. [iii.] 33, 1152). This substance is prepared by the action of magnesium methyl iodide on anthraquinone. It crystallises from methyl alcohol in colourless prisms containing solvent of crystallisation. Some of this it loses on exposure to the air, but the last molecule is not driven off unless the substance is exposed *in vacuô* to a temperature of 100°. The anhydrous compound melts at 181° and dissolves in sulphuric acid with a green colour, changing on standing to yellow. When treated with alcohols the corresponding ethers are produced. Thus ethyl alcohol yields the diethyl ether of the anthracene derivative.

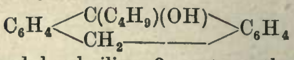


9 - Methyl - 9 - hydroxy - 10 - methenedihydroanthracene $C_6H_4<\begin{array}{c}\overset{\overset{CH_2}{\|}}{C}\\\underset{CH_3}{C}(OH)\end{array}>C_6H_4$ is obtained when the dihydroxy compound (*v. supra*) is boiled with acetic acid. It is a canary yellow crystalline powder melting at 223°, and sparingly soluble in organic solvents. It dissolves in sulphuric acid to a clear yellow solution.



*iso***Butylanthracene** (Liebermann, Annalen, 212, 107) $C_6H_4<\begin{array}{c}C(C_4H_9)\\|\\CH\end{array}>C_6H_4$ is obtained by boiling an alcoholic solution of *iso*butyl hydranthranol ($C_{18}H_{19}OH$) with picric acid or hydrochloric acid. It crystallises from alcohol in fluorescent needles; m.p. 57°. The picrate crystallises in long brownish-red needles.

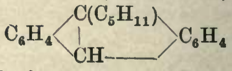
*iso***Butylhydranthranol**



$$C_6H_4<\begin{array}{c}C(C_4H_9)(OH)\\CH_2\end{array}>C_6H_4$$

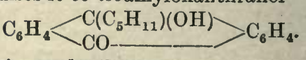
is prepared by boiling 3 parts anthraquinone with 10 parts of zinc-dust, 50 parts of caustic soda solution (10 p.c.), and 2·4 parts of *iso*butyl bromide. It crystallises in needles, which melt at 71°–72°.

*iso***Amylanthracene** (Liebermann, *l.c.*)



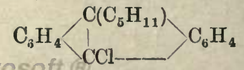
$$C_6H_4<\begin{array}{c}C(C_5H_{11})\\|\\CH\end{array}>C_6H_4$$

is prepared from *iso*amylhydranthranol (*v. Isobutylanthracene*). Long, colourless sea-green needles, m.p. 59°. Very soluble in benzene, CS_2,$CHCl_3$ light petroleum, and hot alcohol; difficultly soluble in cold alcohol. The solutions fluoresce blue. The solution in sulphuric acid is green; on warming it becomes red. Chromic acid oxidises it to *iso*amyloxanthranol



$$C_6H_4<\begin{array}{c}C(C_5H_{11})(OH)\\CO\end{array}>C_6H_4.$$

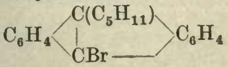
Chlor*iso*amylanthracene



$$C_6H_4<\begin{array}{c}C(C_5H_{11})\\|\\CCl\end{array}>C_6H_4$$

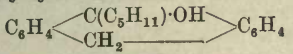
is obtained by passing chlorine into a solution of *iso*amylanthracene in chloroform. It crystallises from alcohol in pale-yellow needles, which melt at 70°–71°. The solutions fluoresce blue. The picrate crystallises in red needles, which melt at 108°.

Bromo*iso*amylanthracene

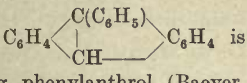
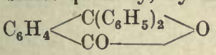
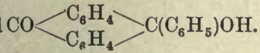


is obtained by adding the calculated quantity of bromine to the solution of the hydrocarbon in 20–30 parts of CS_2. Orange-yellow needles, m.p. 76°. The picrate crystallises in orange-yellow needles, which melt at 110°.

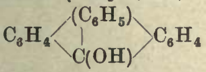
***iso*Amylhydroanthranol**



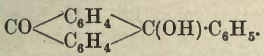
(*v. Isobutylhydranthranol*). Needles, m.p. 73°–74°. Very readily soluble in alcohol; insoluble in water.

Phenylanthracene  is obtained by distilling phenylanthrol (Baeyer, Annalen, 202, 61) $C_{20}H_{13}(OH)$ with zinc-dust; also, but in very small quantity, by distilling diphenylphthalid  or triphenylmethane carboxylic acid $C_{20}H_{16}O_2$ with zinc-dust. It is also produced, together with anthracene and other hydrocarbons, by the action of aluminium chloride on a mixture of chloroform and benzene (Friedel and Crafts, Ann. Chim. Phys. [vi.] 1, 495). It crystallises from alcohol in plates which melt at 151°–153°, and boil at 417°. It is readily soluble in hot alcohol, ether, CS_2, $CHCl_3$, and benzene, the solutions possessing a blue fluorescence. Oxidation with CrO_3 and acetic acid converts it into phenyloxanthranol . The *picrate* crystallises in red needles. Reduction with hydriodic acid converts it into a dihydride $C_{20}H_{16}$, which melts at 120°–120·5°.

Phenylanthranol (Baeyer, *l.c.*)

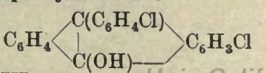


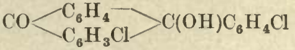
is formed by dissolving triphenylmethane carboxylic acid $(C_6H_5)_2CH{\cdot}C_6H_4{\cdot}COOH$ in 3 parts of sulphuric acid and pouring the mass into water. The precipitate is collected, washed with dilute sodium carbonate, and recrystallised from alcohol. Yellow needles, which melt at 141°–144°, with slight decomposition. It dissolves readily in ether, forming a yellowish solution, which possesses a greenish-yellow fluorescence. It dissolves also in hot alcohol, petroleum spirit, and acetone. Oxidation with CrO_3 converts it into phenyloxanthranol



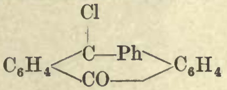
The *acetate* $C_2H_3O_2{\cdot}C_{20}H_{13}$ crystallises from alcohol in yellow needles which melt at 165°–166°.

Dichlorophenylanthranol

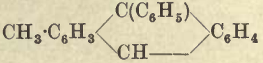


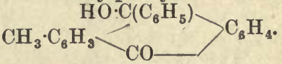
is formed by boiling phenolphthalideïn chloride  with zinc-dust and acetic acid. It crystallises from alcohol in needles, which melt at 170°. It is very sparingly soluble in alcohol, moderately soluble in acetone and ether, readily soluble in benzene or CS_2, forming bluish-green fluorescent solutions.

Phenyloxanthranolchloride

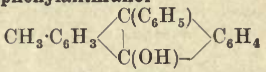


(Haller and Guyot, Bull. Soc. chim. 1897, [iii.] 17, 873) is obtained by warming diphenylphthalide with phosphorus pentachloride. It crystallises from benzene in large, colourless, transparent prisms, melting at 164°. Water changes it to phenyloxanthranol, whilst with methyl alcohol it yields phenyloxanthranol methyl ether.

Methylphenylanthracene (Hemilian, Ber. 16, 2367)  is formed by the distillation of methylphenylanthranol with zinc-dust (*v. infra*). It crystallises from alcohol in yellow crystalline masses (melting-point not given). The alcoholic solution fluoresces greenish-blue. It is readily oxidised by CrO_3 and acetic acid to methylphenyloxanthranol



Methylphenylanthranol

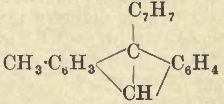


is similarly prepared by heating methyltriphenylmethane carboxylic acid

$$(C_6H_5)_2CH{\cdot}C_6H_3(CH_3)COOH$$

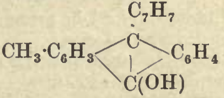
with sulphuric acid to 100°. It crystallises from alcohol in glittering plates, which on heating become brown at 130°, and melt at 156°–157°. It is readily soluble in ether, boiling alcohol, and glacial acetic acid.

Methyl-*p*-tolylanthracene



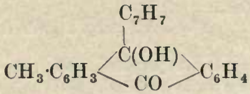
(Limpricht, Annalen, 299, 291) is obtained by the distillation of methyl-*p*-tolyloxanthranol with zinc-dust in a stream of hydrogen. It forms yellow needles of m.p. 191°. On oxidation with chromic acid in acetic acid solution, it yields methyl-*p*-tolyloxanthranol.

Methyl-*p*-tolylanthranol



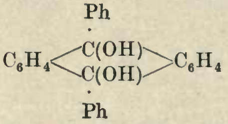
This substance is easily produced by dissolving di-*p*-tolylphenyl methane *o*-carboxylic acid in concentrated sulphuric acid. On pouring the solution into water, small yellow crystals, melting at 117°, separate. The compound is easily changed to

Methyl-*p*-tolyloxanthranol



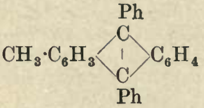
by oxidation with chromic acid. This derivative crystallises from toluene in colourless needles, melting at 206°.

9 : 10 - **Diphenyl** - 9 : 10 - **dihydroxydihydroanthracene**



(Haller and Guyot, Compt. rend. 138, 327). This compound is produced in 10 p.c. yield by the action of magnesium phenyl bromide on anthraquinone. It crystallises from methyl alcohol in colourless needles, containing solvent of crystallisation. This is lost on exposure to air, the crystals falling to a white powder, melting at 247°. The solution in sulphuric acid is indigo blue, changing to orange-yellow on heating. The colourless solution in glacial acetic acid exhibits blue fluorescence.

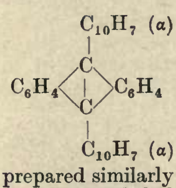
2-**Methyl**-9 : 10-**diphenylanthracene**



(Guyot and Staehling, Bull. Soc. chim. [iii.] 33, 1104). When phenyl magnesium bromide acts on 2-methylanthraquinone the product varies according to the conditions employed. If the organo-metallic derivative is slowly added to a benzene solution of the quinone, then Hemilian's 2-methyl-9-phenyloxanthranol (*v. supra*) is the main product. On boiling the quinone with a solution of magnesium phenyl bromide for many hours, then 2-methyl-9 : 10 - diphenyl - 9 : 10 - dihydroxydihydroanthracene is produced. This crystallises in cubes and melts at 240°. On treatment with zinc-dust in acetic acid solution it is reduced to 2-methyl-9 : 10-diphenylanthracene.

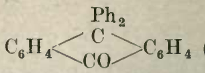
The latter crystallises from benzene and alcohol in yellow green dichroic plates, melting at 213°, and soluble in organic solvents with intense violet-blue fluorescence. Chromic acid changes it to 2-methyl-9 : 10-diphenyl-9 : 10-dihydroxydihydroanthracene.

Di-α-naphthylanthracene



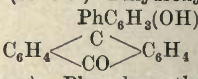
(Guyot and Staehling, *l.c.*) is prepared similarly to the above diphenyl derivative. α-Naphthyl magnesium bromide and anthraquinone yield 9 : 10 - di-α-naphthyl - 9 : 10 - dihydroxydihydroanthracene, which forms colourless crystals from toluene, and contain 1 molecule of toluene of crystallisation. It dissolves in sulphuric acid with a malachite-green colour. Di-α-naphthylanthracene is obtained from this di-ol by reduction with zinc and acetic acid. It forms yellow crystals, soluble in benzene, and exhibiting a most intense violet fluorescence.

Diphenylanthrone



(Haller and Guyot, Bull. Soc. chim. 1897, [iii.] 17, 873). This compound is obtained by the action of aluminium chloride on a benzene solution of phthalyltetrachloride. The latter may be replaced by anthraquinone chloride or phenyloxanthranol chloride, which are probably intermediate products of the reaction. The substance crystallises from acetic acid in colourless needles, or from benzene in large transparent prisms, melting at 192°. Although undoubtedly a ketone, it does not react with phenylhydrazine. It forms a molecular compound with nitrobenzene.

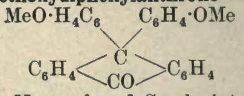
2′ : 4′- (or 3′5′) **Dihydroxy** - 9 : 9 - **diphenylanthrone**



(Liebermann and Lindenbaum). Phenyloxanthranol chloride (*v. supra*) furnishes this substance when it is treated with resorcinol in boiling benzene solution. Other phenols react similarly. The resorcinol derivative crystallises from alcohol in the form of colourless needles, which, when heated, lose solvent at 125°, and then melt at 259°–261°. The solution in concentrated sulphuric acid is yellow. On boiling with acetic anhydride and sodium acetate a diacetate is produced, and this compound crystallises from alcohol in plates and melts at 191°.

Scharwin and Kusnezof (Ber. 36, 2020) have condensed anthraquinone with phenols and with resorcinol, using for the former condensation, tin tetrachloride, and for the latter, zinc chloride. The substances produced are hydroxy derivatives of diphenylanthrone.

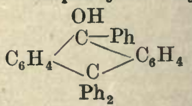
***p*-Dimethoxydiphenylanthrone**



(Scharwin, Naumof and Sandurin).

Anthraquinone chloride condenses with anisole to form this substance, when the solution of the mixture in carbon disulphide is treated with aluminium chloride. It crystallises from alcohol in yellow rhombohedra of m.p. 208°. It is soluble in the usual organic solvents, and in sulphuric acid with red-violet colour. On hydrolysis with aluminium chloride it yields phenolanthraquinone identical with the product obtained by Scharwin and Kusnezof (*l.c.*) from anthraquinone and phenol.

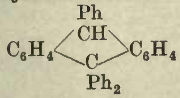
9 : 10 : 10 - **Triphenyl** - 9 - **hydroxydihydroanthracene**



(Haller and Guyot, Compt. rend. 139, 9). This substance can be obtained by dropping a benzene solution of diphenylanthrone (*v. supra*) into an ethereal solution of magnesium-phenyl bromide. After the addition of water, and acidification, the solvent is evaporated, when the carbinol crystallises in colourless voluminous needles, which contain 1 molecule of ether of crystallisation. This is removed at 120°, and the substance then melts at 200°. It dissolves in sulphuric acid with orange-red colour.

The methyl ether is obtained by adding methyl alcohol containing hydrochloric acid to the boiling toluene solution of the carbinol. The colourless leaflets melt at 218°. The corresponding ethyl ether melts at 250°.

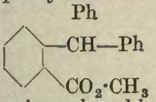
Triphenyldihydroanthracene



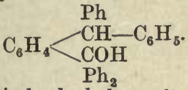
is prepared—

(*a*) By boiling the above carbinol or its ethers with zinc-dust and acetic acid.

(*b*) Methyltriphenylmethane-*o*-carboxylate



reacts with magnesium-phenyl bromide, yielding the tertiary alcohol and



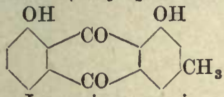
$$C_6H_4 \langle \begin{matrix} \overset{Ph}{CH}—C_6H_5. \\ \underset{Ph_2}{COH} \end{matrix}$$

This crystallises from methyl alcohol as its methyl ether, m.p. 215°. The orange-red solution of this methoxyl compound in sulphuric acid quickly becomes colourless, and on dilution triphenyldihydroanthracene is precipitated. This last change is still better effected by the agency of hydrochloric acid in glacial acetic acid solution.

Triphenyldihydroanthracene forms colourless crystals from a mixture of benzene and alcohol, and melts at 220°. Its solution in sulphuric acid is colourless.

METHYLANTHRACENE DERIVATIVES OCCURRING IN NATURE.

Chrysophanic acid (*Chrysophan, Chrysophanol*)



Occurrence.—In various species of lichens, *Parmelia parietina* (Ach.), *Lecanora* (*Placodium*) *elegans* (Ach.), *Cassia speciosa* (Schrad.), *Rhamnus frangula* (L.), *Rhamnus Purshiana* (D.C.), (as glucoside), in the root of *Rumex obtusifolius* (L.), in senna leaves, and in Chinese rhubarb. From this latter source a definite glucoside chrysophanein $C_{21}H_{20}O_9$ has been isolated by Gilson (Arch. internat. de Pharmako-dynamie et de Therapie, 1905, vol. 14, 487).

Preparation.—Chrysophanic acid is usually obtained by the oxidation of chrysarobin (*v. infra*) (Liebermann, Seidler, Annalen, 212, 36), which is mixed with dilute potassium hydroxide solution and a current of air passed until the liquid has acquired a deep reddish colour. The quinone is precipitated into HCl and extracted with ligroin (b.p. 50°–60°). On evaporation of the solvent a yellow residue is obtained which can be crystallised from alcohol. The melting-points found for chrysophanic acid by various authors range from 154° to 190°, and this has been shown to be due to the fact that the substance commonly contains an admixture of its methyl ether. Repeated crystallisation leads to a product containing only 0·36 p.c. methoxyl, and this melts at 188°. Oesterle (Arch. Pharm. 243, 434) obtained a methoxyl free chrysophanol by treatment with anhydrous aluminium chloride in benzene solution. After crystallisation from ligroin, alcohol, and benzene, the pure chrysophanol melted at 196°. This melting-point was also found by Gilson (*l.c.*) for the hydrolysis product of the pure glucoside chrysophanein. The analysis of the pure substance agreed excellently with the formula $C_{15}H_{10}O_4$. As ordinarily obtained chrysophanol crystallises in orange needles, which sublime, partially with decomposition, in the same form. The methoxyl free substance consists of shining brown-yellow leaflets, when crystallised from benzene. It is almost insoluble in water, but soluble in ether, benzene, and glacial acetic acid. It is difficultly soluble in ammonia and alkaline carbonates, but readily so in potassium hydroxide, forming a deep-red solution. Distilled with zinc-dust chrysophanic acid yields methylanthracene (Liebermann, Annalen, 183, 169).

The absorption spectrum of a solution of chrysophanic acid (Liebermann and Kostanecki, Ber. 19, 2330) in sulphuric acid, which resembles very closely that of chrysazin, is shown in Fig. 4.

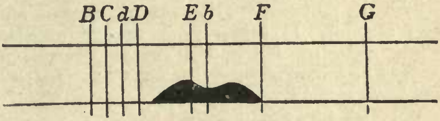


FIG. 4.

Since chrysophanic acid diacetate is converted by oxidation, with chromic acid in acetic acid and acetic anhydride solution, into diacetyl rhein, the positions of the groups are evidently identical in the two substances.

Derivatives of chrysophanic acid. *Tetranitrochrysophanic acid* (Liebermann and Giesel, Annalen, 183, 175) is obtained when chrysophanic acid is warmed with concentrated nitric acid. It occurs in yellow micro leaflets, which decompose on heating. The substance is quite insoluble in water, soluble in acetic acid, and behaves as a strong acid. It resembles chrysammic acid.

Amino derivatives. Aminodeoxychrysophanic acid (Liebermann and Giesel, *l.c.*) was obtained by heating chrysophanic acid with concentrated ammonia at 200°, or by leaving the acid with strong ammonia for a long time at the ordinary temperatures (Hesse, Annalen, 309, 32). It is a cherry-red powder forming easily soluble purple-violet salts with alkalis. It is sparingly soluble in ether, comparatively readily so in alcohol. In this compound, either one of the hydroxy groups of the chrysophanic acid is replaced by amino, or one of the carbonyl oxygens by imino.

Diamino-de-dioxy-chrysophanic acid (Liebermann and Giesel, *l.c.*) is obtained when chrysophanic acid is heated at 150° with a small quantity of aqueous ammonia. Since this substance is soluble in alkalis it may probably be more correctly designated as diiminochrysophanic acid. On boiling with acetic anhydride it yields acetylchrysophanic acid imide (so called) having the composition $C_{15}H_8(C_2H_3O)NO_2$. This substance crystallises from chloroform in violet needles, having a metallic reflex.

Monoacetylchrysophanic acid $C_{15}H_9(C_2H_3O)O_4$ (Hesse, *l.c.*) is obtained by the action of acetic anhydride on chrysophanic acid. It is dissolved by gently warming and then allowed to remain 48 hours. It crystallises from acetic acid in yellow needles of m.p. 152°.

Diacetylchrysophanic acid $C_{15}H_8(C_2H_3O)_2O_4$ (Liebermann, *l.c.*) is the product when chrysophanic acid is boiled with sodium acetate and acetic anhydride. Oesterle (*l.c.*) gives the melting-point of the pure substance as 208°. It crystallises in light yellow leaflets, and can be oxidised by chromic acid to diacetyl rhein (Fischer, Falco and Gross, J. pr. Chem. 1911, [ii.] 83, 208).

Dibenzoylchrysophanic acid $C_{15}H_8(C_7H_5O)_2O_4$ (Warren de la Rue and Müller, J. 1862, 323) obtained by the Schotten-Baumann reaction, crystallises in pale yellow needles, melting at 200°–208° (Tutin and Clewer, Chem. Soc. Trans. 99, 956).

Chrysophanic acid monomethyl ether

$$C_{15}H_8O_2(OH)(OCH_3)$$

(Oesterle, *l.c.*) is the main product when chrysophanic acid is methylated by means of methyl sulphate and potassium hydroxide. After a process of purification, it can be crystallised from alcohol. It forms clear orange needles which melt at 204°. Its acetyl derivative consists of lemon yellow needles when crystallised from alcohol, m.p. 204°.

Chrysophanic acid dimethyl ether

$$C_{15}H_8O_2(OCH_3)_2$$

is also produced when the acid is treated with a large excess of methyl sulphate and alkali. It crystallises in orange needles, m.p. 195°, either from acetic acid or aqueous alcohol. It dissolves with red colour in concentrated sulphuric acid.

Chrysophanein (Gilson, *l.c.*) is as already mentioned the glucoside of chrysophanic acid. It crystallises in needles from 92 p.c. alcohol and melts at 242°–249°. It is tasteless, and this in conjunction with its other properties renders the formulation of barbaloin as a glucoside of aloemodin and arabinose open to criticism.

Chrysophanhydranthrone $C_{15}H_{12}O_3$. Since chrysarobin (*see* below) gave chrysophanic acid on oxidation, attempts were made to realise the reverse process. Liebermann (Ber. 21, 436) reduced chrysophanic acid with tin and hydrochloric and acetic acids, and obtained a compound which crystallised from benzene in yellow leaflets and melted at 196°. It was not chrysarobin and was termed chrysophanhydranthrone. Hesse (Annalen, 284, 194) obtained the same substance by heating chrysophanic acid with hydriodic acid. Jowett and Potter (Chem. Soc. Trans. 1902, 1584) obtained in this reaction chrysarobin; but Hesse obtained chrysophanhydranthrone by heating chrysarobin with concentrated hydrochloric or hydriodic acid. The melting-point of the pure hydranthrone is 205°–210°. On distillation with zinc-dust β-methylanthracene is obtained. It yields a diacetyl derivative which crystallises from acetic acid in needles of m.p. 238°–240°.

Chrysarobin $C_{15}H_{12}O_3$ (?). This derivative of chrysophanic acid is a remedy indispensable to the dermatologist, and was first obtained from Goa powder by Attfield (Pharm. J. 5, 721) by extraction with chloroform. Liebermann and Seidler (Annalen, 212, 34) prepared the compound in a pure condition. The so-called Goa powder separates out in the pith hollows of certain trees belonging to the genus *Andira* in Brazil and India. It is extracted with benzene, the solution evaporated, and the residue repeatedly crystallised from glacial acetic acid. Small yellow needles, m.p. 170°–178°. Insoluble in water and ammonia, difficultly soluble in alcohol and ether, more readily soluble in benzene, glacial acetic acid, and chloroform. Insoluble in very dilute potassium hydroxide, but soluble with a dark-green fluorescence in strong solutions. This solution is readily oxidised by the oxygen of the air, yielding chrysophanic acid. Distilled with zinc-dust, chrysarobin yields methyl anthracene. Chrysarobin has no dyeing properties. It may be the anthranol of chrysophanic acid, although a double molecular formula has been ascribed to it by several authors.

The acetyl derivatives of chrysarobin and of the dichrysarobin obtained by heating the solution in acetic acid have been carefully investigated by Hesse (Annalen, 309, 60).

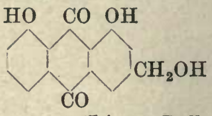
Monoacetyl derivative is obtained by 3–4 hours' boiling with acetic anhydride. The yellow leaflets obtained on crystallisation from acetic acid melt at 188°–190°.

Diacetyl derivative is produced when chrysarobin is boiled 6 hours with acetic anhydride. It crystallises in rhombic prisms, m.p. 216°; the solutions fluoresce blue. A β-diacetate of m.p. 265°–270° has also been isolated.

Triacetyl chrysarobin can be prepared by heating either chrysarobin or chrysophanhydranthrone with acetic anhydride and sodium acetate for 1 hour. It crystallises in prisms, m.p. 234°.

Hexaacetyl dichrysarobin is produced by boiling chrysarobin with sodium acetate and acetic anhydride for many hours. It is amorphous, and melts at 125°.

Aloemodin



Aloemodin occurs (Léger, Bull. Soc. chim. [iii.] 23, 785) together with barbaloin and *iso*-barbaloin in Barbados aloes, and in smaller quantities in all other varieties of aloe.

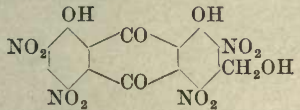
It may be prepared best by the action of alcoholic hydrochloric acid on barbaloin (Oesterle, Arch. Pharm. 237, 699). The dried reaction product is extracted with hot toluene, the solution treated with animal charcoal and concentrated; when on cooling orange-yellow needles separate. The substance is purified by many recrystallisations from toluene and from acetic acid. After sublimation the pure aloemodin melts at 224°. Léger, and Jowett and Potter have obtained aloemodin by the oxidation of barbaloin with sodium peroxide. Tetrachloraloemodin and tetrabromaloemodin are produced by the oxidation of tetrachlor- and tetrabrombarbaloins with the same reagent.

When heated with a little sulphuric acid and subsequently treated with dilute ammonia solution, aloemodin gives a violet colour; frangula emodin under the same conditions gives a cherry red. Aloemodin when oxidised with chromic acid in acetic acid solution yields rhein $C_{15}H_8O_6$. This is a carboxylic acid, so that aloemodin $C_{15}H_{10}O_5$ must be recognised as the corresponding primary alcohol, and further as hydroxychrysophanic acid.

Diacetylaloemodin $C_{15}H_8O_5(COCH_3)_2$ is obtained by boiling aloemodin with acetic anhydride and sodium acetate for an hour. It crystallises from acetic acid in small yellow needles, m.p. 177°–178°. Although aloemodin yields a diacetate, tetrachloraloemodin has three hydroxyl groups which can be acetylated.

Tribenzoyl aloemoin $C_{15}H_7O_5(COPh)_3$ is obtained by the Schotten-Baumann reaction. It crystallises well from ethyl acetate as greenish-yellow micro leaflets, m.p. 235°.

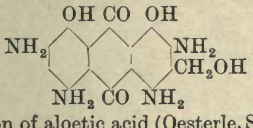
Tetranitroaloemodin



is the so-called *aloetic acid,* which is obtained together with chrysammic acid, by the action of nitric acid on barbaloin. The substance was first obtained by Scheele, who termed it aloë bitter, and subsequently by a number of chemists, but it was first isolated in the pure condition by Mulder (Annalen, 1849, 72, 286). Oesterle proved that the substance is tetranitroaloemodin since he applied to it the process by which Liebermann and Giesel (Annalen, 183, 184) converted chrysammic acid into chrysazin, and obtained aloemodin.

Aloetic acid is a yellow crystalline powder which becomes red on standing in the air. It is fairly soluble in water to an intense red solution. It is also soluble in ether, chloroform, alcohol, benzene, and ethyl acetate. Léger (Compt. rend. 1911, 153, 114) finds that on further oxidation with nitric acid, aloetic acid yields chrysammic acid and 2 : 4 : 6-trinitrometahydroxybenzoic acid.

Hydroaloetic acid



The reduction of aloetic acid (Oesterle, Schweizer Wochenschr. f. Ch. u. Ph. 1906, No. 31) is accomplished by an aqueous solution of potassium hydrogen sulphide. Hydroaloetic acid is a blue-black amorphous substance very sparingly soluble in most solvents. The solution of the substance in concentrated sulphuric acid was treated with nitrous fumes and then boiled with an excess of alcohol. It was found possible to isolate aloemodin by acetylating the product, purifying the diacetate and hydrolysing with alcoholic potash. The aloemodin obtained melted at 223°.

Frangula emodin (emodin)

$C_{15}H_{10}O_5$, or $C_{14}H_4(CH_3)(OH)_3O_2$

(position of OH groups unknown, but probably the same as those in flavopurpurine).

Occurrence.—In rhubarb root, the bark of the alder tree, in *Rhamnus Purshiana* (D.C.) (cascara sagrada) and *Rhamnus cathartica* (Linn.).

Preparation.—Alder bark is extracted with dilute sodium hydroxide, the solution precipitated with HCl, and the precipitate purified by repeated recrystallisation from absolute alcohol.

Orange-red, silky needles, m.p. 245°–250° (Liebermann, Annalen, 183, 161).

Moderately soluble in benzene, more readily so in alcohol and acetic acid; soluble in dilute ammonia, forming a cherry-red solution. Does not dye mordanted cloth. Distilled over zinc-dust β-methylanthracene results. The absorption spectrum of a solution in concentrated sulphuric acid is shown in Fig. 5 (Liebermann and Kostanecki, Ber. 19, 2330):

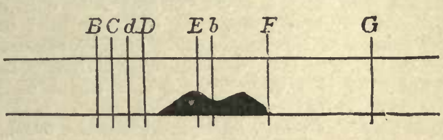


FIG. 5.

and closely resembles that of flavopurpurin.

The triacetate (Liebermann, *l.c.*)

$C_{15}H_7(C_2H_3O)_3O_5$

crystallises from acetic acid in yellow needles, m.p. 190°.

Tribenzoate. Tutin and Clewer (Chem. Soc. Trans. 99, 954) obtained this derivative by applying the Schotten-Baumann reaction to emodin. It crystallises from glacial acetic acid in small pale yellow needles, and melts at 186°.

Dibenzoyl emodin, m.p. 225°, has also been described, but there appears to be some uncertainty as to its existence.

Emodinmonomethyl ether

$CH_3{\cdot}C_{14}H_4O_2(OH)_2OCH_3$

was found by Perkin and Hummel in *Ventilago maderaspatana* (Chem. Soc. Trans. 65, 940), by Tutin and Clewer in rhubarb root and in *Rumex Ecklonianus* (Meissn.), whilst Oesterle and Johann (Arch. Pharm. 1910, 248, 476) show that it is the methylated compound usually associated with chrysophanic acid.

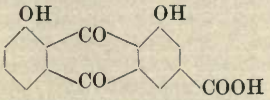
Jowett and Potter (Chem. Soc. Trans. 1903, 77, 1330) obtained the substance by heating the potassium salt of emodin with methyl iodide. It crystallises from benzene in long, orange-red needles, m.p. 200°. It is sparingly soluble in alcohol or acetone. A nitro derivative melts at 217°, and a tetranitro derivative at 275° with decomposition. The former is obtained by using nitric acid of sp.gr. 1·42, the latter when nitric acid (sp.gr. 1·54) is employed.

Its diacetate crystallises in golden needles, m.p. 185°, and the dibenzoate prepared by the Schotten-Baumann method melts at 228°.

Frangulin. This emodin derivative was first obtained in a pure condition by Casselmann (Annalen, 104, 77), although Binswanger (Repert, Pharm. 104, 151) had previously obtained it in a crude state from the bark of *Rhamnus frangula* (Linn.). It crystallises from alcohol in lemon-yellow, silky needles, melting at 226°. Acids hydrolyse it with formation of emodin and rhamnose so that the body is a rhamnoside of emodin. Its precise composition is at present uncertain. *Polygonin* is another glucoside of emodin, although the nature of the sugar is unknown. It was extracted by A. G. Perkin from *Polygonum cuspidatum* (Sieb. et Lucc).

(Chem. Soc. Trans. 67, 1084). It crystallises in slender, orange-yellow needles, m.p. 202°–203°.

Rhein



Rhein occurs in rhubarb, from which it was first isolated by Hesse (Annalen, 1899, 309, 43). He gave it the formula $C_{15}H_{10}O_6$, and considered it a tetrahydroxymethylanthraquinone. Tschirch and Heuberger (Arch. Pharm. 1902, 240, 611), however, made analyses from which they concluded that rhein is $C_{15}H_8O_6$, and since only a diacetate could be prepared, they assigned to the substance the constitution of a methylene ether of a tetrahydroxyanthraquinone. In support of this view it was also urged that on distillation with zinc-dust rhein yields anthracene. Oesterle and Tisza (Schweiz. Woch. Chem. Pharm. 1908, 46, 701) carefully purified rhein, by crystallisation from pyridine, and sublimation in cathode ray vacuum, and support the empirical formula of Tschirch and Heuberger. Rhein is best prepared by the oxidation of barbaloin or the acetyl derivative of barbaloin. Oesterle (Schweiz. Woch. f. Chem. Pharm. 1903, 50) obtained a small yield by oxidising barbaloin with chromic acid in aqueous solution, but when tetraacetylbarbaloin is oxidised with chromic acid in acetic anhydride solution, a 50 p.c. of diacetylrhein is easily obtained, and rhein is thus shown to be a dihydroxyanthraquinone carboxylic acid (Robinson and Simonsen, Chem. Soc. Trans. 95, 1085). Rhein crystallises from pyridine in combination with a molecule of the solvent in glistening orange needles. These fall to a powder at 130°, and the pure rhein then melts at 318° (Tutin and Clewer, *l.c.*). Oesterle's purest rhein melted at 321°–321·5°. It is sparingly soluble in organic solvents, but dissolves readily in sodium carbonate solution. It dyes both mordanted and unmordanted wool clear yellow shades.

Diacetate. Various melting-points have been assigned to this substance ranging from 236° to 258°. The latter value is probably correct, and was obtained by Tutin and Clewer (*l.c.*), who prepared this derivative by heating rhein with a large excess of acetic anhydride and a little camphor sulphonic acid. After concentration the compound separates in rosettes of pale yellow needles, m.p. 258°. It is soluble in sodium carbonate solution, and on hydrolysis with alcohol and sulphuric acid yields the ester of rhein.

Dibenzoyl rhein (Tutin and Clewer, *l.c.*) obtained by the Schotten-Baumann reaction, crystallises from acetic acid in yellow-brown prisms, m.p. 262°.

Rhein methyl ester $C_{14}H_5O_2{\cdot}(OH_2){\cdot}CO_2Me$ (Robinson and Simonsen, *l.c.*) forms deep orange needles by crystallisation from methyl alcohol, and melts at 174°. It is insoluble in sodium carbonate solution.

Rhein ethyl ester $C_{14}H_5O_2{\cdot}(OH)_2CO_2Et$ is obtained by esterifying either rhein or diacetyl rhein with alcohol and sulphuric acid. Orange needles from alcohol, m.p. 159°. It yields a diacetate, melting at 170°, which is quite insoluble in cold aqueous potash.

Dimethylrhein $C_{14}H_5O_2(OMe)_2COOH$ (Robinson and Simonsen, *l.c.*) is prepared by treating an alkaline solution of rhein with methyl sulphate in the cold. The substance was isolated by means of its sparingly soluble potassium salt. It crystallises from alcohol in light brown needles, and melts when pure at 283°–284°. It dissolves in alkali to orange-yellow solutions, and can be neither acetylated nor benzoylated. Its ethyl ester melts at 185°–187°, and is insoluble in alkalis.

Dimethyl rhein chloride $C_{14}H_5O_2(OMe)_2COCl$ is produced from the acid by the action of thionyl chloride. It is crystallised by adding ligroin to its solution in chloroform. Canary-yellow prisms melting at 190° are obtained. On treatment with ammonia—

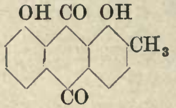
Dimethyl rhein amide

$$C_{14}H_5O_2(OMe)_2{\cdot}CO{\cdot}NH_2$$

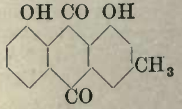
is obtained. This very insoluble substance can be crystallised from a large quantity of ethyl acetate. It occurs in microscopic hexagonal plates, m.p. 287°. It is a fact of great importance that this amide undergoes the Hofmann reaction, and can be converted in this way into an aminodimethoxyanthraquinone, which, after removal of the amino group and demethylation, yields chrysazin. Rhein is thus chrysazin carboxylic acid.

CONSTITUTION OF CHRYSOPHANIC ACID, ALOEMODIN, AND RHEIN.

The relationship of chrysophanic acid, aloemodin, and rhein is expressed by the scheme, RCH_3, $RCH_2{\cdot}OH$, RCOOH, since both chrysophanic and and aloemodin yield rhein on oxidation and rhein is a carboxylic acid (Robinson and Simonsen, *l.c.*). Now chrysophanic acid is derived from β-methylanthracene whilst rhein can be degraded to chrysazin. Accepting the usual 1 : 8-configuration for chrysazin, this leaves two possible formulæ for chrysophanic acid, namely—



and



That the latter (and therefore the corresponding formulæ for aloemodin and rhein) must be taken as correct is proved by the fact that aloetic acid (*see* above) is oxidised by nitric acid with formation of 2 : 4 : 6-trinitro-*m*-hydroxybenzoic acid. W. H. P. & R. R.

METHYLANTHRANILIC ACID *v.* AMINO ACIDS (AROMATIC).

METHYLARBUTIN *v.* GLUCOSIDES.

METHYLASPIRIN *v.* SYNTHETIC DRUGS.

METHYLATED SPIRIT *v.* ALCOHOL.

METHYLAURIN *v.* AURIN.

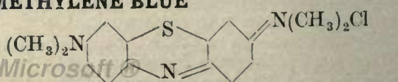
α-METHYLBUTYRIC ACID *v.* VALERIC ACIDS.

METHYLDIBUTYL ACETIC ACID *v.* HENDECATOIC ACIDS.

METHYLDIETHYL ACETIC ACID *v.* HEPTOIC ACIDS.

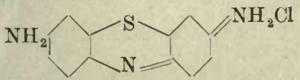
METHYLDIPHENYLAMINE *v.* DIPHENYLAMINE.

METHYLENE BLUE

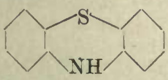


A colouring matter first obtained by Caro in

1876 by the oxidation of dimethyl-*p*-phenylenediamine in presence of sulphuretted hydrogen. By treating *p*-phenylenediamine with sulphuretted hydrogen and oxidising agents, or by heating it with sulphur and subsequently oxidising, Lauth obtained a violet basic colouring matter containing sulphur, known as 'Lauth's violet' or thionine.



The comparatively small yield of the colouring matter (15–20 p.c. of the *p*-phenylenediamine taken), together with the difficulties attending the preparation of the materials required, prevented its manufacture on the large scale. Lauth's reaction, however, became of industrial importance through Caro's discovery of the method of manufacture of nitrosodimethylaniline whereby it was readily possible to obtain dimethyl-*p*-phenylenediamine. This compound, when treated by Lauth's reaction, gave rise to a methylated Lauth's violet, which differed from the parent substance in being of a pure blue colour, and also in being more easily obtained and in much larger quantity. The new colouring matter came into commerce under the name of *Methylene blue.*[1] Its constitution, together with its relation to Lauth's violet (thionine), was first established by Bernthsen (Annalen, 1885, 230, 73). He showed that both these substances were derived from thiodiphenylamine



from which by nitration, reduction, and subsequent oxidation, Lauth's violet could be obtained, methylene blue being the tetramethyl derivative.

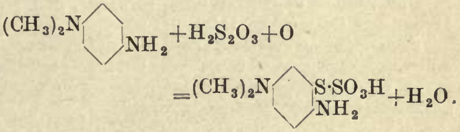
The method of manufacturing methylene blue formerly adopted by the Badische Anilin und Soda-fabrik (Eng. Pat. 3751, 1887; D. R. P. 1886; Amer. Pat. 204796; *cf.* also Mühlhäuser, Dingl. poly. J. 1886, 262, 371) consists in reducing nitrosodimethylaniline $NO{\cdot}C_6H_4{\cdot}N(CH_3)_2$, made by the action of sodium nitrite on dimethylaniline by means of zinc or sulphuretted hydrogen; the dimethyl *p*-phenylenediamine so obtained is treated in dilute acid solution with sulphuretted hydrogen and some oxidising agent (*e.g.* ferric chloride)

$$2C_8H_{12}N_2+H_2S+3O+2HCl$$
$$=C_{16}H_{18}N_3SCl+NH_4Cl+3H_2O.$$

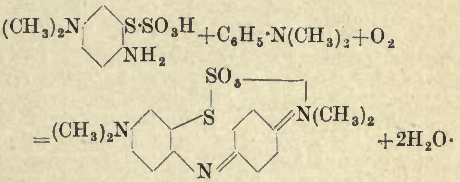
By the gradual addition of the ferric chloride the liquid becomes deep blue, and the resulting colouring matter is 'salted out' by adding common salt and zinc chloride, and purified by re-solution in water and 're-salting out.' This double salt, which constitutes the methylene blue of commerce, crystallises in copper-coloured crystals, readily soluble in pure water, but sparingly soluble in solution of zinc chloride.

Tetramethyldiaminodiphenylamine when oxidised in presence of sulphuretted hydrogen yields only traces of methylene blue. Similarly in the simultaneous oxidation of dimethyl-*p*-phenylenediamine and dimethylaniline in presence of sulphuretted hydrogen, the dimethylaniline enters but slightly into the reaction. On the other hand, if the tetramethyldiaminodiphenylamine, or the mixture of dimethyl-*p*-phenylenediamine and dimethylaniline, is oxidised in presence of sodium thiosulphate, a peculiar sulphoacid results, which on boiling with acids decomposes into sulphur dioxide and *leuco-methylene blue.* By the oxidation of this body methylene blue is readily obtained (Ulrich, Eng. Pat. 43, 1886; D. R. PP. 38573, 39757). According to D. R. P. 38573 a mixture of the neutral salts of aminodimethylaniline and dimethylaniline is oxidised in presence of the thiosulphate; in No. 39757 a solution of nitrosodimethylaniline hydrochloride is heated with dimethylaniline and sodium thiosulphate.

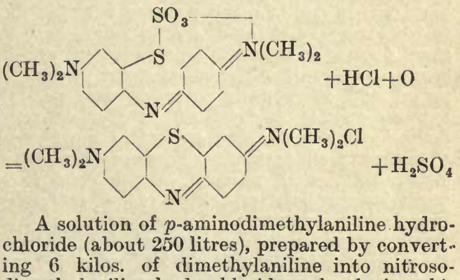
The process by which methylene blue is now manufactured (Eng. Pat. 10314, 1888; 8221, 1893; D. R. PP. 45839, 46085, 47374) is as follows: *p*-aminodimethylaniline (dimethyl-*p*-phenylenediamine) is mixed with sodium thiosulphate and the mixture oxidised by potassium dichromate to the thiosulphonic acid, thus—



Dimethylaniline is now added and the indamine is formed by oxidation with dichromate



The indamine is now boiled with dilute acid or zinc chloride solution whereby the colouring matter is formed



A solution of *p*-aminodimethylaniline hydrochloride (about 250 litres), prepared by converting 6 kilos. of dimethylaniline into nitrosodimethylaniline hydrochloride and reducing this with zinc-dust, is neutralised at 18°–20° with sodium hydroxide solution until a faint turbidity is produced. 16 kilos. of aluminium sulphate are now added, the mixture stirred for half an hour and then a concentrated solution of 13 kilos. of sodium thiosulphate is quickly poured in, followed at once by a solution of 4·8 kilos. of potassium dichromate in 75 litres

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[1] Methylene blue appears on the market under this name and also with the following marks: 2B (Badische Co.); 2B powder extra (Berlin Co.); DBB zinc-free (Cassella & Co.); BG conc. zinc salt (Ter Meer); 4BE (Poirrier). It is manufactured in England by Read Holliday and Sons, Ltd., Huddersfield, and Claus and Co., Ltd., Manchester.

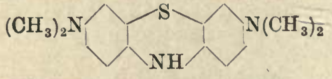
of water. In order to complete the formation of the thiosulphonic acid the mixture is stirred for an hour. The whole is diluted to 600 litres and 6 kilos. of dimethylaniline hydrochloride are added. For the preparation of the indamine a saturated solution of 14 kilos. of potassium dichromate is now run in quickly at a temperature of 10°–12°, the whole being well stirred, 75 kilos. of a solution of zinc chloride (sp.gr. 1·53) added and the mixture heated for half an hour to 100°. On cooling the precipitated methylene blue is filtered off and purified by redissolving and precipitating with zinc chloride. (The amount of potassium dichromate added in the last operation is sufficient both to form the indamine and to oxidise the leuco-methylene blue produced.)

By using methylethylaniline instead of dimethylaniline a much greener dyestuff is obtained (*Methylene blue, M.E.* Cain, 7th Int. Cong. App. Chem. London, 1909, sect. iv. B, 95).

(For the preparation of methylene blue on the laboratory scale see Cain and Thorpe, Synthetic Dyestuffs, 1905, 258; Möhlau and Bucherer, Farbenchemisches Praktikum, 1908, 262.)

Methylene blue may be estimated by titrating a boiling solution with titanous chloride in a current of carbon dioxide (Knecht, J. Soc. Dyers and Colourists, 1905, 21, 9).

Concentrated sulphuric acid dissolves methylene blue with a green colour. By reducing agents it is readily transformed into its leuco base, *tetramethyldiaminothiodiphenylamine*



This substance forms yellow needles, melting at 185° (Landauer and Weil, Ber. 1910, 43, 198); it rapidly oxidises on exposure to moist air, and is transformed into methylene blue.

Methylene blue is, with the exception of Victoria blue, the only basic blue colouring matter which has any technical importance, and it is preferable to Victoria blue on account of its greater fastness to light. It resists the action of neutral soaps and dilute solutions of chloride of lime. It is largely used in cotton-yarn dyeing and in calico-printing with tannin, or with tannin and tartar emetic mordants. It gives a greenish-blue inclining to indigo, and is frequently shaded with methyl violet, malachite green, and other basic colouring matters. It has no special applications in silk or wool dyeing. For pure blue cotton is mordanted with aluminium acetate, aged, passed through a chalk bath, well washed, passed through a weak tannin bath and dyed at a gradually increasing temperature. The colour is added in small portions to the dye-bath, which should not be warmer than 20°–25° at the beginning, and after some colour has been taken up it should be heated very gradually to 70°–80°, or higher if required; a small amount of acetic acid in the dye-bath acts favourably for level dyeing. For very dark indigo shades cotton, mordanted with tannin and antimony, may be passed through a weak solution of pyrolignite of iron; or a bath of pyrolignite of iron (6° Tw.) may be substituted for tartar emetic; after the treatment with iron liquor the cotton should be passed through weak lime water and finally well washed before dyeing (Knecht, Rawson and Loewenthal, A Manual of Dyeing, 2nd ed., 1910, 484). For method of detection on dyed fabrics, *v.* vol. ii. p. 298.

Methylene blue is of considerable value as a staining material in bacteriological and histological research; *v.* Ehrlich, Centralb. Medic. Wissensch. 1885; Dresser, Zeitsch. Biol. 1885, 41; A. B. Lee, The Microtomist's Vade-Mecum; J. W. H. Eyre, The Elements of Bacteriological Technique. J. C. C.

METHYLENE GREEN. A substance obtained by treating methylene blue with nitrous acid, or with nitric acid in sulphuric or acetic acid solution. It is a mono-nitro derivative of methylene blue. The leuco compound forms brown needles melting at 146°–147°. It is applied to cotton in the same way as methylene blue, and gives a full bluish-green shade.

Literature.—Eng. Pat. 8992, 1886; D. R. P. 38979; Fr. Pat. 177331; Ber. 1906, 39, 1020; Z. Farben. Ind. 1906, 5, 285; J. pr. Chem. 1907, [ii.] 76, 401; Ber. 1910, 43, 198.

J. C. C.

METHYLENE VIOLET *v. Safranines*, art. AZINES.

METHYLETHYL ACETIC ACID *v.* VALERIC ACIDS.

METHYLETHYLALLOXAN *v.* ALLOXAN.

METHYLETHYLBENZENE *v.* CUMENES.

METHYLGLUCOSIDE *v.* CARBOHYDRATES.

METHYLGRANATONINE *v.* KETONES.

METHYL GREEN *v.* TRIPHENYL METHANE COLOURING MATTERS.

METHYLHEXYL ACETIC ACID. NONOIC ACID (*q.v.*).

METHYLHYDROXYBENZENE *v.* PHENOL AND ITS HOMOLOGUES.

METHYLINDENE *v.* INDENE.

METHYLINDOLES *v.* INDOLES.

METHYL*iso*PROPYL ACETIC ACID *v.* CAPROIC ACIDS.

METHYL*iso*PROPYL PROPIONIC ACID *v.* HEPTOIC ACIDS.

METHYLMALIC ACID *v.* MALIC ACID.

METHYLNAPHTHALENES. α- and β-methylnaphthalene occur in creosote oil (Schulze, Ber. 1884, 17, 842, 1527), and, together with naphthalene and di-, tri-, and tetra-methylnaphthalene, in crude petroleum or naphtha (Tammann, D. R. P. 95579, 1897). The separation of these substances from their homologues can be effected either by fractional sulphonation or distillation, and their purification by means of picric acid (Tammann, *l.c.*; Wichelhaus, Ber. 1891, 24, 3918; Wendt, J. pr. Chem. 1892, [ii.] 46, 319). The azo dyes prepared from aminomethylnaphthalenes (Akt-G., D. R. P. 15647; Eng. Pat. 750, 1881) have no technical value.

α-Methylnaphthalene, b.p. 240°–242°, forms a *picrate* crystallising in needles, m.p. 116°–117° (Ciamician, Ber. 1878, 11, 272); a *nitro* derivative, b.p. 194°–195° under 27 mm. (Scherler, Ber. 1891, 24, 3932); and two isomeric *sulphonic acids*, separable by means of their barium salts (Wendt, *l.c.*).

β-Methylnaphthalene, monoclinic prisms, m.p. 32·5°, b.p. 240°–242°, forms a *picrate* crystallising in needles, m.p. 115° (Schulze, *l.c.*);

a *nitro* derivative, needles, m.p. 81° (*ibid.*), and two isomeric *sulphonic acids*, separable by means of their barium slats (Wendt, *l.c.*).

METHYL ORANGE *v.* Azo- colouring matters.

METHYLPHENYL HYDRAZINE *v.* Hydrazines.

METHYLPHENYL HYDRAZONES *v.* Hydrazones.

METHYLPROPYL ACETIC ACID *v.* Caproic acids.

METHYLPROPYLBENZENE *v.* Cymenes.

METHYLPYRROLE *v.* Bone oil.

METHYL VIOLET *v.* Triphenyl methane colouring matters.

METHOXYBENZENE *v.* Anisole.

METOL. Trade name for methyl-*p*-aminophenol sulphate. Used as a photographic developer.

METOQUINONE. Trade name for a photographic developer obtained by the action of methyl-*p*-aminophenol sulphate (metol) on hydroquinone (quinol).

METTERNICH GREEN. A double salt of zinc chloride with the chlormethyl-hexamethyl rosaniline hydrochloride. Known also as *iodine green* or *night green.* Obtained by the action of methyl iodide or chloride upon rosaniline (Hofmann and Girard, Ber. 2, 442; Appenzeller, *ibid.* 6, 965).

MEXICAN ELEMI *v.* Oleo-resins.

MEXICAN MYRICA WAX *v.* Waxes.

MEZEREON RESIN *v.* Resins.

MIARGYRITE. Silver sulphantimonite $AgSbS_2$, occurring as small, usually indistinct, monoclinic crystals. These are black and opaque, with a metallic lustre, but thin splinters transmit a deep crimson colour; streak dark cherry-red; sp.gr. 5·2. Crystals were formerly found at Bräunsdorf, near Freiberg in Saxony, and compact masses of some size are met with in the silver mines of Bolivia. L. J. S.

MICA (Ger. *Glimmer*). A name applied to a group of minerals characterised by the facility with which they split into thin laminæ, which are flexible and more or less elastic. It is now believed that all micas belong to the monoclinic system, but the crystals often affect a hexagonal habit. The perfect cleavage, on which the micaceous structure depends, is parallel to the basal plane. A similar structure is seen in the group of chlorites, but their laminæ, though flexible, are not elastic. The hardness of the micas is between 2 and 3; while their sp.gr. ranges from 2·7 to 3·1. The optical characters and chemical composition are subject to considerable variation in different species. Broadly speaking, there is a group of potash-micas, generally of pale colour, and having the optic axes separated by wide angles; and a group of magnesian, or ferro-magnesian, micas, usually of dark colour, with the optic axes in some cases so close that the mineral becomes apparently uniaxial. On sharply striking a plate of mica with a needle-point, a six-rayed star is produced (*percussion-figure*); while pressure with a blunt instrument develops a similar figure (*pressure-figure*), having each ray at right angles to one in the percussion-figure.

All the micas are complex silicates, containing aluminium and potassium, generally with magnesium, but rarely with calcium. The potassium is frequently replaced in part by lithium and sodium, while iron may be substituted for the magnesium and aluminium. Water is always present, and many micas contain fluorine. The chemical constitution of the group of micas has been discussed by Rammelsberg (Min. Chem.) and by Tschermak (Zeitsch. Kryst. 1878, 2, 14; 1879, 3, 122), and later by F. W. Clarke (Amer. Chem. J. 1889, 38, 384; Bull. United States Geol. Survey, 1895, No. 125). The following analyses will serve to illustrate the composition of the principal species:—

—	I	II	III	IV
Silica . .	46·74	50·43	44·81	40·91
Alumina .	35·10	28·07	10·87	17·79
Ferric oxide .	4·00	—	—	11·02
Manganese oxide	—	0·88	—	—
Ferrous oxide .	1·53	—	0·31	—
Magnesia .	0·80	1·42	28·90	19·04
Potash . .	9·63	10·59	8·40	9·96
Soda . .	—	1·46	0·38	—
Lithia . .	—	1·23	0·08	—
Fluorine. .	1·05	4·86	—	—
Water . .	3·36	—	5·42	—
	102·21	98·94	99·17	98·72

I. Muscovite from Easton, Pennsylvania, by Rammelsberg. II. Lepidolite from Rozena, Moravia, by Reuter. III. Phlogopite from Edwards, St. Lawrence Co., New York, by Penfield; notable for the absence of fluorine. IV. Biotite from Vesuvius, by Chodnew.

Muscovite, or potash-mica $H_2KAl_3(SiO_4)_3$, is the common species widely distributed as a constituent of granite, gneiss, and mica-schist. It is usually white, grey, or yellow; and the angle of the optic axes may be as much as 70°. Some forms of muscovite have been mistaken for talc, as in the granitic rock of the Alps called protogine, and in certain so-called talc-schists. *Sericite* is a silky talc-like mica, occurring in the schists of the Taunus. A rare variety of muscovite containing 6 p.c. of baryta has been called *oellacherite* or baryta-mica. *Fuchsite*, or chrome-mica, of a bright-green colour, is a variety containing about 4 p.c. of chromic oxide. The *paragonite* of St. Gotthard, closely related to muscovite, is a soda-mica $H_2NaAl_3(SiO_4)_3$.

Lepidolite, or lithia-mica, with the approximate formula $KLi[Al(OH,F)_2]Al(SiO_3)_2$, is generally of peach-blossom colour, but sometimes grey or white, with a pearly lustre. It occurs in certain granites, especially with minerals containing fluorine, like topaz and tourmaline. Small amounts of rubidium and cæsium are sometimes present in lepidolite. The best-known locality for the typical kind is near Rozena in Moravia, where it forms a beautiful rock, occasionally polished as an ornamental stone. During recent years lepidolite has been extensively mined at Pala in California for the supply of lithium salts largely used in the manufacture of lithia-water. *Zinnwaldite* is a greyish lithia-bearing mica, occurring in the tin-mining districts of Saxony, Bohemia, and Cornwall.

Phlogopite $[H,K,(MgF)]_3Mg_3Al(SiO_4)_3$ includes certain magnesian micas, usually of reddish or bronze colour, occurring in crystalline limestone and in serpentine. The angle of the optic axes ranges from 0° to 17°. It is notable that certain phlogopites exhibit by transmitted light luminous stars, due to the presence of multitudes of included acicular crystals definitely orientated; the best examples of this asteriated mica being yielded by some of the Laurentian limestones of Canada. The mica mined in Canada and Ceylon for commercial purposes is phlogopite.

Biotite includes a number of magnesian and ferro-magnesian micas, generally of dark colour, and transparent only in thin laminæ. Frequently occurring in six-sided plates, and having a very small optic angle, they were formerly referred to the hexagonal system. In thin sections they exhibit strong pleochroism. They are generally denser than muscovite, and their cleavage-laminæ are less elastic. Biotite is often found, in association with muscovite, in granite, gneiss, and mica-schist, and the two micas are sometimes closely intergrown. The biotitic micas also occur in mica-syenite, mica-porphyry, and trachyte; while sharply developed crystals are not uncommon in the ejected blocks of Monte Somma. The Vesuvian dark micas were termed by Breithaupt *meroxene*, and this name has been revived by Tschermak for all the true biotites, while he uses the term *anomite* to distinguish a similar mica, differing only in optical characters. *Rubellane*, an opaque red mica from certain volcanic rocks, is merely an altered biotite, which has lost its elasticity. In *lepidomelane*, the aluminium of an ordinary biotite is largely replaced by iron, and the mica becomes black and is attracted by a powerful magnet. Heddle's *haughtonite*, of the Scottish granites, differs from biotite by containing less magnesium, and from lepidomelane by having most of its iron in the condition of FeO, the average percentage of this oxide being 17·22.

The vanadium-mica, or *roscoelite*, occurring with gold ores in California and Colorado, contains as much as 28·85 p.c. V_2O_3. *Margarite*, or lime-mica, $H_2CaAl_4Si_2O_{12}$ is sometimes placed in the mica group, though more usually it is classified with the clintonites or 'brittle micas.'

The mica of commerce comes mostly from India, the United States, and Canada. Large sheets of sufficient purity to be profitably worked are of very limited occurrence; they are usually found in veins of pegmatite or giant granite, where the constituents crystallise on a large scale, and are often associated with rare minerals such as beryl and columbite. In India the chief mica-mining districts are those of Hazáribágh in Bengal and of Nellore in Madras; from the former the mica (muscovite) is usually of a pale ruby tint, and from the latter of a greenish shade. In the Inikúrti mine, Nellore, 'books' of mica measuring 10 feet across the basal plane and up to 15 feet across the folia have been found. Rectangular sheets measuring 30×24 inches and free from flaws have frequently been obtained. A single mica crystal from North Carolina has been known to weigh nearly 2000 pounds. Mica has been worked at Alstead, in New Hampshire, where sheets have been found measuring 4 feet across. Mining for mica has also been carried on in the Black Hills of South Dakota, in Virginia, and in New Mexico. Several mines have now been opened up in the Uluguru Mountains, in German East Africa.

Of the various micas, muscovite and phlogopite are the only ones of commercial importance; and these, strangely enough, often pass in trade under the name of 'talc.' Muscovite was formerly called 'Muscovy glass,' in allusion to its use in Russia as a substitute for window-glass. At the present day it is employed chiefly as a transparent fire-resisting medium in the doors of stoves and furnaces, and for lamp-shades and gas-covers. It is also used for the dial-plates of compasses, while in the East, especially in India, it is applied to various ornamental purposes. Paintings on mica, executed by native artists, are well known to collectors. Sheets of mica, used as a decorative material, have been found in the prehistoric mounds of the Mississippi Valley.

The preparation of mica for the market is very simple. The blocks of rough mica, having been freed from associated minerals, or dressed, are split into plates, which are then 'scribed,' or marked out into patterns, and along this scribing the mineral is cut by means of shears. A good deal of refuse is necessarily produced. This mica-waste is ground and used as a lubricating agent, and as an absorbent for nitroglycerin in the preparation of certain explosives; it has also been employed in the ornamentation of wall-papers, and to a limited extent as a substitute for asbestos.

Many other practical uses of mica might be mentioned. Its most extensive application at the present day depends on the fact that it is a bad conductor of electricity. The smooth, flexible sheets are used in the construction of the armatures of dynamos and in other parts of electrical machinery. Extensive use is also made for insulating purposes of a manufactured material known as *micanite* or *micanite cloth*. This consists of scraps of mica cemented by shellac on to cloth or paper.

References.—T. H. Holland, The Mica Deposits of India (Mem. Geol. Survey, India, 1902, 34, 11–121). The Mining and Preparation of Mica for Commercial Purposes (Bull. Imperial Institute, 1904, ii. 278–291). F. Cirkel, Mica, its Occurrence, Exploitation, and Uses (Mines Branch, Ottawa, 1905, 148 pp.). G. P. Merrill, The Non-metallic Minerals, 2nd ed. 1910.

L. J. S.

MICA POWDER *v.* Explosives.

MICACEOUS IRON ORE *v.* Hæmatite; also Iron.

MICHLER'S KETONE *v.* Ketones.

MICROBALANCE. Nernst and Riesenfeld (Ber. 1903, 36, 2086) described a torsion balance sensitive to 0·0005 mgrm. with a load of several milligrams (for applications of same, *v.* Jänecke, Zeitsch. anal. Chem. 1904, 43, 547; Brill, Ber. 1905, 38, 140; Brill and Evans, Chem. Soc. Trans. 1908, 93, 1442). The zero of this balance is inconstant, and its sensitiveness varies greatly with the load. Ordinary gravity balances have been made by Steele and Grant (Proc. Roy. Soc. 1909, A. 82, 580), and modified by Gray and Ramsay (*ibid.* 1911, A. 84, 536; 1912, A. 86, 270) to carry loads ranging from 1 or 2 mgrms. to 1 decigram with a sensitiveness of 1×10^{-7} to 4×10^{-9} grm. The zeros of these balances remain constant over long periods of time.

The beam (Fig. 1) consists of a framework of thin silica rods, total length 10 cms. (Fig. 2 (*a*) shows a more rigid beam); it turns on a compound quartz knife-edge resting on a quartz plate A at the top of the brass pillar B. The vibrations of the balance are followed by passing a beam of light, from a Nernst lamp, through the window C in the side of the air-tight brass case, on to a tiny platinised quartz mirror, sealed to the balance frame at D so that it revolves with the latter without undergoing displacement. The light is reflected on to a mm. scale some distance away. The three-way tap E allows the interior of the balance case to be put into communication with either the atmosphere or a vacuum pump; the manometer F records the pressure within the case. A fine quartz thread fused to the beam at G supports (i.) a quartz bulb H of known volume V c.c. (either filled with air or vacuous), (ii.) the scale-pan J, and (iii.) a quartz counterpoise K. The whole hangs within the tube L (fitted to the case by the ground-glass joint M), and is counterpoised by a solid bead of silica at N. A little uranium oxide inside the case ionises the air and eliminates disturbing electrical effects; and calcium chloride in L keeps the interior dry.

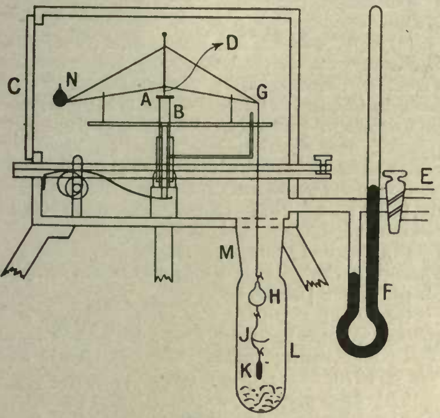


FIG. 1.

To perform a weighing, the pressure in the case is suitably lowered (to P_1 at temp. T_1 abs.), and the position of the reflected spot of light on the scale taken as the zero. The substance is then placed on the pan J, and a new pressure (P_2 at temp. T_2 abs.) determined under which the zero of the balance is recovered. The weight of the substance is then given by the expression (σ_0=wt. of 1 c.c. air at N.T.P.)

$$\frac{273V\sigma_0}{760}\left(\frac{P_2}{T_2}-\frac{P_1}{T_1}\right)$$

The usual vacuum correction is, of course, necessary. Only weights less than the weight of air that the bulb H can hold may be thus determined. To measure greater weights, the counterpoise K is replaced by a lighter one; a series of such counterpoises is required, and the differences between their weights may be measured on the microbalance itself. It is convenient (Fig. 2*b*) to make the bead N counterpoise the bulb, scale-pan, and a set of weights (ranging from 2 to 0·1 mgm.; made from capillary quartz tubing, and calibrated on the balance). In weighing a substance, weights are removed to obtain a coarse adjustment; the pressure within the case is then altered, thereby making the (variable) buoyancy of the air on the bulb H effect the fine adjustment. The absolute accuracy of the weighings is limited to the accuracy with which V may be determined; their relative accuracy is much greater.

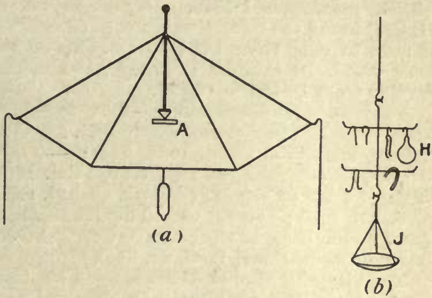


FIG. 2.

In a balance constructed by Steele and Grant, the beam, &c. weighed 0·93 grm., the bulb H had a capacity of 0·422 c.c. and contained $5{\cdot}04\times10^{-4}$ grms. of air; the balance had a period of 33 secs., and was sensivitive to 4×10^{-8} grm.

MICROCLINE *v.* FELSPAR.

MICROCOSMIC SALT. *Ammonium sodium hydrogen phosphate* $NH_4{\cdot}NaHPO_4,4H_2O$, used as a flux in blow-pipe tests.

MICROSAL. Trade name for a disinfectant made by mixing a solution of crude sulphophenolic acid with copper carbonate.

MIDDLETONITE *v.* RESINS.

MIEMITE. A dolomite of an asparagus-green colour found in Tuscany, *v.* DOLOMITE.

MIKADO ORANGE, -YELLOW *v.* AZO-COLOURING MATTERS.

MILK. Milk is the term usually restricted to the liquid secreted by the mammary glands of the class of animals called mammalia. Certain secretions, however, which are produced by birds and by some species of plants more or less resemble ordinary milk in their general physical and chemical characters.

Milk is generally white in colour, with a faint yellow or bluish tinge; it is homogeneous and opaque, the opacity being due to particles of fat (milk globules) and to casein, the characteristic protein of milk, which in combination with lime and calcium phosphate exists in pseudo solution. When fresh it has a characteristic aroma. Immediately after drawing, it has in addition a faint odour of an exhalation from the skin which disappears on exposure to the atmosphere. The sp.gr. of milk in general varies between 1·018 and 1·045 (Scherer); that of human milk averages 1·032 (Simon), 1·03267 (1·02561–1·04648) (Vernois and Becquerel), 1·0313 (1·0353–1·0260) (Leeds, Chem. News, 50, 263); that of cow's milk varies between 1·029 and 1·033 (Bouchardat and Quevenne). The average of English cows' milk is 1·0322 (Vieth), of German cows 1·031 (Fleischmann).

The specific heat of milk is 0·96, varying slightly according to the percentage of fat (Richmond) and 0·9457 (Fleischmann, J. Landw.

1902, 50, 33), and it attains its maximum density between 0° and 1° (Fleischmann, L. V. S.[1] 17, 251). The refractive index of cow's milk was found by Valentin (Pfl. Arch. 1879, 78) to average 1·35 with Abbe's refractometer. The refractive index of human milk varies from 1·3475 to 1·3494, maximum 1·3518. Jorgenssen (L. J. 11, 699) found the refractive index of 23 samples of milk to vary from 1·347 to 1·3515; on the other hand, 29 samples of whey gave indices varying from 1·3465 to 1·3433.

The freezing-point of milk is —0·54° to —0·58° mean —0·554° (Beckmann, Milch. Zeit. 23, 702; Lajoux, J. Pharm. Chim. 1905, 577); —0·556° to —0·574° (Hamburger, Rec. trav. chim. 1896, 349); —0·55° to —0·57° (Winter, Compt. rend. 1895, 121, 696); —0·55° to —0·59° (Carlinfanti, Gazz. chim. ital. 1897, 460); —0·55° ±0·03° (Atkins, Chem. News, 1908, 97, 241).

The viscosity of milk depends upon the temperature, but the diminution in viscosity with rise of temperature is much more rapid in milk than in water.

The reaction with litmus varies according to the species. Human milk is normally alkaline, whilst that of the carnivora is generally acid; cow's milk may appear faintly alkaline or faintly acid, or show both reactions (amphoteric).

Abnormally, milk may be bluish-white, deep-yellow, brown, pinkish-red, blue, or black in colour, watery, slimy, stringy, sandy, or heterogeneous in consistency, putrid or otherwise offensive in odour, and salty, sour, bitter, or astringent in taste.

The liquid secreted by the female immediately before or after parturition is termed colostrum or beestings, and differs considerably from normal milk in both physical and chemical characters.

Reaction.—Soxhlet (J. pr. Chem. [ii.] 6, 1) has shown that cow's milk, in common with all liquids containing both neutral and acid phosphate in solution, is amphoteric—*i.e.* it will exhibit both acid and alkaline reactions. With the recognition of the facts that litmus is an acid of appreciable strength, and that the change of colour is due to a setting up of equilibrium between the bases combined with the phosphoric acid and litmus respectively, the amphoteric reaction of milk is simply explained. All milks are acid to phenolphthalein, the average degree of acidity of cow's milk being about equal to 20 c.c. of normal acid per litre; the exact degree varies slightly according to the amount of phenolphthalein used, and the temperature.

Composition.—The ancients were acquainted with only three of the constituents of milk, viz. fat, caseïn, and water. Bartoletus of Bologna (1619) discovered a fourth constituent, the 'nitrum seri lactis,' afterwards renamed by Testi (1698) *zucchero di latte* (sugar of milk). Geoffrey (1737) separated the soluble salts and identified sodium chloride among them. Scheele (1780) found calcium phosphate in the ash.

At the present time the following substances are stated to be normal constituents of fresh milk.

(*a*) *Proteins*: Caseïn, opalisin (Wroblewski, Zeitsch. physiol. Chem. 1898, 308); and the mucoid-protein of Storch (Analyst, 1897, 148); albumin (lactalbumin); globulin (Sebelien, Zeitsch. Chem. 9, 445; Hewlett, J. Physiol. 1892, 13, 798; Arthus, Arch. Physiol. 1893, 673).

(*b*) *Extractive matters*: Urea (Lefort, Compt. rend. 62, 190); creatinine (Weil, Ber. 11, 2175); traces of lecithin, cholesterol, and hypoxanthine (Schmidt-Muhlheim, P. Arch. 30, 379).

(*c*) *Organic acids*: Lactic acid (Marchand, J. Pharm. Chim. [iv.] 29, 311; Hoppe-Seyler, Virch. Arch. 17, 443; Manetti and Musso, Zeitsch. Chem. 16, 397), though it is doubtful if this exists in perfectly fresh milk; citric acid (Henkel and Soxhlet, Bied. Zentr. 17, 787); acetic acid (Béchamp, Compt. rend. 76, 836); orotic acid (Biscaro and Belloin, Mon. Scient. [iv.] 19; i. 384; and Ann. Soc. Chim. Milano, 11, 1905).

(*d*) *Carbohydrates*: Sugar of milk, and a second carbohydrate discovered by Ritthausen, (J. pr. Chem. [i.] 57, 348).

(*e*) *Other organic bodies*: Alcohol (Béchamp, Compt. rend. 76, 836); lactochrome, an organic colouring matter (Blyth, Chem. Soc. Trans. 1879, 531); and a bitter principle.

(*f*) *Inorganic acids* (*in combination*): Phosphoric, hydrochloric, sulphuric (Musso and Schmidt, Bied. Zentr. 1179, 865); thiocyanic (Musso); but its presence is accidental from mustard oil in food (Stoecklin and Crochetelle, Compt. rend. 1910, 150, 1530).

Enzymes.—A proteoclastic enzyme (Babcock and Russell, 14th Ann. Report, Wisconsin Exp. Stat. 1897); an oxydase, a catalase (Loew, Zeit. Biol. 1902, 256; Wender, Chem. Zentr. 1903, i. 592), a reductase (Schardinger, Zeitsch. Nahr. Genussm. 1902, 1113; Reiss, Chem. Zentr. 1905, i. 604), and a kinase (Hongardy, Bull. acad. Roy. Belg. 1906, 888). Wohlgemuth and Strich (Sitzungsber. K. Akad. Wiss. Berlin, 1910, 520) state that carbohydrate and fat splitting enzymes are present, also oxydase, reductase and catalase, but show that proteoclastic enzyme is due to bacteria; there is a glycyltryptophan enzyme. Tromsdorff (Centr. Bakt. Par. 1909, 1, 291) finds no reductase in quite fresh sterile milk. Bordas and Touplain (Compt. rend. 1909, 1057) reject the enzyme nature of peroxydase, and state that the reactions are due to casein.

(*g*) *Bases*: Potash, soda, lime, ferric oxide, magnesia, ammonia (Latschenberger, J. 14, 222).

(*h*) *Gases* (*in solution*); carbon dioxide, oxygen, nitrogen.

Microscopic characters.—Viewed under the microscope fresh milk appears as a clear colourless liquid in which are suspended—(*a*) milk globules and more rarely (*b*) granular bodies, the so-called colostrum corpuscles. Haidenhain (Handb. der Phys.) states that the following morphological structures have been observed in human and to a less extent in cow's milk:—

(1) Semiglobular fat drops with a finely granular substance.

(2) Clear cells containing one or two fat drops and an eccentric nucleus.

(3) Round clear bodies easily coloured by eosin and picrocarmine, supposed to be free nuclei.

(*a*) The milk globules may vary in diameter from 0·01 to 0·0015 mm., but generally range from 0·005 to 0·0033 mm.

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[1] L. V. S. = Landwirthschaftliche Versuchs-Stationen.

According to Bohr (J. 1880, 183) the diameter may vary from 0·0063 to 0·00014 mm.

Under the highest powers of the microscope they appear merely as more or less irregularly shaped globules of fat, without the faintest trace of a limiting membrane; nevertheless, all the earlier observers (Henle, Mitscherlich, Lehmann, Moleschott, &c.) believed in the existence of an external envelope, principally because ether, when shaken up with milk, will not dissolve out the fat unless acetic acid or potash is previously added. These substances were supposed to dissolve the enveloping membrane of the globules and release the fat. This view has been again advocated by Struve (J. pr. Chem. [ii.] 27, 249), who thinks the globules have a coat of insoluble casein; by Babcock (Milch.-Zeit. 17, 809), who states they are covered with an envelope of milk-fibrin, and by Béchamp (Compt. rend. 107, 772). Storch (Analyst, 1897, 198) affirms the existence of a semi-gelatinous membrane; but his conclusions have been adversely criticised by Richmond (Analyst, 1897, 207; 1904, 183) and Wood (American Medicine, 1907, 416).

The weight of evidence appears, however, to be against the existence of a solid membrane. Soxhlet holds that the milk is a simple emulsion of fat particles with casein, calcium phosphate, &c., and that the addition of acetic acid or sodium carbonate deprives the casein of its emulsifying power. He found that when a small quantity of ether was added it also entered into an emulsion with the fat and casein, &c., and only separated out with extreme slowness. If a large excess of ether or a mixture of ether and alcohol is shaken up with milk, the fat is completely extracted, without any previous addition of acid or alkali, whereas benzene and chloroform, which are equally good solvents for fat, will not extract it from the globules even after the addition of potash. If acetic acid is added to the milk in quantity just sufficient to convert the phosphates present into acid phosphates, but not to coagulate the milk, the fat cannot be extracted with ether. If a current of CO_2 is then passed through the milk, coagulation ensues and the fat can very readily be extracted with ether. The CO_2 cannot be supposed to be capable of dissolving any membrane (L. V. S. 19, 118). If milk be dried in a vacuum over H_2SO_4 the fat can easily be extracted from the residue with ether, but if the residue is redissolved in water the solution resists the action of the ether.

Duclaux (Chem. Biol. 667) finds that if the globules are kept warm while under the microscope, they may be squeezed out and broken by pressing on the cover glass, the altered globules only differing in size from the original ones. Babcock (Milch.-Zeit. 15, 393) also found that if milk be heated to 100° and whipped, the globules are doubled in number but present the same microscopic outline as before. By passing milk through small orifices under great pressure (homogenising) the fat globules can be broken up into very minute particles. From the above facts it is certain that the only membrane is a liquid layer condensed round the globules by the surface tension. Refer also to De Sinety (Arch. de Phys. 1874, 479), Herer (J. 1871, 120), Hoppe-Seyler (Arch. Path. Anat. 17, 417). The milk globules consist mainly of various fats, but analysis shows the presence of traces of cholesterol, lecithin, and of a yellow colouring matter spectroscopically identical with luteïn.

(*b*) The colostrum cells or corpuscles occur very sparingly in normal milk, but abundantly in the colostrum. They consist of irregular conglomerations of very small fat vesicles embedded in a granular protoplasmic matrix; occasionally one or more eccentric nuclei may be observed. They are about four or five times as large as the milk globules, the diameter varying from 0·014 to 0·055 mm. Heidenhain (Handb. der Phys.) finds that if a drop of warm perfectly fresh milk be examined on a Strecker's warm stage, and the temperature regulated to 38°C. amœboid movements of these cells can be observed resembling in all respects those of the white blood corpuscles, from which indeed Heidenhain considers them to be derived by a process of infiltration with milk fat.

The fat of these corpuscles is much more readily dissolved by ether than that of the milk globules. They are disintegrated by potash or acetic acid, iodine water colours them intensely yellow, hence they consist of very small globules of fat embedded in an albuminous substance.

Abnormal milk may contain hematin, biliary colouring matters, mucin, blood corpuscles, pus, mucus, fibrous clots, and many varieties of fungi and bacteria.

Changes in milk.—Milk commences to undergo change from the moment it is drawn. If left exposed to the air it very soon loses its dissolved CO_2 and takes up oxygen. Cow's milk, in which the alkaline reaction is said to be more distinct whilst in the udder, soon shows the acid reaction markedly. On standing for a time a thick yellowish-white stratum, rich in fat, collects on the surface (cream), whilst the lower portion becomes bluish-white, poorer in fat, and increases in sp.gr. Recknagel (Bied. Zentr. 1884, 16) finds that 2 or 3 hours after the milk has been drawn the sp.gr. commences to rise, the milk attaining its maximum density in 6 hours if the temperature is kept down to 5°, but only after the lapse of 2 or 3 days at 15°. This property he considers to be due to the swelling up of the casein suspended in the milk. Vieth (Milch.-Zeit. 18, 141) found the average sp.gr. of 15 samples to be 1·0296, half an hour after milking, and 1·0309, 16 hours later.

This phenomenon is chiefly, if not wholly, due to the slow solidification of the fat globules; fat in the liquid state has a density of 0·92, and when solid of 0·93, and the experiments of H. D. and S. O. Richmond (Dairy Chemistry, 338; and Analyst, 1901, 117) prove that the fat melts at about 32°–34°, and the liquid globules slowly solidify if cooled below this temperature.

If milk is cooled to 10° it acquires a viscous consistency which increases rapidly as the temperature falls. Hoppe-Seyler (Ph. C. 723) states that on standing the quantity of albumin falls and that of casein increases.

On boiling, CO_2 is expelled, and it is stated that H_2S is also given off (Schreiner, L. V. S. 22, 60; Rettger, Amer. J. Physiol. 1902, 450; Utz, Milch.-Zeit. 1903, 354). Arnold (Bied. Zentr. 1882, 131) states that unboiled milk colours tincture of guaiacum blue, but that boiled milk does not; potassium iodide and starch are rapidly turned blue by unboiled milk, but only slowly by boiled milk.

These reactions are due to the oxydase present in milk; there are, however, a large number of other reagents, which, when added to fresh milk, give on addition of a little hydrogen peroxide coloured oxidation products; among these may be mentioned paraphenylene diamine (Dupuoy, J. Pharm. Chim. 1897, 397; Storch, Bied. Zentr. 1898, 711; Leffmann, Analyst, 1898, 85); metaphenylene diamine (Richmond and Rosier, Analyst, 1900, 231); ortol (ortho methylamino phenol and quinol); Saul (Brit. Med. J. 1903, 664); benzidine (Wilkinson and Peters, Zeitsch. Nahr. Genussm. 1908, 172); most photographic developers (Macadie, Pharm. J. 1907, 207; *cf.* also Siegfeld, Zeitsch. angew. Chem. 1903, 764).

As in all fairly alkaline liquids, the alkaline reaction in cow's milk becomes more evident while hot (Soxhlet, J. pr. Chem. [ii.] 6, 1), but recovers its previous intensity on cooling. Boiled milk also coagulates less readily, and is less sensible to the action of ferments and bacilli (Richet, Compt. rend. 88, 750). Very considerable chemical change must therefore have taken place, but it is still not very clear what is the nature of this change.

If heated over 60° milk acquires a slimy consistency, which has also been attributed to a change in the state of the suspended casein; this sliminess retards the subsequent separation of cream.

By heating milk to 100° (or even to lower temperatures) the rising of cream is hindered (Cazeneuve and Haddon, Bull. Soc. chim. 1895, 13, 500; Richmond and Boseley, Analyst, 1897, 95).

When milk is evaporated in a vacuum at the ordinary temperature, or at the ordinary pressure at a temperature of 50°, a skin gradually forms on the surface and is renewed as often as it is removed. This skin is due to the desiccation of the proteins by the surface evaporation, and to the concentration of the hydrogen ions. It was formerly thought to consist of albumin only (Hoppe-Seyler, Virch. Arch. 17, 417), and the statement was made that, on boiling milk, the albumin separated out; but Sembritzki (Pogg. Ann. 37, 460) found that by continually removing the skin, he could obtain 1·023 p.c. of the milk in that form. Since the albumin is not present in such quantity, it follows that some other body such as casein must enter into its composition.

When milk is heated for a long time at a high temperature it coagulates; Cazeneuve and Haddon (Compt. rend. 1895, 120, 1272) attribute this to the formation of formic acid by the action of heat on lactose; but Bardach (Monatsh. 1897, 199) shows that the formic acid produced is insufficient in quantity for this, and find that it is due to complex changes in the caseïn.

On slowly freezing milk, the ice first formed contains a greater proportion of fat, but the mother liquor contains more casein, milk-sugar, and salts, but if the freezing takes place quickly the fat is equally distributed (Kaiser and Schmeider, Bied. Zentr. 1887, 267).

For composition of ice found on freezing milk, *cf.* Vieth, Analyst, 1891, 65; Bordas and de Raczkowski, Compt. rend. 1901, 133, 759; Richmond, Analyst, 1893, 53.

If, however, the milk is agitated, the milk-ice is richer than the mother liquor in slow freezing, but more watery and poorer in both solids and fat when quickly frozen (Henzold, Milch.-Zeit, 15, 461).

Souring of milk.—Under certain circumstances, the homogeneous structure of milk undergoes a change, and a curd is thrown down in the form of a flocculent or compact precipitate. This change is termed curdling or coagulation, and is caused by the development of lactic acid by the action of micro-organisms, *e.g.* the *B. acidi lactici*, which are constantly present in milk, even when drawn from the udder (Hueppe, Bied. Zentr. 85, 408), and precipitation of the caseïn.

Spontaneous coagulation is characterised by the gradual souring and thickening of the milk; it takes place more readily when the temperature is raised, and when the atmosphere is charged with electricity.

Soxhlet found fresh milk to coagulate in 19 hours at 39°; in 29 hours at 25°; in 48 hours at 20°; in 63 hours at 17·5°; in 88 hours at 15°; in 99 hours at 10°; and he kept milk for 14 days without much change in taste at 1°–2°.

Though the nature of the organisms varies the amount of acid produced in a given time at any temperature is fairly constant (*cf.* Thorner, Chem. Ziet. 1891, 1108; Van Slyke and Hart, Amer. Chem. J. 1904, 145). Richmond and Miller (Analyst, 1907, 144) have plotted out a curve showing the relation of acidity and time at 20°, and state that at other temperatures the form of the curve remains the same, but the time taken to reach a given point increases (or decreases) 2·075 times for each 10° above or below 20°. The curve is logarithmic up to 45° acidity, at which point a break occurs; this appears to be due to this being the point at which the micro-organisms do not increase (Revis and Payne, J. Hygiene, 1906, 216); from this point the development of acidity is expressed by another parabolic curve. Revis and Payne (*l.c.*) conclude that as milk turns sour, calcium phosphate is split off from the casein complex, and when curdling takes place practically all the calcium phosphate is removed.

Though the lactic fermentation is the most common in milk, other substances are produced by the action of micro-organisms; both *d*- and *l*-lactic acids are produced, and acetic, propionic, and butyric acids may be formed (*cf.* Kozai, Bied. Zentr. 1903, 273; Tissier and Gastling, Ann. Inst. Pasteur, 1903, 540; v. Freudenreich and Jensen, Centr. Bakt. Par. 1906, 529; Thorpe Chem. Soc. Trans. 1905, 206; Richmond and Miller, Analyst, 1906, 317; Beyerinck, Proc. K. Akad. Wetensch. Amsterdam, 1907, 17), and succinic acid, together with ammonia and trimethylamine has been found in two cases by Kozai (*l.c.*). Alcohol in small quantities is almost always present in sour milk, and usually proteolysis occurs (*cf.* Kozai, and Richmond and Miller, *l.c.*; Pennington, J. Biol. Chem. 1908, 353).

When milk is boiled for some time, *most* of the organisms contained in it are destroyed, and spontaneous coagulation cannot occur unless it is again impregnated by contact with the air.

A temperature of 100° is, however, insufficient to destroy all the organisms present in milk.

Duclaux (Le Lait, Paris, 1887) kept milk unchanged for 5 years by removing all the air from the vessel, and subsequently by heating to 120° for some time.

Spontaneous coagulation is retarded by the addition of antiseptics, which inhibit the action of the bacilli themselves, and also by alkaline substances which merely neutralise the acid formed by their action. As antiseptics the following substances are sometimes added to milk, viz. boric acid, salicylic acid, formaldehyde, benzoates &c. (For a quantitative study of the action of preservatives, *cf.* Richmond and Miller, Analyst, 1907, 144.)

Coagulation by acids.—Most acids coagulate milk in the cold, more readily when heated. 1 p.c. of acetic acid is required to precipitate milk fully at the ordinary temperature, but 0·4 p.c. is sufficient at 35° and 0·2 p.c. at 100°. Even carbonic acid will coagulate milk at an elevated temperature. Duclaux (*Le lait*) found that on saturating milk in the cold with CO_2 and heating it in a closed vessel at 115°–120°, coagulation ensued.

Many salts such as NaCl, $MgSO_4$, &c., coagulate milk. Alcohol and acetone act in a similar manner.

Coagulation by rennet.—This is by far the most important of all the methods of coagulating milk, and the phenomena merit the closest attention. Unfortunately the action is very complex, and there still exists some divergence of opinion as to its nature. The old theory, that coagulation was in this case also preceded by the formation of lactic acid, held by Simon, Liebig, Soxhlet, &c., is now entirely abandoned, and it is generally admitted that the action of rennet depends upon the specific property of a chemical ferment present in it. This was first isolated by Deschamps (Dingl. poly. J. 1840, 445), who termed it *chymosin.* Hammarsten (Bull. Soc. chim. [ii.] 22, 352) fully investigated the properties of this ferment. He found that it does not give the xanthoprotein reaction, is not precipitated by nitric acid, alcohol, iodine, tannin, nor by neutral acetate of lead, but it is precipitated by basic lead acetate. It is not coagulated at 100°, but its efficiency is destroyed. It is soluble in water and glycerol; the latter solution is precipitated by alcohol.

Hammarsten (J. Pharm. Chim. 5, 267) further proved that it could coagulate milk even in the absence of acids or of milk sugar, and that the precipitate obtained differed in many important particulars from that thrown down by acids. Heintz showed that rennet could produce coagulation even in solutions rendered alkaline with sodium carbonate, provided the temperature were raised to 65°.

The ferment is inactive in the cold, and when present in only very small quantity. Hammarsten has proved that it cannot precipitate a solution of casein unless a small amount of certain soluble salts is present; the salt may be phosphate or chloride or sulphate, but it is essential to have it in solution; calcium phosphate in suspension is entirely useless. Small quantities of sodium phosphate, potassium chloride, the soluble barium, strontium, calcium, and magnesium salts promote the action of the ferment; larger quantities have, however, an adverse influence. The great majority of the sodium, potassium, and ammonium salts invariably retard the action of rennet.

Halliburton (J. Physiol. 1890, 11, 448) and Ringer (*ibid.* 1891, 12, 164) have shown that the ferment splits up the protein, and the curd is precipitated owing to its insoluble lime salt.

The presence of alkalis and alkaline carbonates either delays or entirely prevents coagulation. Small quantities of acids, on the other hand (except boric), hasten the action (A. Weitzel, Arbeiten a. d. Kais. Gesundheitamt, 1902, 19, 126). 1 p.c. of lactic acid greatly accelerates coagulation (Engling, L. V. S. 31, 391).

Pawlow and Parastchouk (Verb. d. Vers. Nordicher Naturfor. u. Äntze in Helsingfors, 1902, 28) have put forward the view that as many ferments contain a rennet-like body, rennet is not a special ferment at all, but that the property of curdling milk is shared by all proteoclastic enzymes.

Constitution of milk.—Chemists have hitherto been unable to agree with regard to the constitution of milk. According to some it is a solution, according to others an emulsion, and others consider it to be a mere mixture.

On filtering milk through a porous cell, the following substances occur in the filtrate in solution:—

The whole of the milk sugar, albumin and extractive matters, soda, potash, hydrochloric and citric acids (in combination), the greater part of the magnesia, about one-third the lime, and one-half the phosphoric acid present in the milk (Richmond, Analyst, 1901, 313, however, found that the albumin was removed). The bulk of the milk solids—viz. the fat, casein, lime, and phosphoric acid—fails to pass through.

The question whether the fat exists in an emulsified state, or in morphologically differentiated structures has already been noticed (*v. Microscopic characters*). The state of the casein, lime, and phosphoric acid, now claims our attention.

Hammarsten (J. Pharm. Chim. 5, 267) found that perfectly pure casein is insoluble in water, and possesses a strongly acid character. It dissolves in the phosphates and carbonates of the alkalis; in the latter case CO_2 is expelled. It also dissolves in a solution of caustic soda, in lime water, and in baryta water. If the solution in lime water is neutralised with phosphoric acid and kept for some time at about 40°, it becomes milk-white in appearance, behaves on filtration like natural milk, and is coagulated by acids or rennet. Other solutions of casein were not affected by rennet, unless calcium and phosphoric acid or a few other substances were introduced.

Hammarsten also observed that milk-casein precipitated by rennet constantly contained 4–5 p.c. of tricalcium phosphate, whilst that precipitated by acids contained a lesser and more variable percentage; the serum obtained from rennet also contained more proteins than that obtained from other precipitants. From these facts he concluded that casein was held in solution in milk by the neutral phosphates of the alkalis, and that the casein thus dissolved was able to take up the insoluble di- and tri-calcium phosphates and enter with them into a turgid, highly hydrated, and colloid condition which he considered the characteristic state of milk-casein, both in his artificial compound and in natural milk.

Coagulation by acids is according to this theory due to the conversion of the neutral phosphates of the alkalis into acid phosphates, which are unable to hold the casein in solution, but at the same time the acids convert part of the insoluble di- and tri-calcium phosphates, into the soluble mono-calcium salts. The milk-casein precipitated by acids is therefore poor in calcium phosphate.

Coagulation by rennet is due, according to Hammarsten, to the decomposition of the milk-casein into two proteins, one of which passes into perfect solution, whilst the other forms an insoluble compound with tricalcium phosphate (cheese). The approximate constancy of the percentage of calcium phosphate in the coagulum, and the excess of proteins in the serum, are thus accounted for (*cf.* Harris, J. Anat. and Physiol. 1894, 188).

On heating milk with an oxalate, calcium oxalate is precipitated; fluorides also easily precipitate the calcium (Arthus, Arch. Physiol. 1893, 673; Ringer and Hammarsten, *l.c.*).

Milk-casein, according to Engling (L. V. S. 31, 391), is casein-tricalcium-phosphate, and is completely decomposed by acids, casein being precipitated and more or less of the calcium phosphate taken up into solution. Rennet again only partially decomposes the casein-tricalcium-phosphate. A portion of the protein is detached and goes into perfect solution as acid albuminate, and as soon as a certain quantity of this is formed its acid character determines the precipitation of the bulk of the casein and tricalcium phosphate as a *basic* salt (cheese).

Hammarsten (*l.c.*) has studied the properties of the soluble portion, which he calls whey-protein; it has the properties of an albumose.

Söldner (L. V. S. 35, 351) made the observation that although the reaction of milk is amphoteric, the bases in the ash of milk are very largely in excess of the acids. It seemed to him *à priori* improbable that a strongly acid body like casein should exist in milk in combination with neutral tricalcium phosphate, and that a quantity of base should be simultaneously present with no acid to neutralise it, and without imparting a basic reaction to the liquid. Hammersten (*l.c.*) had found that casein was soluble in lime-water and Söldner found he could obtain two compounds of casein and lime; one containing 2·36 p.c. CaO reacts alkaline with litmus, but not with phenolphthaleïn, and dissolves in water to form an opalescent fluid which is not coagulated by rennet. The other compound containing 1·55 p.c. CaO, has a slight acid reaction; its solution in water forms after some time a milk-white fluid which is coagulated by rennet. Hammarsten had observed that pure casein contains 0·847 p.c. of phosphorus, and Söldner has proved that a solution of pure casein in lime-water leaves on ignition a residue of calcium pyrophosphate. Söldner therefore concludes that milk-casein is the *unsaturated compound of casein and lime* (1·55 p.c. CaO), and that it does not enter into combination with, nor has any specific solvent power for the insoluble di- and tri-calcium phosphates as such, these salts merely existing *in suspension* in the milk.

The power that *free casein* posessses of dissolving di- and tri-calcium phosphates is due to the acid nature of free casein. Just as it expels CO_2 from carbonates, &c., like other acids, so it abstracts part of the base from the insoluble phosphates, forming a soluble lime-casein compound.

According to Richmond (Analyst, 1900, 116; 1901, 313; 1902, 241) the state in which casein exists in milk has been elucidated by the study of the composition of the substance removed by filtration through a porous cell, and by the action of acids and of rennet.

There is little doubt that casein is a substituted phosphoric acid, and the amount of base in combination with the substance separated by porous earthenware is equal to one atom of sodium and one of calcium, together with half a molecule of tribasic calcium phosphate. The minimum amount of acid necessary to curdle milk on boiling is 8·3 c.c. normal hydrochloric or sulphuric acids per litre, and slightly greater amounts of weaker acids; this quantity is almost exactly equal to that required to combine with the sodium, and the precipitate contains the same amount of calcium, and calcium phosphate as the substance removed by a porous cell; the acidity of the serum is moreover equal to that of the milk. The behaviour of two acids is, however, anomalous, very much larger amounts of oxalic and phosphoric acids being required to curdle milk on boiling, the average quantities being 28·5 c.c. N-oxalic acid, and 35 c.c. N-phosphoric acid per litre; if we consider that oxalic acid removes calcium from milk as insoluble calcium oxalate, and phosphoric acid would form acid phosphates with calcium phosphate, it appears that these two acids break up the sodium-calcium-casein-calcium-phosphate complex.

The action of rennet, though chiefly on the protein portion of the complex, presents many analogies to that of acids on boiling; a portion of the casein molecule is split off as 'whey protein,' and the residue is also a substituted phosphoric acid; the proportion of calcium and calcium phosphate to organic phosphorus in the precipitated curd is the same as that found in the substance separated by porous earthenware, and in the precipitate formed by the minimum quantity of acid on boiling; the sodium is, however, removed, and the difference between the acidities of the milk and the whey is almost exactly 8·3 c.c. N-acid per litre. It appears probable that the action of rennet is even more analogous to that of the minimum quantity of acid on heating, as the amount of protein precipitate in the latter case is never quite equal to that of the casein, indicating that a portion of the protein molecule is removed on boiling; further evidence that this is the case is shown by the fact that while mercury salts are very perfect precipitants of the casein of milk, they do not remove the whole of the casein from a solution that has been heated, a lævo-rotatory substance which is precipitated by phosphotungstic acid remaining dissolved.

By heating milk alone, or by centrifuging, practically no calcium or phosphoric acid is removed, without a corresponding amount of organic phosphoric acid.

The action of acids in the cold is different from that on boiling; at ordinary temperatures at least 6 times the quantity required on boiling is necessary before a precipitate is obtained, and nearly the whole of the calcium and calcium phosphate is removed. At intermediate temperatures the amount of acid is less, and the removal of the inorganic constituents proportionately less.

These facts show that casein exists in milk as a complex of a sodium calcium salt combined with a molecular proportion of calcium phosphate, and that the simple derivatives consist of a similar complex, and are precipitated as acid salts, the sodium being removed. The older view that calcium phosphate was entangled or loosely combined appears to be untenable. This complex forming a solution resembling milk can be artificially prepared, and behaves towards rennet in a manner similar to milk. Casein in solution in alkalis is not curdled by rennet, but the molecule is split up, the hydrolysis proceeding much further than when rennet acts on the complex which exists in milk. This indicates that the final product of the action of rennet on the casein as it exists in milk is determined by a simple derivative which forms an insoluble acid salt.

It is not known in what state the albumin exists in the milk; it is not coagulated by raising the temperature to 70°, though it has been shown by Faber (Analyst, 1889, 144) and Stewart (Brit. Med. J. 1896, 626) that at this temperature it is converted into a form which is precipitated by acids or magnesium sulphate.

It has been stated that it is in combination with the casein, but the experiments of Richmond (Analyst, 1902, 240) appear to negative this view.

Lecithins, which are compounds of choline, glyceryl-phosphoric acid, and fatty acids such as stearic, are found in milk, and are probably of considerable importance in nutrition. They have been studied by Bordas and de Raczkowski (Compt. rend. 1902, 134, 1592; 135, 302, and 354) who state that the greatest amount is found in the first month; they show that by removing 98 p.c. of the cream 69 p.c. of the lecithin is removed, and this is confirmed by Glikin (Biochem. Zeitsch. 1909, 348). Nerking and Haensel give the quantity as 0·0109–0·0833 p.c. (Biochem. Zeitsch. 1908, 348).

Citric acid. Henkel (Bied. Zentr. 17, 787) found that on saturating the serum left after removing proteins, &c., with calcium salts, and slowly evaporating, a crystalline deposit of calcium citrate was formed. The amount of citric acid was estimated from this as 0·08–0·12 p.c.; but the quantity present is probably considerably greater.

Söldner (L. V. S. 35, 351) estimates it as 0·25 p.c., and Richmond (Analyst, 1901, 316) as 0·264 p.c.

It evidently exists as a soluble salt, since the same quantity separates out from whey and from serum (by cell filtration). The concretions in condensed milk consist of pure calcium citrate.

Salts. These consist principally of phosphates, chlorides, and citrates of the alkalis and alkaline earths. Musso also found 0·0391–0·0831 gram of sulphuric acid per litre. This would amount to 0·558–1·19 p.c. of SO_3 in the ash. Musso also found 0·0021–0·0046 gram NaCNS per litre of milk.

The amount of ash in cow's milk varies from 0·65 to 0·85 p.c.; generally from 0·7 to 0·8 p.c.

The ratio of ash : proteins : sugar is very constantly 2 : 9 : 13 in cow's milk, 1 : 5 : 10 in human, 1 : 6 : 23 in mare's milk (Vieth, Analyst, 13, 49). The following are average analyses of milk-ash:

	Percentage in milk	Percentage in ash
K_2O	0·1728	24·5
Na_2O	0·0868	11·0
CaO	0·1608	22·5
MgO	0·0243	2·6
Fe_2O_3	0·0005	0·3
P_2O_5	0·1922	26·5
Cl	0·1146	15·6
SO_3	0·0061	1·0

(Fleischmann).

More sulphuric acid is actually found in the ash than that shown, but it is due to the oxidation of the sulphur in the albuminoids; only that determined by Musso is taken into account. On the other hand, a deduction must be made for increase of weight by oxidation. Fleischmann deducts 3·5 p.c. of the weight of the ash for this error.

Söldner has shown (L. V. S. 35, 351) that, owing to the excess of base present in milk-ash, the whole of the phosphorus in the casein is oxidised to phosphoric acid, and appears in the ash as calcium phosphate. From 25 to 40 p.c. of the P_2O_5 in the ash may be due to this source. The composition of the ash therefore still requires revision.

Söldner (*supra*) has made an estimate of the amounts of salts as actually existing in the milk. Assuming the presence of 0·25 p.c. citric acid, he calculates:

Sodium chloride	0·962
Potassium chloride	0·830
Monopotassium phosphate	1·156
Dipotassium phosphate	0·835
Potassium citrate	0·495
Dimagnesium phosphate	0·336
Magnesium citrate	0·367
Dicalcium phosphate	0·671
Tricalcium phosphate	0·806
Calcium citrate	2·133
Lime (in combination with casein)	0·465

Rona and Michaelis (Biochem. Zeitsch. 1909, 114) state that 40–50 p.c. of the calcium is diffusible, and that much of it is combined with proteins. Richmond (Analyst, 1901, 310) considers that the citrates exist in milk as dibasic salts and gives the following as the distribution of the phosphoric acid in milk:

	P.c.
P_2O_5 as casein combined with CaNa	0·0605
„ $Ca_3(PO_4)_2$	0·0625
„ R_2HPO_4	0·077
„ RH_2PO_4	0·020

Latschenberger (Monatsh. 5, 129) found 0·02106 p.c. of ammonia in milk. Sherman, Berg, Cohen, and Whitman (J. Biol. Chem. 1907, 171) give the amount as 0·004 p.c.

Schrödt and Hansen (L. V. S. 31, 55) found the amount of chlorine in the ash to be greater at the end than at the beginning of the period of lactation (17·63 p.c.). There was also relatively more soda than potash, though the total alkalis were the same.

The ash is almost always 8 p.c. of the solids not fat (Vieth, Analyst, 13, 63).

Gases in Milk.—Pflüger (Pafl. Arch. 2, 166) found:

	O	CO_2 (pumped out)	CO_2 (expelled by phosphoric acid)	N
1.	0·1	7·6	0·00	0·7
2.	0·09	7·4	0·2	0·8

v. also Hoppe-Seyler (Virch. Arch. 17, 417); Setchenow (Zeit. rat. Med. 1861, 285).

Colostrum is, immediately after parturition, a yellow or brownish-yellow dirty-looking liquid, slimy, viscous, and often heterogeneous in consistency. It has a peculiar smell, a stale salty taste, and generally a slight acid reaction. It coagulates on boiling. The sp.gr. at 15° varies from 1·040 to 1·080.

The presence of colostrum corpuscles is characteristic (*v. Microscopic characters*).

The character of colostrum rapidly changes, and the following analyses by Engling (Bied. Zentr. 1879, 214) will show this:

Time after calving.	Sp.gr.	Total solids	Fat	Casein	Albumin	Sugar	Ash
Immediately	1·068	26·93	3·54	2·65	16·56	3·00	1·18
10 hours	1·046	21·23	4·66	4·28	9·32	1·42	1·55
24 „	1·043	19·37	4·75	4·50	6·25	2·85	1·02
48 „	1·042	14·19	4·21	3·25	2·31	3·86	0·96
72 „	1·035	13·36	4·08	3·33	1·03	4·10	0·82

Cf. also Vaudin (J. Pharm. Chim. 1894, 30, 337) and Sutherst (Chem. News, 1902, 1) who states that what is called albumin by Engling contains a large proportion of globulin; he finds 5·32 p.c. of this on the first day, and 2·05 p.c. on the second.

The proteins in colostrum vary greatly. Casein is always somewhat greater than in normal milk; albumin varies from a little above that of ordinary milk to over three times that amount. Globulin is always an essential constituent. Extractive N is a little higher than in ordinary milk. Engling (*l.c.* 96) states that at first colostrum contains no milk sugar, but only carbohydrates, resembling grape sugar. Sebelien and Sunde (Zeitsch. angew. Chem. 1908, 2546) find that the sugar is chiefly lactose, and suggest the presence of 0·05 p.c. of arabinose. The colostrum fat differs from ordinary butter in smell, taste, consistency, and melting-point. It melts at 40°–44°. This is due, according to Nilsson (Bied. Zentr. 17, 171) to the smaller quantity of volatile acids. Nuclein has been found up to 2 p.c. Cholesterol and lecithin also occur in some quantity. Urea is higher than in ordinary milk.

Engling found the ash of colostrum to consist of

K_2O	Na_2O	CaO	MgO	Fe_2O_3	P_2O_5	SO_3	Cl
7·23	5·72	34·85	2·06	0·52	41·43	0·16	11·25

The higher percentage of phosphoric acid and lime, and the low alkalis, are particularly noteworthy.

ABNORMAL MILK.

Blue milk. This is characterised by the appearance of blue spots, which gradually increase till the whole surface is covered. It is due to a bacillus (*B. cyanogenus*). If the reaction of the milk is acid the colouration is deep blue; in other cases it is a slaty blue, changing to deep blue on addition of acids. The colouring matter is identical with triphenylrosaniline (Martiny and Fürstenberg, Milch.-Zeit. 10, 594).

Stringy milk. Some milk, on standing for a short time, becomes thick and stringy. It is due to a special ferment, which sets up mucic fermentation. Sound milk is infected by addition of a little of the stringy milk, but the ferment can be destroyed by heating to 65° or by the addition of strong antiseptics.

Red milk is due either to colouring matter in the food of the animal or more frequently to the presence of blood from the rupture of a small blood vessel in the udder; on warming the milk and centrifuging the blood may be separated and identified by the usual methods.

Bitter milk is principally due to the food, but it is occasionally obtained from cows just before the end of lactation.

For particulars of other abnormalities in milk, *v.* Kirchner's Milchwirthschaft. For milk in disease, *v.* Blyth's Foods, where other references will be found.

ANALYSIS OF MILK.

Specific gravity. This may be determined by the lactodensimeter, the pyknometer, or by the Westphal balance.

The lactometer or lactodensimeter. This is merely a special form of hydrometer with a large bulb and a slender stem, which is graduated from 15°–45° corresponding to sp.grs. of 1·015 to 1·045; in some forms the range is even less. The milk should be at 60°F., or if the determination is made at another temperature, the readings of the lactometer should be corrected by means of a table.

The milk should be stirred, and the instrument very gently lowered till it sinks no further. The reading of the lower edge of the meniscus should be taken.

The form of pyknometer which gives the best results with milk is the Sprengel tube—a U-tube with narrow capillary ends; this should be filled with milk, immersed in a vessel of water at 60°F. till the volume is constant, and weighed. The weight of milk divided by the weight of water at 60°F. will give the specific gravity.

The Westphal balance consists of a counterpoised thermometer of exactly 5 or 10 c.c. displacement, suspended by a fine platinum wire from one end of a graduated lever. The thermometer or plummet is immersed in the milk at 15° and equilibrium restored by suspending a series of riders from the lever, which is graduated for the direct reading of the sp.gr.

Determination of the total solids. About 5 grams of milk are rapidly weighed out into a tared platinum, porcelain, nickel, or aluminium dish, and dried on a water-bath till successive weighings at one hour's interval differ by less than a milligram. This generally occupies 4–5 hours.

Richmond (Analyst, 14, 121) states that the most satisfactory results are obtained by taking not more than 2 grams of milk, and drying for 1½ hours in a wide, flat-bottomed basin.

Babcock (Dept. Agric. Rept. 13, pt. i. 81) dries the milk on asbestos, and very accurate results are thus obtained. For the rapid determination of total solids, Revis (Analyst, 1907, 284) adds 1 c.c. of acetone to 2·5 grams of milk in a wide basin and dries for 2 hours.

Determination of the ash. The total solid matter obtained by evaporating a portion of the milk to dryness is ignited at the lowest possible temperature until the ash is perfectly white; a barely visible red heat should be employed. If the temperature is raised to a visible red heat, serious loss may be incurred owing to the volatility of the chlorides in the ash. In a series of experiments Vieth (Analyst, 12, 60) found that the ash lost 25 p.c. in weight after heating at a bright red heat for half an hour. On heating for 5, 10, and 20 minutes respectively, the ash lost 6, 19, and 24 p.c. in weight. The percentage of chlorine in the ash was simultaneously reduced by $15\frac{1}{2}$, 69, and 96 p.c. of its total amount, so that over two-thirds of the chlorides volatilise in 10 minutes, and nearly the whole in 20 minutes. The ash must not be kept even at the lower temperature longer than necessary. Vieth found that it lost 6 p.c. in weight in 30 minutes when kept at a dark-red heat.

Determination of the milk-fat. The fat is the most valuable and important constituent of milk, and its determination with exactness is therefore indispensable for commercial and analytical purposes. Formerly the dried milk solids were exhausted with ether or petroleum, the ether evaporated from the solution obtained and the fat weighed. This method is almost entirely abandoned, as 20–25 p.c. of the fat is left unextracted, and concordant results are unattainable.

The following methods are now in use:—

Gravimetric methods. In consequence of the discrepancies between the results obtained by different analysts by processes in general use in 1884–5 (Wanklyn, or modifications), the Society of Public Analysts appointed a committee to compare the principal methods then known. The report of the committee, presented in 1886, and adopted by the society, stated that 283 comparative analyses had been made, and that the most concordant, and most trustworthy results had been obtained by the use of *Adams's process.* It was accordingly resolved that public analysts should use that process in preference to any other. The advent of methods such as Schmidt's and Gottlieb's has, however, caused this recommendation to be generally ignored.

Adams's process. The original method (Analyst, 85, 48) as modified by Allen and Chattaway (*ibid.* 86, 74) is carried out as follows. A strip of blotting paper 22 inches long, $2\frac{1}{2}$ inches wide, is thoroughly exhausted with ether and dried at 100°C. to constant weight. It is then rolled up into a coil of about 1 inch diameter with a piece of thin string (previously boiled with sodium carbonate) placed in a cap of (fat free) filter paper, and attached to it by means of the ends of the string. 5 c.c. of milk are distributed with a pipette over the upper surface of the coil, it is then transferred to the water oven and roughly dried on a glass plate. The dry coil is transferred to a 'Soxhlet's extractor,' and exhausted with ether, light petroleum, or carbon disulphide for $1\frac{1}{2}$ to 3 hours, the fat solution evaporated to dryness and weighed.

If the milk is sour it is preferable to mix it well, transfer a portion into a tared basin, weigh, pour it on to the coil, wash out the basin with 2 or 3 drops of water, adding these also to the coil, then proceed as above.

Sour milk may also be rendered homogeneous by adding a few drops of ammonia. A definite volume may then be used (the sp.gr. being known).

There is some difficulty in completely exhausting the blotting paper before use. Richmond (Analyst, 14, 123) states that this can be very perfectly done by treating for 3 or 4 hours with alcohol containing 10 p.c. of acetic acid, in a large Soxhlet extractor.

Adams's method gives low results if the fat is in a finely divided condition, *e.g.* in homogenised milk.

Storch's method. 10 grams of milk are evaporated on pumice, which is then ground to a fine powder, and extracted in a Soxhlet extractor; the pumice is then dried and reground and further extracted. Many other substances can be used in place of pumice; thus plaster of Paris was used for many years, and if the fine grinding (the essential part of the method) is adhered to, gives excellent results, but if only broken up roughly the results are low. Nilsson recommends kaolin (Chem. Zeit. 1891, 37), but the substance which gives the best results is kieselguhr (Analyst, 14, 124).

Schmidt (Zeitsch. anal. Chem. 27, 464) takes a test tube of 50 c.c. capacity, graduated in the upper part to $\frac{1}{10}$ c.c., introduces 10 c.c. of milk, adds 10 c.c. of strong HCl, boils with shaking until the liquid turns dark brown, cools the tube in cold water, adds 30 c.c. of ether, shakes round, and, after standing, measures the volume of the ethereal solution and draws off 10 c.c. This he evaporates down in a weighed porcelain capsule on the water-bath, and finally in the air-bath at 100°C. He then weighs and calculates for the original quantity of the ethereal solution. If the process has been properly conducted, the ether separates from the aqueous solution quite clear, without the slightest turbidity. The ethereal solution as it flows out from the pipette should not show any watery drops. With proper arrangements the operations can be carried out in 15 minutes. Stokes, who has devised special forms of tube for this method (Analyst, 14, 30), finds the results by this method agree with those obtained by Adams's process.

Instead of taking an aliquot portion of the ethereal solution, as much as possible should be withdrawn, and the tube washed out with successive portions of ether; the whole of the fat is thus obtained and weighed.

Gottlieb's method (L. V. S. 40, 1). This is a modification of the method of Röse (Zeitsch. angew. Chem. 1888, 4), and is thus carried out: 10 c.c. of milk are measured into a tall, narrow cylinder, graduated in 0·5 c.c., and holding 100 c.c., 1 c.c. of ammonia (sp.gr. 0·96) is added, and then 10 c.c. of alcohol; the mixture is well shaken. 25 c.c. of ether, which need not be dry, are added, and the contents of the tube well mixed; finally 25 c.c. of light petroleum are added and the mixture again well shaken. It is essential that the contents of the tube be mixed after the addition of each reagent, or the results may be very low. The cylinder is then left for 6 hours, the volume of the ethereal solution measured, and 50 c.c. removed, evaporated, and the fat dried and weighed .Popp (Milch.-Zeitung, 1904, 20) states that 1 hour is sufficient for the separation, and that the sp.gr. of the ammonia may be varied between 0·91 and 0·96 without affecting the results.

A more rapid procedure is to follow the method as above described, as far as the addition of the light petroleum (the quantities being halved throughout if desired, though it is essential to adhere to the proportions given); the contents of the tube are mixed, allowed to stand a minute or two till separation takes place, again mixed, and allowed to separate. As much as possible of the ethereal layer is removed, and the residue of the fat extracted by three further shakings with a mixture of equal quantities of ether and light petroleum (the recovered solvent answers admirably for this purpose). The combined ethereal extracts are evaporated in a wide-necked flask, and the fat dried in the water oven, with frequent blowing in of air until the weight is constant. The fat is then washed out of the flask with a little light petroleum, and the flask with any small residue of non-fatty substance again weighed (Fahrion, Chem. Zeit. 1906, 267; Richmond, Analyst, 1908, 389). This last procedure should be applied to the fat determinations by all methods, especially the Schmidt method, if accurate results are to be obtained.

Gottlieb's method is perhaps the easiest and best of all the methods of fat estimation, and is probably destined to supplant all the others; it is applicable with certain obvious modifications to all milk products.

Siegfeld (Milchw. Zentr. 1906, 1) finds that 0·0029–0·0036 p.c. cholesterol and 0·0079–0·0166 p.c. lecithin are contained in the fat separated by Gottlieb's method.

The maceration method being particularly suited to the analysis of sour milk will be described later.

Volumetric methods. A number of methods have been described in which the milk is treated with a solvent which dissolves everything in the milk except the fat, and this is separated by centrifugal force into the narrow graduated neck of a bottle, and there measured. Of these it is only necessary to describe the Gerber acid method, and to mention the Sinacid and Sal alkali methods.

Gerber's acid method. The reagents employed are sulphuric acid (first proposed by Babcock, Seventh Ann. Rep. Agr. Expt. Stat. Univ. Wisconsin, 1889, 98) to dissolve the casein, and amyl alcohol the use of which was introduced by Leffmann and Beam (Analyst, 1892, 83), to assist the separation of the fat. Gerber has worked out the various details (Milch.-Zeit. 1892, 891; 1893, 363, 656; and 1895, 169), and at the present time is worked as follows: 10 c.c. of sulphuric acid (commercial sp.gr. 1·820–1·825; 90–91 p.c. H_2SO_4) are measured into a bottle with a long graduated stem called a butyrometer; 11 c.c. of milk are added, and 1 c.c. of amyl alcohol (sp.gr. 0·815, b.p. 128°–130°C.). It is important that this order be adhered to, as if the sulphuric acid and amyl alcohol be allowed to mix before the acid is diluted with the milk, an action resulting in the formation of amylene and other products takes place, which substances increase the apparent volume of the fat (Richmond and O'Shaughnessy, Analyst, 1899, 146; Siegfeld, Molkerei-Zeitung, 1899, 433). The butyrometer is closed by a rubber cork, and the contents well mixed by shaking, and inverting several times so that the liquid in the neck becomes thoroughly warm; the fat is brought up into the neck by centrifuging for several minutes at a speed of at least 1000 revolutions per minute. Unless the bottles have been kept warm during centrifuging, by the use of a steam turbine to drive the machine or other device, they must be placed in a water-bath at a temperature of 60°–65° for several minutes. The percentage of fat is read off directly on the scale; to facilitate reading, the bottom of the fat column can be adjusted to one of the main percentage lines, by pushing in or pulling out the rubber cork to a small extent.

There are many types of butyrometers, differing chiefly in the construction of the graduated stem, this being round, square, or flat, or with eccentric bore to magnify the fat layer; for the trained chemist the round stem is the best, and gives the most accurate readings, but to the untrained eye the lateral magnification of the scale appears to be more easy to read. A number of appliances for automatically measuring the sulphuric acid and amyl alcohol have been devised, which are fully described and illustrated in the various manufacturers' catalogues.

With care this method gives good results, usually agreeing within 0·1 p.c. of the figures given by gravimetric analysis. The usual faults made by untrained persons are: (i) insufficient mixing, which may lead to a clear fat layer not being obtained; (ii) insufficient centrifuging, leading to low results; and (iii) unsuitable strength of acid, which may give rise to a dark, fat layer, and to errors in the result.

The layer measured is not pure fat (Richmond, Analyst, 1905, 326), partial hydrolysis takes place, and a portion of the soluble fatty acids is dissolved in the aqueous liquid; a small amount of amyl ester is formed, and also a sulpho-acid. If the conditions of the process are adhered to the volume of the fatty layer is but very slightly in excess of the true fat of the milk. As the whole of the amyl alcohol dissolves in the acid to form amyl hydrogen sulphate, a considerable margin of error in the measurement of the alcohol is without appreciable influence on the result.

The 'Sinacid' and 'Sal' methods. As strong sulphuric acid has certain disadvantages as a reagent, especially in the hands of inexperienced persons, the use of alkaline solutions to dissolve the casein has been introduced by Sichler (Milch.-Zeit. 1904, 417, Sinacid process), and Gerber (*ibid.* 1906, 4, Sal method).

The former method employs a solution containing sodium hydroxide, Rochelle salt, and sodium sulphate, whilst sodium chloride is substituted for the sulphate in the Sal method. Butyrometers, which are practically the same as those used in Gerber's acid method, are employed, and 11 c.c. of alkaline solution, 10 c.c. of milk, and 0·6 c.c. of *iso*butyl alcohol are measured into the boules. The mixing and centrifuging are performed as in the acid method, but the temperature of the water-bath is 45°. The *iso*butyl alcohol used in this method, which is usually coloured red, blue, or green, does not dissolve in the aqueous liquid, but passes into the fat, and hence the measurement must be exact. A drawback is that the corks become slippery, and tend to come out of the bottles.

The 'Neusal' method. A solution containing sodium salicylate, a carbohydrate and *iso*butyl alcohol is employed, and 4 c.c. of this are added to 9·7 c.c. of milk, mixed, warmed to 45° and centrifuged. The results are good, but Golding (Analyst, 1911, 203) has shown that variations in the mixture give erroneous results.

Determination of milk-fat from formulæ. It has been found that the sp.gr. of milk, solids not fat, and the fat are dependent upon each other, so that if two of these quantities are known, the third can be calculated.

Numerous formulæ have been worked out to express the relations between the three data, many of them applicable only to particular methods of analysis, which have now been shown to be incorrect. Owing to the natural variation in composition and specific gravity of the fat and solids not fat, the method is only an approximate one.

The following formula, which, though scientifically incorrect, is simple, gives results which are near the truth :

$$\text{S.n.F.} = \frac{G}{4} + 0{\cdot}2F + 0{\cdot}14 \text{ or } T = \frac{G}{4} + 1{\cdot}2F + 0{\cdot}14.$$

G=lactometer degrees, F=Fat, S.n.F.=solids not fat, T=total solids (Richmond, Analyst, 1905, 57).

A slide rule called the milk scale has been devised to perform the calculation (Analyst, 1898, 2); a scale for the correction of specific gravity for temperature is also included.

Determination of the milk-sugar.—(1) *Gravimetrically, by Soxhlet's method.*—25 c.c. of milk are weighed out, diluted to 400 c.c. ; 10 c.c. of a solution of copper sulphate (69·28 grams per litre) are added, then 6·5–7·5 c.c. of a solution of caustic soda standardised to precipitate an equal volume of the copper solution. The solution should still be slightly acid after the addition of the soda, and contain traces of copper. Scheibe (Milch.-Zeit. 1901, 113) recommends that 20 c.c. of a cold, saturated solution of sodium fluoride should also be added to remove lime salts. It is diluted to 500 c.c., filtered ; 100 c.c. are transferred to a beaker, 50 c.c. of Fehling's solution are added, the whole boiled for 6 minutes, filtered through asbestos, washed with hot water, then twice with absolute alcohol and twice with ether. A special filter is used consisting of a calcium chloride tube, the bulb half filled with asbestos and previously dried and weighed. The tube containing the asbestos and precipitate is cleared of ether by blowing air through, and a stream of hydrogen passed through, whilst the bulb is gently heated for 5 minutes. The reduced copper is allowed to cool in a stream of hydrogen, and weighed. Soxhlet gives the following table :—

Copper obtained (milligrams)	Amount of milk-sugar (milligrams)
392·7	300
363·6	275
333·0	250
300·8	225
269·6	200
237·5	175
204·0	150
171·4	125
138·3	100

The intermediate values are obtained by interpolation.

(2) *By polarisation.*—The proteins in milk affect the determination, and must first be eliminated. This may be done—

By mercuric nitrate (Wiley, Amer. Chem. J. 6, 289).—Mercury is dissolved in double its weight of HNO_3 (sp.gr.=1·42), and an equal volume of water added to the solution.

Vieth (Analyst, 1888, 63) gives the following directions : to 100 c.c. of milk 3 c.c. of this solution are added, the mixture well shaken and filtered. The clear filtrate is polarised, and the percentage of anhydrous milk sugar deduced. If a 200 mm. tube is used, the reading in angular degrees, is multiplied by

$$0{\cdot}95 \times \frac{1}{1{\cdot}05} \times \frac{100 - 1{\cdot}057F}{100} \times \frac{1}{\text{sp.gr.}}$$

This expression reduces the readings to their value in anhydrous milk sugar ; corrects for the volume of the fat (the volume of the proteins is taken as 3 c.c.), and converts percentages by volume into percentages by weight.

Richmond and Boseley (Analyst, 1897, 98) add to 100 c.c. of milk (if a 200 mm. tube is used):

3 c.c. mercuric nitrate solution,

10·85 c.c. of water to reduce angular degrees to percentages of anhydrous milk sugar,

$F \times 1{\cdot}11$ c.c. of water to correct for the volume of fat,

Lactometer degrees $\times \frac{1}{10}$ to convert volume into weight percentages.

The reading in angular degrees gives the percentage direct.

Richmond (Analyst, 1910, 516) has lately shown that mercury salts do not precipitate the whole of the proteins, and recommends the addition of phosphotungstic acid to the mercuric filtrate. With whole milk the error is very small, but is important with dried milks, &c.

Patein (J. Pharm. Chim. 1904, 501) states that milk sugar cannot be estimated polarimetrically in human milk, as this contains a lævorotatory substance not precipitated by mercuric nitrate nor picric acid.

The volume of the precipitate of fat and proteins may be estimated by the method of double dilution, *i.e.* making up the same quantity of milk to two different volumes, one being preferably twice the other; formulæ for correction have been worked out by Bigelow and McElroy (Amer. Chem. J. 25, 694), Wiley and Ewell (Analyst, 1896, 186), and Schiebe (Milch.-Zeit. 1901, 113). Mercuric iodide, and acetate, sodium metaphosphate, picric acid, and zinc ferrocyanide have also been proposed to precipitate the proteins (*cf.* Thibault, J. Pharm. Chim. 1896, 5; Carrez, Ann. Chim. anal. 1909, 187).

The temperature during the process must be kept constant and within 15°–25° (Wiley, Analyst, 13, 196).

Stokes and Bodmer (*ibid.* 10, 12) recommend the use of Pavy's solution (*v.* p. 101).

100 of milk-sugar have the same reducing power as 52 of glucose or 49·4 of cane-sugar. By this method a fair determination may be made by merely diluting the milk so that 6–12 c.c. decolourise about 40 c.c. of Pavy's solution.

Determination of the total proteins.—Ritthausen's method (Zeitsch. anal. Chem. 1878, 241).—The proteins are precipitated by copper sulphate and soda solution (*v. Determination of milk-sugar*). The precipitate is collected on a weighed filter, washed with a little of the clear filtrate, allowed to drain, washed with 80–100 c.c. of hot water, dried, the fat extracted, dried again at 125°–150° and weighed. The precipitate is ignited and the ash deducted. Sebelien (Zeitsch. Chem. 13, 135) points out that this method is not exact, since copper hydroxide does not give up all its water at 125°, but only on ignition. This error is avoided if at least 0·6 gram of protein is present in solution, and the ratio between the copper oxide used and the amount of protein falls between 1·3 and 1·35.

Fleischmann (Lehrbuch der Milchwirtschafe, 1907, 70) states that the error introduced is 0·038 p.c. for each 1 p.c. of protein.

Almen's method. This method gives very exact results, and is particularly recommended by Sebelien (Zeitsch. physiol. Chem. 13, 135). 3–5 grams of milk are taken (2 grams of colostrum, 10 of whey), diluted with 3–4 vols. water; a few drops of solution of some salt (NaCl, $MgSO_4$, &c.), then excess of solution of tannin, is added in the cold. (The tannin solution consists of 4 grams tannin added to 8 c.c. of 25 p.c. acetic acid and 190 c.c. of 40–50 p.c. alcohol.) The precipitate is thoroughly washed with *cold* water, and the nitrogen in the filter and precipitate estimated by Kjeldahl's process. The result, after subtraction of the N in the filter, gives the protein N, and this ×6·38=total proteins (since both casein and albumin contain 15·7 p.c. N); for whey the factor 6·96 gives the most exact results.

Phospho-tungstic acid may also be used to precipitate the proteins.

Total nitrogen. The total nitrogen in milk is best determined directly by Kjeldahl's method. The digestion must be somewhat prolonged to obtain the best results (Kreusler, L. V. S. 31, 248). In absolutely accurate determinations it is not advisable to calculate the total proteins from total N by multiplication by 6·37, because of the presence of nitrogenous extractive matters in the milk. Schmidt-Muhlheim found an average of 0·04–0·05 p.c. of extractive N. This is confirmed by Sebelien (*l.c.*), who finds the same average, with a minimum of 0·03 p.c. and an exceptional maximum (in colostrum) of 0·08 p.c.

(N−0·04)×6·38 gives a very close approximation (Sebelien).

Separate determination of the proteins (casein, albumin, globulin, &c.). Hoppe-Seyler (Handb. der Phys. Chem. Anal.) proceeds as follows. 20 c.c. of milk are diluted with water to 400 c.c., transferred to a deep beaker, and very dilute acetic acid added until a flocculent precipitate just appears. Carbon dioxide is then passed for ¼–½ hour, and the precipitate allowed to subside for 12 hours. The solution, which should be perfectly clear, is passed through a weighed filter, the precipitate washed on with a little of the clear filtrate, allowed to drain, and washed once with distilled water. The precipitate=casein+fat. The latter is extracted as usual. The filtrate is boiled for a few minutes, when the albumin separates out; if the precipitate is not very flocculent, a few drops of very dilute acetic acid may be added. It is collected on a weighed filter, washed with cold water, and dried at 120°–125°.

The filtrate and wash-water are evaporated to the consistency of a thin syrup, the precipitate which settles out gathered on a small weighed filter, well washed with cold water, and weighed.

Van Slyke (Amer. Chem. J. 1894, 712) adds to 10 grams of milk + 90 c.c. of water at a temperature of 40°–42°, 1·5 c.c. of 10 p.c. acetic acid, and allows the liquid to stand 5 minutes; the precipitate of casein is washed, and the nitrogen estimated by Kjeldahl's method. The albumin is precipitated by boiling the filtrate, the nitrogen being estimated in the precipitate. This method has been extended by Van Slyke and Hart (Amer. Chem. J. 1903, 150).

This method cannot be used for human milk nor for that of the mare and ass, because on dilution and treatment with acetic acid and CO_2 the caseïn separates in such a finely divided condition that it cannot be filtered. Blyth (Food: Lond. 88) uses the following modification for human milk; 100 c.c. are diluted to 400 c.c., acidified with dilute acetic acid, saturated with CO_2, and transferred to a tall beaker. A small cylindrical porous battery cell, closed by a perforated plug connected with a mercury pump, is immersed in the liquid. A good vacuum is maintained, and ultimately the whole of the solution passes through. The caseïn is left behind, and is washed, dried, and weighed. The albumin is precipitated by boiling, &c.

Pfeiffer and Schmidt (Zeitsch. Chem. 23, 445) modify Hoppe-Seyler's method in the following way for human milk: 20 c.c. of milk are diluted to 400 c.c., heated to 40°, acetic acid added drop by drop till a granular precipitate commences to form; CO_2 is then passed in for half an hour and the precipitate allowed to subside for 24 hours. The caseïn is then weighed, and the filtrate treated in the ordinary way.

Tolmatscheff's method.—(1) *Casein.* 20 c.c. of milk are saturated in the cold with crystallised $MgSO_4$ (it is best to make the crystals into a paste with water), 100 c.c. of a very concentrated solution of $MgSO_4$ are added, the precipitate filtered off, well washed with a concentrated solution of $MgSO_4$, the fat extracted, and the residue dried, weighed, and the ash deducted.

(2) *Albumin.* The filtrate and wash-water from the caseïn are acidified with dilute acetic acid, heated to boiling, filtered, washed, with water and alcohol, dried at 120°–125°, and weighed. Sebelien (*l.c.*) advises that in each case the N should be determined in the precipitate by Kjeldahl's process, and the albuminoid found by multiplication by 6·37. The results are accurate.

The following scheme is recommended for scientific purposes (Sebelien):—

(1) Determine total N by Kjeldahl's method.

(2) Total proteins by precipitation with tannin (N by Kjeldahl).

(3) Casein+globulin by precipitation with $MgSO_4$ (N by Kjeldahl).

(4) Casein by precipitation with dilute acetic acid (N by Kjeldahl).

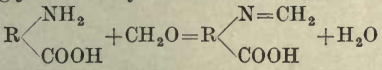
The difference between (2) and (3) gives the albumin, between (3) and (4) the globulin, between (1) and (2) the non-protein or extractive N. The latter may also be determined directly by Kjeldahl's method, in the filtrate from the tannin (2).

Opalisin, which is scanty in cow's milk, but abundant in human milk, is estimated by precipitation of the casein by acetic acid, and saturation of the filtrate by sodium chloride (Wroblewski, Zeitsch. physiol. Chem. 1898, 308).

Schlossmann (*ibid.* 1896, 197) precipitates casein with a little saturated alum solution at 37°, globulin in the filtrate by saturating with magnesium sulphate, and estimates albumin from the difference between the total protein nitrogen and that of the casein and albumin.

For general review of the methods of protein estimation, *cf.* Simon, Zeitsch. physiol. Chem. 1901, 466.

Rapid estimation of proteins.—The aldehyde method. Steinegger proposed that the acidity developed in milk by the addition of formaldehyde should be used as an analytical method (Zeitsch. Nahr. Genussm. 1905, 659), and showed that it was due to the conversion of the practically neutral amino-acid groups into strongly acid methylene-amino-acid radicles.



$$R\begin{cases}NH_2\\COOH\end{cases}+CH_2O=R\begin{cases}N{=}CH_2\\COOH\end{cases}+H_2O$$

Richmond and Miller (Analyst, 1906, 224) studied the method, and pointed out that the value depended on the nature of the base used for titration, the use of soda giving lower results than strontia, which they recommend (*cf.* also Sorensen, Biochem. Zeitsch. 1907, 45).

The method is as follows: to 10 or 11 c.c. of milk (the latter volume is convenient if the Gerber fat estimation is performed) at least 1 c.c. of 0·5 p.c. phenolphthalein solution is added, and the milk neutralised with N/11 (approx.) strontia; to the faintly pink solution 2 c.c. of 40 p.c. formaldehyde solution is added, and the titration continued till a faint pink colour again appears; the acidity of the formaldehyde added is deducted, and the aldehyde figure is calculated as c.c. of N acid per litre; this multiplied by 0·170 gives the percentage of proteins in normal cow's milk. On no account must the formaldehyde solution be neutralised previous to use with soda, as the strong neutral solution becomes very appreciably alkaline on dilution; the same figure for acidity of the formaldehyde is, however, obtained when strontia is used whatever the dilution. The factor for converting aldehyde figure to proteins varies with different milks and milk products; thus it is 0·125 for whey, 0·136 for human milk, and 0·154 for asses' milk. When milk turns sour the aldehyde figure rises (Analyst, 1906, 328; and 1908, 115), due to proteolytic fermentation. The method, although extremely rapid, and approximately accurate, must be used with reservation.

Acidity. By titration of milk with an alkali solution using phenolphthalein solution as indicator, a measure of the acidity is obtained; unfortunately there are several modes of expression of acidity. Soxhlet and Henkel (Chem. Zentr. 1887, 229) titrate 50 c.c. of milk with N/4 soda solution, and call the number of cubic centimetres of soda used degrees of acidity; Thörner (Milch.-Zeit. 1893, 58) dilutes 10 c.c. of milk with 20 c.c. of distilled water, and titrates with N/10 soda, and expresses as degrees of acidity the number of c.c. of normal solution required per litre of milk; many others use 10 c.c. of milk undiluted and titrate with N/10 solution, and express the acidity in the same terms as Thörner, but as the sodium salts of the acids present in milk dissociate on dilution the degrees determined by Thörner's method do not agree with those determined by using undiluted milk. It is not unusual, though of course incorrect, to express the acidity as grams of lactic acid per 100 c.c., and Dornic (Le Contrôle du Lait, 1897) proposes the use of N/9 soda solution (1 c.c. = 0·01 gram lactic acid), and calls the grams of lactic acid per litre degrees. The amount of phenolphthalein used and the temperature have some influence on the end-point of neutrality (Richmond and Miller, Analyst, 1907, 152).

Experience has shown that the most satisfactory and concordant results are obtained by the use of strontia solution (about N/11) as the alkali at the ordinary room temperature (15°–20°), and employing at least 0·005 gram phenolphthalein for 10 c.c. of milk, and the most convenient mode of expression is c.c. of N acid per litre or degrees. The tint equal to that produced by 1 drop of an 0·01 p.c. alcoholic solution of rosaniline acetate added to 11 c.c. of milk may be taken as a standard. The normal acidity of cow's milk is about 20 degrees, and the acidity is nearly always within 2 degrees of the aldehyde figure (*q.v.*; Richmond, Analyst, 1908, 115); in a few abnormal cases it is much lower.

Analysis of sour milk. A practical method for the analysis of sour milk, by means of which the composition, when fresh, can be deduced, has been devised at the Government Laboratory. Originally described by Bell (Food and its Adulterations, 1883, pt. 2), it has been modified and placed on a scientific basis by Thorpe (Chem. Soc. Trans. 1905, 206); Richmond and Miller (Analyst, 1906, 317) have examined and criticised the method, and while suggesting a few minor modifications, agree in the main with Thorpe as to its substantial accuracy. The following is an abridged description, but for full working details the original papers should be consulted.

Maceration method for fat and solids not fat. 10 grams (*circa*) are weighed into a flat-bottomed platinum dish provided with a flattened glass stirrer, neutralised with strontia solution, using phenolphthalein as indicator, and evaporated to a stiff paste on a steam-bath; the residue is treated with successive quantities of ether, and ground up to a fine powder under the ether, which is passed through a weighed filter, and collected in a flask; the ether is evaporated and the fat dried and weighed. The fat should be washed out of the flask with light petroleum, and the residue of phenolphthalein subtracted from the weight (R. and M.). It is advisable to continue the extraction with ether and the grinding of the solids not fat till no more fat is obtained. The solids not fat in the basin and on the weighed filter are dried to constant weight in the water oven. A correction is made or the added alkali by deducting 0·00428 gram or each c.c. of N/10 strontia added.

Corrections for loss owing to decomposition.—(*a*) *The alcohol correction.* 75 grams (more or less according to the amount of sample available) are half neutralised with soda and distilled, the distillate is neutralised, using litmus paper as indicator, and redistilled a convenient volume (say 25 or 50 c.c.) being collected, and the density taken; the difference between the density found and 1000, multiplied by 0·977, will give the quantity of anhydrous milk-sugar equivalent to the alcohol per 100 c.c. of distillate.

(*b*) *Volatile acid correction.* 10 grams of milk are half neutralised with N/10 soda, and a little phenolphthalein added; the mixture is evaporated to dryness with frequent stirring, taken up with 20 c.c. of boiling water, and titrated with N/10 soda. The difference between volume of N/10 soda used for the original acidity, and that after evaporation multiplied by 0·0255 gives the correction due to loss of milk-sugar p.c. by conversion into volatile acids.

If the milk has undergone the butyric acid fermentation, which is not common, but which is easily recognised, this method gives totally erroneous results, and the methods described by Thorpe or Richmond and Miller (*l.c.*) must be substituted.

(*c*) *Ammonia correction.* 2 grams of milk are made up to 100 c.c. with ammonia free water, and filtered clear; the ammonia is estimated by Nesslerising in 10 c.c. of the dilute solution, the standard solution receiving an addition of 10 c.c. of a clear solution of 2 c.c. of fresh milk slightly acidified in 100 c.c. of water. The ammonia found multiplied by $500 \times 5{\cdot}2$ will give the loss of casein p.c. The three corrections, of which that due to alcohol is generally by far the largest, are added to the solids not fat to obtain the solids not fat in the fresh milk.

Richmond and Miller introduce some further corrections for lactic acid, aldehyde taken up from the ether, loss of butyric acid (if present) on drying, and for hydrolysis of the proteins, but these, except in special cases, are small, and tend in opposite directions; they may be omitted, as a rule, without greatly affecting the results. Specific gravity of sour milk may be determined by adding ammonia to dissolve the curd, and making a correction for the density of the added ammonia (*cf.* Weibull, Milch.-Zeit. 1894, 247, and 413; Richmond and Harrison, Analyst, 1900, 207).

ADULTERATIONS.

The principal adulterations practised are the addition of water and the removal of cream. Carbonates of the alkalis and borax, or boric acid, formaldehyde, and more rarely, salicylic acid, are also introduced to keep milk from souring.

The addition of water or removal of cream is shown by the analysis.

Clause 4 of the Sale of Food and Drugs Act, 1899, gives power to the President of the Board of Agriculture to fix limits below which a presumption is raised till the contrary is proved that the milk is not genuine; these limits are 8·5 p.c. of solids not fat and 3·0 p.c. of fat. It sometimes happens that genuine milk yields a percentage of fat below 8·5 p.c. of solids not fat (*cf.* Wauters, Rev. internal. Falsific. 1902, 67; Malpeaux and Dorez, Ann. Agronom. 1901, 449; and Billitz, Milchw. Zentr. 1905, 113). Richmond (Analyst, 1893, 271) considered that genuine milks of this character contained above 0·7 p.c. of ash and 0·5 p.c. of nitrogen, but as he has himself found lower percentages of nitrogen (Analyst, 1903, 281, and 1910, 231) his views have undergone modification. His present view is that normal milk should contain at least 4·5 p.c. of lactose, 0·5 p.c. nitrogen, and 0·7 p.c. ash, and that abnormal milks low in solids not fat should conform to these limits in at least two of the constituents.

For the monthly variations of the composition of milk, the daily variations and the variation between morning and evening milk, *see* numerous papers in the Analyst since 1882, by Vieth and Richmond.

Soxhlet has proposed the following direct test for the addition of water, based upon the presence of nitrates in water and their total absence in milk.

The milk is coagulated by a solution of calcium chloride free from nitrate; the serum is now treated with a solution of diphenylamine in concentrated H_2SO_4, in the same way as with the ferrous sulphate test. This test has frequently been rediscovered. Szilasi (Ann. Chim. Phys. 33) measures out 1 c.c. of a solution of diphenylamine sulphate into a porcelain dish, and adds a few drops of milk; nitrates gradually give a blue colouration. These tests are not sufficiently delicate for pure water.

Fritzmann (Chem. Zentr. 1898, i. 218) adds formaldehyde and pure sulphuric acid; in the presence of nitrates a blue colour is developed.

Richmond (Analyst, 1894, 83) has found nitrates in the milk of cows that received 1 gram of potassium nitrate with their food.

Carbonates of the alkalis are best determined by taking 500 grams of milk and determining the CO_2 in the ash. The ash of pure milk should not contain more than 2 p.c.

Boric acid is detected by Meissl as follows. 100 c.c. are made alkaline with milk of lime, evaporated and incinerated. The ash is dissolved in as little concentrated HCl as possible, filtered, the filtrate evaporated to dryness, and the HCl expelled. The residue is moistened with a drop or two of an alcoholic extract of turmeric and evaporated on the water-bath. Mere traces of boric acid give a cinnabar or cherry-red colouration.

A more rapid though less delicate test consists in neutralising a quantity of milk with caustic soda, using phenolphthalein as indicator; portions of this are poured into the test tubes, and to one an equal volume of water is added, and to the other an equal volume of neutral 50 p.c. glycerol. In the presence of boric acid the glycerol tube will be much lighter in colour, usually quite white.

Salicylic acid is detected by Pellett by mixing 100 c.c. of milk, 100 c.c. of water at 60°, 5 drops acetic acid, 5 drops of a solution of mercuric nitrate, filtering off the proteins, shaking with 50 c.c. of ether, allowing to settle, removing the ether, evaporating to dryness, dissolving the residue in a few drops of water, and adding ferric chloride. The quantity of salicylic acid can be approximately known by comparing the violet colouration produced with a series of standard solutions.

Boric acid is estimated (Richmond and Miller, Analyst, 1907, 144) by adding to milk half its volume of 0·5 p.c. phenolphthalein solution, and neutralising to a faint pink colour while boiling; at least 30 p.c. of glycerol is now added, and the boric acid titrated with N/10 alkali (1 c.c. = 0·0062 gram H_3BO_3). R. T. Thomson (Analyst, 1893, 184) neutralises first to methyl orange, and then titrates in the presence of glycerol to phenolphthalein. Another method, due originally to Gooch, depends on the volatilisation of boric acid as methyl borate by distillation with methyl alcohol (*cf.* Cassal, Analyst, 1890, 230, and Hehner, *ibid.* 1891, 141). Formaldehyde may be detected by numerous methods, the most simple of which is due to Hehner (*ibid.* 1896, 94); when strong sulphuric acid is added to milk it forms a violet-blue colouration at the junction of the two liquids in the presence of formaldehyde, provided that a small quantity of an oxidising agent be present. Leonard (Analyst, 1896, 157) and Farnsteiner (Chem. Zentr. 1897, i. 133) have shown that ferric chloride is the best oxidising agent, and Rosenheim (Analyst, 1907, 106) has pointed out that this last is a tryptophan reaction.

Other tests are those of Trillat with dimethylaniline (Compt. rend. 1892, 891), Richmond and Boseley with diphenylamine (Analyst, 1895, 155), Rideal with Schiff's reagent (*ibid.* 1895, 158; *cf.* Richmond and Boseley, *l.c.*, and Hehner, *l.c.*), Mitchell with Nessler's reagent (Analyst, 1897, 97), Jorissen with morphine (Bull. Soc. chim. 1897, 17, 167), Vanino with phloroglucinol (Chem. Zentr. 1899, i. 710), Gabutti with carbazole (Boll. Chim. Farm. 1907, 349).

Preservation of Milk.

To preserve milk for any length of time at the ordinary temperature it must be sterilised. This may be done either by means of antiseptics, such as salicylic acid, borax, or boric acid, &c. —the presence of which is highly undesirable in food—or, as is more generally practised, by the agency of heat. For the action of drugs, *v.* Soxhlet, J. Pharm. Chim. 6, 118; Mayer, Milch.-Zeit. 1882, 321. A temperature of 100° is insufficient to sterilise milk completely. Dietzell found that milk heated for 20 minutes to 105°–110° only kept sweet for a few weeks, whilst that heated to 100°–115° for 20 minutes (5 minutes at 115°) was perfectly sweet 3 years later.

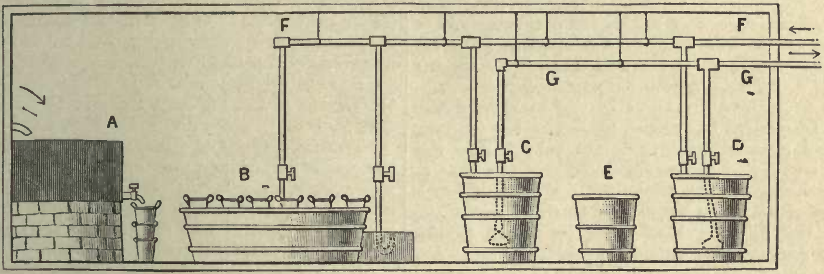


Fig. 1.

Duclaux kept milk unchanged for 5 years by exhausting the air from the containing vessel and subsequently heating to 120°.

Milk can, however, be preserved unchanged by mixing it with a considerable percentage (not less than 12 p.c. of its weight) of sugar, evaporating to a semi-solid mass, and excluding the air.

Fleischmann gives the following account of the process of manufacture of condensed milk *with* addition of sugar. The milk on delivery is weighed, filtered through a wire sieve, and thrown into a reservoir communicating with the tank A (Fig. 1), tapped into cans 20–30 inches deep. A number of these are placed in the water-bath B which is heated by steam from a perforated coil at the bottom, communicating with the steam-pipe F. (Beside each water-bath is a smaller bath for cleaning the cans.) When the milk has attained a temperature of 87°–94° it is transferred to the vats C or D, which have false copper bottoms, into which steam can be introduced to prevent the milk from cooling. The vat E contains the necessary quantity of *cane-sugar*—12 p.c. of the weight of the milk, hot milk is thrown in, stirred, and passed back to C through a filter, and this is repeated till all the sugar is dissolved.

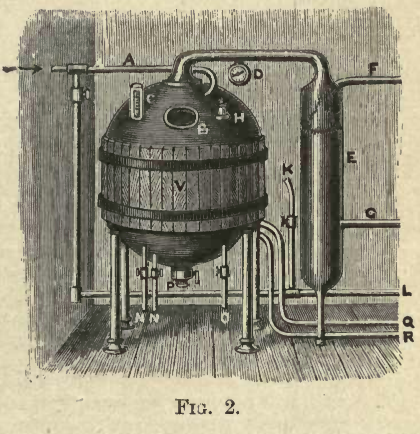


Fig. 2.

The milk in C is then sucked up by the pipe G, which terminates in a sieve, into the vacuum V (Fig. 2). This is a spherical copper vessel, with a wooden jacket round the middle and with a false bottom, into which either steam or cold water can be introduced. There is also a copper coil inside the vacuum, into which steam and cold water can be passed. A (Fig. 2) is the pipe through which the sugared milk is introduced; B is a sight-hole, hermetically closed with a thick glass plate; C is a thermometer; D a manometer; E a condenser; F the cold-water pipe for the condenser; G the pipe leading to the air-pumps; H an air-cock; I is an exhaust pipe for the condensed water; K and L are cold-water pipes for clearing the vacuum; M an exhaust pipe for the waste water from the space between the two bottoms; N an exhaust pipe for the coil inside the vacuum; O a pipe for drawing samples of milk; P the delivery pipe for the condensed milk; Q a steam pipe for supplying the space under the false bottom; R a supply pipe for the coil. On the other side of the vacuum there is another sight-hole resembling B, behind which a light is placed, whilst the progress of the operation is continually watched through B. The air-pumps are set to work, but no steam is passed in until the milk is seen to be *boiling briskly*; the temperature is then regulated to 60°. The pressure inside the vacuum is generally 60–100 mm.

When a sample taken out and cooled is of the right consistency, cold water is turned on in both the coil and false bottom, and after a short time the milk is run out and quickly cooled to 15°. It is then tapped into canisters; the covers, which are pierced with a fine hole, are soldered on—the heat of the operation causes the greater part of the residual air to be expelled; the hole is then quickly soldered over.

Various modifications of the above process are adopted. In some places, for instance, special precautions are taken to regulate the temperature of the water-bath, and the heat is not allowed to rise above 60°–75°; in others a series of ledges are arranged in the vacuum, so that the milk trickles down from one to the other and is more quickly condensed, &c., &c. Grandeau and Kramer (J. Pharm. Chim. 16, 267) state that at Zurich the addition of sugar is made to the milk heated to 35°, and the temperature in the vacuum is not allowed to rise above 52°.

In many cases part of the cream is removed before condensation.

ANALYSIS OF CONDENSED MILK (SWEETENED).

—	Nestlé	Nestlé	Anglo-Swiss Co.	Anglo-Swiss Co.	Cham	Gerber & Co.
Water .	15·30	24·48	24·94	25·63	27·67	23·68
Fat . .	8·85	11·23	8·90	6·13	9·33	9·74
Albuminoids	9·98	10·97	9·68	12·65	16·53	9·80
Milk-sugar .	13·62	11·19	13·29	12·50	13·20	12·93
Cane-sugar .	50·08	39·95	41·24	41·21	30·65	41·80
Ash . .	2·17	2·08	1·95	1·88	2·20	2·05

MILK CONDENSED WITHOUT ADDITION OF SUGAR.

In America the milk is filtered, heated to 60° or 70°, filtered again and condensed in a vacuum at 40°–45° to about ⅓ of its bulk. A portion of the cream is often abstracted before condensation.

This milk will not keep for more than a few days. The milk prepared at Romanshorn (Switzerland) keeps better, but the process of manufacture is not known. It is believed that the milk is heated to about 120° in its preparation, as about ⅔ of the albumin is coagulated, whilst in ordinary (sweetened) condensed milk only about half the albumin is coagulated. A portion of the cream is abstracted before condensation on account of the rancidity which a large amount of fat quickly occasions.

Scherff's process, which is in use at Stendorff, consists in first sterilising the milk by heating it to 100°–113° for 1–2 hours in sealed vessels under a pressure of 2–4 atmospheres. It is then condensed either to ½ or to ⅓ of its bulk in a partial vacuum at a temperature of 65°–70° and a pressure of 11 mm.

Voelcker gives the following analyses of unsweetened milk:

	I	II
Water . . .	57·96	51·72
Fat . . .	16·02	14·33
Casein . . .	8·50	11·69
Milk-sugar . .	16·32	19·51
Ash . . .	2·20	2·75

KEPHIR.

Milk does not readily undergo the alcoholic fermentation by the action of yeast, though a small amount of alcohol is formed during the lactic fermentation.

In the Caucasus a special ferment (kephir grains) is used which has the property of speedily inducing alcoholic fermentation in milk. Kern (Biol. Zentr. 2, 137) found in the grains two of the organisms of ordinary yeast (*Saccharomyces cerevisiæ*) and a bacillus (*Dispora caucasica*).

For the manufacture of kephir, *v.* Krannhals (J. Pharm. Chim. 14, 191), Haccius (Bied. Zentr. 1885, 265).

The milk-sugar is changed by the action of the grains partly into carbon dioxide and alcohol and partly into lactic acid; small quantities of glycerol, acetic, succinic, and butyric acids are also formed. The casein and albumin are partly peptonised.

Kephir is an agreeable nourishing drink with a slightly sour taste. It is best relished when two days old, and three days after preparation it is decidedly sour and stronger in alcohol.

König gives the following average composition of kephir:

Water	91·21
Alcohol	0·75
Fat	1·44
Sugar	2·41
Lactic acid	1·02
Casein	2·83
Albumin	0·36
Hemialbumose . . .	0·26
Peptone	0·039
Total proteins . . .	3·49
Ash	0·68

A simple method of making kephir consists in taking some of the good 3-days' old product, adding 4–5 parts of cow's milk, and allowing it to ferment for 2 days with occasional shaking. The consumption of kephir has made considerable progress, and it is now the custom to take it medicinally, although its preparation in reference to the production and significance of the so-called kephir grains is still obscure. In the Caucasus kephir is prepared from milk, particularly sheep's and goat's milk, in peculiar leather pipes (*burdinks*) by adding to it kephir grains as ferment. Struve has investigated the formation of this ferment and studied its properties. Since the augmentation of the kephir grains takes place when the milk is kept in leather pipes their growth must necessarily be affected by the milk constituents, and although it was *à priori* impossible to determine what changes the ingredients consumed during this process undergo, it was assumed that the substances belonging to the group of proteins would maintain their general type to a greater or less degree. 100 parts of the grain dried in the air gave :

Water	11·21
Fat	3·99
Peptones soluble in water .	10·98
Proteins soluble in ammonia .	11·32
Proteins soluble in potash .	30·39
Insoluble residue . . .	33·11

On digesting the insoluble residue in a dilute solution of potash and subjecting it to microscopical examination, it showed an intimate mixture of yeast fungi with the bacteria described by Kern under the name of *Dispora caucasica.* Struve concludes that only 33·11 p.c. of the total substance of the grains constitutes the active ferment. With kephir grains of the above composition a drink is prepared which, according to Podwisozky, contains only traces of alcohol after 24 hours' bottling, whilst in 48 hours it becomes brisk and contains a considerable amount of alcohol, the latter increasing still further after the lapse of another 24 hours. On subjecting the three drinks characterised by the difference in the duration of the fermentation to analysis it was found that although the percentage of casein was the same in each case, the latter was not completely soluble in a mixture of dilute ammonia and potash. In the solution of the casein of the kephir of one day's fermentation only traces of a precipitate were observed ; the kephir 2 days old gave 0·05 p.c. and that 3 days old 0·22 p.c. of residue. Microscopical examination of the residues showed that yeast fungi only were present, bacteria or other forms of fungi being entirely absent. From this Struve infers that the fermentation of the milk is dependent upon the growth of the yeast fungus (*Saccharomyces mycoderma, Mycoderma cerevisiæ et vini*) contained in the kephir grains, whilst the bacteria *Dispora caucasica* take no active part in the fermentation. This conclusion is confirmed by the fact that the finished kephir is capable of fermenting fresh portions of milk. From the results of this investigation Struve concludes (1) During the fermentation the yeast fungus, under the influence of the power of vegetation and of osmotic laws, enters into animal as well as vegetable tissues, and disposes them to a variety of changes. (2) The development of the yeast fungus in the interior of organic tissues may, under favourable conditions, assume the character of a special process of fermentation. (3) The effects of such a process are increased when the evolution of carbon dioxide is retarded. (4) Animal tissues into which the yeast fungus has entered exhibit in sugar solutions as well as in milk all appearances of vinous fermentation. They can therefore be used instead of kephir grains for the preparation of kephir. (5) The formation of the kephir ferment is the cause of a peculiar growth of the yeast fungus within the tissues of the leather pipes during the process of fermentation, its fungoid form being due to the development of carbon dioxide. (6) The bacteria *Dispora caucasica* must be regarded as residues of fibrils of the tissues of the leather pipes (Ber. 17, 1364 ; J. Soc. Chem. Ind. 3, 493).

Milk powder. By evaporating condensed milk in a vacuum chamber it is reduced to a solid form. Many patents have been taken out for drying milk ; Just and Hatmaker use rollers heated by steam above the temperature of 100°, the milk being fed on to them at such a rate that it is nearly dry by the time that the adhering film reaches knives touching the surface of the rollers, that remove it continuously. A small quantity of alkali is added to render the milk powder soluble in water. The rollers may be surrounded by a jacket through which a current of air passes, or from which the air is exhausted, in which case the temperature of the rollers is not so high, and a more soluble product is obtained.

Under the Stauf, Merrell-Soule, and Bevenot de Neveu patents, milk is sprayed through small orifices under pressure, into a large chamber through which warm air is passed ; evaporation takes place, and the solid milk falls in very minute particles ; this method produces a very soluble powder, without the addition of alkali, and the fat does not separate in oily globules, as it does from milk powders prepared by other methods. Milk powders prepared from skim milk keep well, but those containing the fat have a tendency to turn rancid or tallowy ; this is partly due to oxidation, a large surface of the fat being exposed to the air, and partly to the action of the neutral enzymes of the milk, which are not destroyed at the temperatures employed.

The following are typical analyses of milk powders :

Designation	Moisture	Fat	Milk sugar	Proteins	Mineral matter
Enriched .	1·4	36·8	33·8	22·8	5·2
Full cream	4·7	29·2	35·7	24·8	5·6
Half cream	4·9	16·4	43·6	28·5	6·6
Skim .	3·4	2·1	54·5	31·8	8·2
Whey .	2·7	0·7	76·5	14·0	8·1
Sweetened	1·6	17·7	22·6 cane sugar 38·9	15·6	3·6

Cream. On allowing milk to stand, the fat globules rise to the surface, and form a layer of cream on the surface ; under the influence of gravity the rate of rise of the fat globules is slow, and the whole of the cream cannot be obtained before the milk turns sour. By centrifugal force the rate of motion of the fat globules can be much increased, and practically the whole of the cream removed ; the modern cream separator consists of a steel bowl rotated at a high rate of speed (5000–10,000 revolutions per minute) into which the milk is fed by a central inlet tube ; from this it passes to a series of chambers (usually formed by a number of conical discs—the Alfa device), in which the heavier portion—the skim milk—pass to the outside of the bowl, while the lighter fat globules collect in the centre, and escape by an outlet at the top of the bowl, the skim milk being removed from near the periphery by a series of tubes or a special chamber, and discharged at a lower level. Provision is made by an adjustment of the cream outlet for varying the proportion of skim milk and cream removed, and thus the thickness of the cream.

Qualitatively cream has the same composition as milk, but differs quantitatively in containing a very much larger percentage of fat; the other constituents, except those soluble in the fat (lecithin), or those existing in the solid form (the cellular elements) are depressed in proportion to the increase of the fat.

Clotted or Devonshire cream is prepared by setting milk in pans, and when a layer of cream has risen to the surface, heating on a water-bath nearly to boiling; the cream is removed on the following day. As evaporation takes place from the surface, not only is the percentage of fat raised, but the non-fatty solids are proportionately high.

COMPOSITION OF MAMMALIAN MILK.

	Water	Fat	Sugar	Casein	Albumin	Ash
Cow .	87·25	3·75	4·75	3·00	0·40	0·75
Woman .	88·20	3·30	6·80	1·00	0·50	0·20
Goat .	86·04	4·63	4·22	3.49	0·86	0·76
Sheep .	81·31	6·86	5·23	4·62	1·00	0·98
Buffalo .	82·63	7·61	4·72	3·54	0·60	0·90
Mare .	89·80	1·17	6·89	1·84		0·30
Ass .	90·12	1·26	6·50	1·32	0·34	0·46
Mule .	91·50	1·59	4·80	1·64		0·38
Bitch .	75·44	9·57	3·09	6·10	5·05	0·73
Cat .	81·63	3·33	4·91	3·12	5·96	0·58
Rabbit .	69·50	10·45	1·95	15·54		2·56
Llama .	86·55	3·15	5·60	3·00	0·90	0·80
Camel .	86·57	3·07	5·59	4·00		0·77
Elephant	67·85	19·57	8·84	3·09		0·65
Sow .	82·34	6·71	4·97	5·96		1·02
Porpoise	41·11	48·50	1·33	11·19		0·57
Whale .	48·67	43·67	7·11			0·46

HUMAN MILK.

Human milk differs in important particulars from that of the cow. It is not curdled by rennet, appears thinner, and contains more sugar and less proteins.

Fat. The fat of human milk contains a very much smaller quantity of volatile acids than that of cow's milk, and a larger amount of unsaturated acids (Laves, Zeitsch. physiol. Chem. 19, 369; Ruppel, Zeit. Biol. 31, 1; Pizzi, Staz. Sper. Ag. 1894, 615; Sauvaitre, Ann. Chim. Anal. 1902, 143). The refractive index is higher, and decreases as lactation advances and free fatty acids are present (Carter and Richmond, B. M. J. 1898, 199).

Sugar. According to Radenhausen (Zeitsch. Chem. 5, 13) and Denigès (J. Pharm. Chim. [v.] 27, 413), the sugar of human milk is lactose; the last author, however, states that there is another carbohydrate which modifies the properties, whilst Denigès finds a second dextrorotatory carbohydrate present. Carter and Richmond (*l.c.*) give the specific rotatory power as 48·7°, and state that it crystallises in rhomboid plates; they consider that more than one sugar is present.

Proteins. The casein of human milk, though closely related, differs from that of cow's milk; it is not curdled by rennet, does not exist in combination with calcium phosphate, and is thrown down by acids in a very finely divided state. Dogiel (Zeitsch. Chem. 9, 591) attributes this to the small amounts of salts present; if the salts are raised to the standard of cow's milk, the casein comes down in flakes. Kobrak (Pfluger's Archiv. 1900, 69) says that it is less acid, and by repeated precipitation with acid and solution in dilute alkali, a product like the casein of cow's milk is obtained; he considers it as a nucleo- protein plus histon or protamine. Lehmann and Hempel (Pfluger's Archiv. 1894, 56, 558) find 1·09 p.c. of sulphur and 3·2 p.c. ash, as against 0·72 and 6·47 p.c. respectively in the casein of cow's milk. Sikes (J. Physiol. 1906, 464) gives the proportion of Ca to proteins as 1·06 : 100. Wroblewski (Diss. Berne, 1894) also finds more sulphur, and states that no nuclein is present. Abderhalden and Schittenhelm (Zeitsch. physiol. Chem. 1906, 458) find that whilst biological tests show that the casein of human milk differs from that of the cow, the proportion of amino-acids is very similar (*cf.* also Tangl and Czókás, Pfluger's Archiv. 1908, 534; also Abderhalden and Langstein, Zeitsch. physiol. Chem. 1910, 8, find no difference in yield of amino-acids).

Wroblewski (*ibid.* 1898, 308) states that the amount of opalisin (*q.v.*) is abundant in human milk. Camerer and Soldner (Zeitsch. Biol. 1898, 277) find 40 p.c. of unknown protein in human milk. The ratio of protein nitrogen to total nitrogen is 0·88 (Camerer and Söldner, *l.c.*), 0·91 (Munk, Virchow's Archiv. 134, 501).

Salts. Human milk contains only about 0·03 p.c. calcium and 0·029 p.c. P_2O_5 (Sikes, *l.c.*), or 0·044 p.c. P_2O_5, according to Stoklasa (Zeitsch. physiol. Chem. 1897, 343); of the P_2O_5 0·012 p.c. belongs to the proteins (Sikes). These quantities are very much lower than those found in cow's milk. Citric acid is present.

Gases. Külz (Zeitsch. Biol. 1895, 180) finds O 1·07–1·44, CO_2 2·35–2·87, and N 3·37–3·81 p.c. by volume.

Enzymes. Oxydase does not appear to be normally present in human milk, but there is much catalase, which is destroyed at 75° (Jolles, Zeitsch. Biol. 1903, 248). A proteoclastic enzyme is also found. Béchamp (Compt. rend. 76, 836) describes an amylolytic ferment.

Composition.—The most extensive studies of the composition of human milk are those of Leeds (Chem. News, 50, 263, 280), Pfeiffer (J. Pharm. Chim. 13, 163), Carter and Richmond (*l.c.*), Lehmann and Hempel (*l.c.*), Szilasi (Chem. Zeit. 14, 1202), Camerer and Söldner (Zeitsch. Biol. 1896, 43 and 535), and V. and J. S. Adriance (Pamphlet Abstr. J. Chem. Soc. 1899, ii. 115).

It is difficult to deduce a mean composition from the results, as human milk appears to undergo a progressive change of composition; the table below is an abstract of the results of the observers:

Date from birth	Total solids	Fat	Sugar	Proteins	Ash
1st day (colostrum)	15·7	3·0	4·0	8·3	0·4
1st week . .	12·9	3·5	6·1	3·0	0·3
2nd week . .	12·35	3·35	6·6	2·15	0·25
3rd & 4th weeks .	12·1	3·4	6·75	1·75	0·22
After 1st month .	11·8	3·3	6·8	1·5	0·2

The fat is the most variable of the constituents, the maximum found being 9·05 (P.) and the minimum 0·47 (C. and R.). Forster (Ber. 14, 591) states that the last portions drawn from the lowest are richer than those preceding, 1·71, 2·77, and 4·5 p.c. being found in three successive samples. Carter and Richmond, however, find, from the examination of 37 samples taken before suckling and 37 after, that there is little difference in the fat; in 15 cases the fat was higher, and in 21 cases lower, while in one (where the reaction was excessive) the composition before and after suckling was identical. The maximum difference (with a very deficient supply) was shown in a case where 0·98 p.c. was found before suckling and 4·07 p.c. after. The cases in which the fat was found higher before suckling generally occurred when the mother was lying down, and hence it would seem that the separation of cream was largely mechanical.

When lactation is established the sugar usually varies between 6 and 7 p.c., though Carter and Richmond record a sample containing 8·89 p.c. and the proteins between 1 and 2 p.c.

Reaction.—Human milk always appears alkaline to litmus, and the acidity to phenolphthalein averages 3 c.c. N acid per litre.

Healthy children of both sexes discharge, from their seventh to their twelfth day from birth, a white secretion from the breast (*Haeenmilch*), which resembles human milk in composition

MILK OF OTHER ANIMALS.

Mare's milk is white, sp.gr. 1·035 (1·034–1·036). It is much sweeter than cow's milk, but contains less fat and proteins. Mare's milk is distinguished from all others by its small amount of fat.

Koumiss is a vinous liquor made by the Tartars by the fermentation of mare's milk. It is a white, sweetish, effervescing liquid, somewhat sour when old. The sugar gradually diminishes with age, whilst the alcohol and the lactic acid increase.

It is prepared by adding 1 part of old koumiss to 10 of fresh milk, and warming for 2–3 hours to 20°–25°. Carbon dioxide then comes off, and the liquid is bottled and left to mature. (For manufacture and analyses, *v.* Vieth, Analyst, 13, 2; L. V. S. 31, 353; Biel, J. 4, 166.) A similar preparation in imitation of the true Russian koumiss is made in Switzerland and in this country from cow's milk by adding a small quantity of sugar and yeast to skim milk; it contains more sugar and less lactic acid than old Russian koumiss, and on account of the much greater proportion of casein contained in cow's milk differs considerably from that prepared from mare's milk (Phil. Trans. [iii.] 1, 861, 888).

H. Suter-Naef (Ber. 5, 286) gives the composition of Swiss koumiss (sp.gr. 1·1286), manufactured at Davos, as follows:

	In 100 grams	Per litre
Water	90·346	1019·64 grams.
Alcohol	3·210	36·23 ,,
Lactic acid	0·190	2·14 ,,
Sugar	2·105	23·75 ,,
Albuminates	1·860	20·99 ,,
Butter	1·780	20·09 ,,
Inorganic salts	0·509	5·74 ,,
Free carbonic acid	0·177	2·00 ,,

For observations on the changes and action of Russian koumiss *v.* Jagielski (Pharm. J. [iii.] 1, 861, 885); J. T. George (Phil. Trans. [iii.] 3, 544).

Ass's milk is white, and sweeter than cow's milk. Sp.gr. between 1·023–1·035.

It readily turns acid, and easily undergoes fermentation. (For composition, *v.* Table, p. 540.)

Goat's milk is white, of insipid, sweetish taste and peculiar odour. It is a little richer in solids than cow's milk. Sp.gr. 1·030–1·035. On coagulation its casein forms thick clots. (For composition, *v.* Table p. 540.)

Sow's milk. Petersen and Oekhen (Bied. Zentr. 1897, 711; and Milch.-Zeit. 1896 ,655), Henry and Woll (Ann. Rep. Ag. Exp. Stat. Wisconsin, 1897, 10), and Woll (Exp. Stat. Record, 1900, 84) have examined the milk. The average composition is

Fat	Sugar	Proteins	Ash	Solids not fat	Sp.gr.
6·71	4·97	5·96	1·02	11·95	1·0389

The fat varies from 2·4 to 12·1.

Sheep's milk. Besana (Staz. Sper. Ag. Ital. 1892, 572), Hucho (Landw. Jahr. 1897, 497), Trillat and Forestieri (Compt. rend. 1902, 134, 1517; Ann. Chim. anal. 1902, 321; Bull. Soc. chim. 1903, 29, 286), Pizzi (Staz. Sper. Ag. Ital. 1894, 615; Fleischmann (Book of the Dairy, 1896, 56). Mean composition:

Fat	Sugar	Protein	Ash	Solids not fat	Sp.gr.
6·86	5·23	6·52	0·98	11·83	1·0385

Buffalo's milk. F. Strohner (Zeitsch. Nahr. Genussm. 1888, 88), W. Fleischmann (Book of the Dairy, 1896, 57), A. Pizzi (Staz. Sper. Ag. Ital. 1894, 615), Windisch (Zeitsch. Nahr. Genussm. 1904, 273), Leather (Analyst, 1901, 200, Indian Buffalo), Pappel and Richmond (J. Chem. Soc. Trans. 1891, 246, Egyptian Buffalo).

H. D. R.

MILK-TREE WAX, COW-TREE WAX, *v.* WAXES.

MILLERITE. Native nickel sulphide. Occurs in brass-yellow capillary crystals *v.* NICKEL.

MILLET. A name somewhat loosely applied to many species of grasses, growing in tropical or sub-tropical countries. As examples may be given the following:—

Great millet, *Sorghum vulgare* (Pers.). Other names given to varieties of this plant are dhurra or durra, African millet, Kaffir corn, millo maize. American broom corn and joar.

Little millet, *Panicum miliare* (Lam.).

Common millet or **Indian millet,** *Panicum miliaceum* (Linn.).

Texas millet, *Panicum texanum* (Vasey).

Sauwa millet, *Panicum frumentaceum* (Roxb.).

Japanese broom corn, *Panicum Crus-galli* (Linn.).

Golden or **Italian millet,** *Setaria italica* (Beauv.). Varieties of this constitute German millet or Hungarian grass, Japanese millet, Boer manna, and Californian green molia.

Pearl millet, *Pennisetum typhœdeum* (Rich.). Also known as Egyptian or cat's tail millet.

Polish millet, *Panicum sanguinale* (Linn.).

Koda millet, *Paspalum scrobiculatum* (Linn.).

The seeds of some varieties are used as human food, also in the preparation of certain fermented drinks, and as food for horses, cattle, and poultry. Broom corn is so called because its seed heads, after being deprived of the seeds, are employed in making brooms. The whole plants, cut green, are employed either as green fodder, or hay for farm animals.

Many of the millets grow to a height of only 2–4 feet, but Pearl millet sometimes attains 6 feet, while great millet or Kaffir corn reaches 8 or even 10 feet.

The following analyses, many of them by Church (Food Grains of India, 1886 and 1891), will serve to show the composition of the seeds of many 'millets.'

Species	Water	Protein	Fat	N-free extract	Crude fibre	Ash
Sorghum vulgare .	12·5	9·3	2·0	72·3	2·2	1·7
,, *saccharatum*	12·8	11·8	3·0	68·3	3·0	1·1
Pennisetum typhoideum .	11·3	10·4	3·3	71·5	1·5	2·0
Setaria italica[1] .	10·2	10·8	2·9	73·4	1·5	1·2
Panicum miliare .	10·2	9·1	3·6	69·0	4·6	3·5
,, *miliaceum*[1]	12·0	12·6	3·6	69·4	1·0	1·4
,, *frumentaceum*	12·0	8·4	3·0	72·5	2·2	1·9
,, *sanguinale* .	13·4	14·9	4·1	64·5	1·1	2·0
,, *texanum* .	(?)	4·7	2·1	47·1	23·2	(?)
Paspalum scrobiculatum[1]	11·7	7·0	2·1	77·2	0·7	1·3
'Rangoon millet' .	12·4	10·6	3·1	70·3	1·4	2·2
'Millet' . .	12·9	11·1	4·5	59·5	7·5	4·5
Dhurra . .	11·5	9·0	3·8	70·1	3·6	2·0
Sorghum vulgare .	15·2	9·3	3·3	68·0	2·5	1·7
Pearl millet[2] .	9·2	12·9	5·1	68·5	2·1	2·2

The various millets are largely used as fodder plants, but cases of death among animals fed upon young plants (of *Sorghum* in particular) have been numerous. It has been shown by Dunstan and Henry (Phil. Trans. 1902, A, 399) that the young leaves and shoots of *Sorghum vulgare* contain a glucoside, *dhurrin*, which readily hydrolyses by the action of an enzyme also present in the plant, yielding *p*-hydroxybenzaldehyde, *d*-glucose, and hydrocyanic acid. Brünnich (Chem. Soc. Trans. 1903, 788) obtained as much as 2·44 grains of hydrocyanic acid from 1 lb. of green sorghum at 5 weeks old, corresponding to 13·38 grains per 1 lb. of dry matter. The amount rapidly diminishes as the plant grows: at 9 weeks old, the same sorghum only yielded 0·20 grain per 1 lb. of green material (0·76 grain HCN per 1 lb. dry matter).

Brünnich was also able to detect hydrocyanic acid in several other varieties of millet.

When sufficiently grown, however, the various millets afford good fodder, and the smaller varieties, nutritious and palatable hay. The following are analyses of some millet hays grown in the Transvaal:—

	Water	Protein	Fat	N-free extract	Crude fibre	Ash
Boer manna . .	7·2	4·9	1·5	43·0	36·5	6·9
Golden millet . .	7·9	11·1	1·0	29·5	41·0	9·5
Californian green moba	8·0	10·5	1·2	35·6	35·6	9·3
Jap. broom corn .	9·6	6·8	1·2	38·8	34·8	8·8

H. I.

MILLON'S REAGENT *v.* Albuminoids.

MILORY GREEN. *Chrome green v.* Pigments.

MIMOSA *v.* Primuline and its Derivatives.

MIMOSA BARK *v.* Tannins.

MINERAL ACIDS. Acids of inorganic origin, *e.g.* sulphuric, nitric, hydrochloric, phosphoric, &c.

MINERAL ALKALI. A term originally given to soda in contradistinction to potash, which was termed the *vegetable alkali*.

MINERAL BLUE. *Antwerp blue v.* Pigments.

MINERAL CAOUTCHOUC. Syn. with *Elaterite* (*q.v.*).

MINERAL CARBON. *Anthracite v.* Fuel.

MINERAL CHAMELEON. *Sodium* or *potassium manganate v.* Manganese.

MINERAL COTTON. A name given to slag-wool.

MINERAL GREEN. *Scheele's green, Hydrocupric arsenite* $CuHAsO_3$ *v.* Arsenic.

MINERAL INDIGO. A name given to the blue oxide of molybdenum *v.* Molybdenum.

MINERAL KERMES. Amorphous antimony sulphide containing the trioxide (*v.* Antimony).

MINERAL OILS *v.* Petroleum.

MINERAL PURPLE. *Purple of Cassius v.* Gold, purple.

MINERAL TALLOW. *Hatchettine.* A variety of fossil resin or wax resembling dysodil, ozokerite, &c.

MINERAL TURPETHUM. *Mercuric sulphate v.* Mercury.

MINERAL WATERS *v.* Aerated waters; also Water.

MINERAL YELLOW. A term occasionally given to lead oxychlorides when used as pigments *v.* Lead.

MINIUM *v.* Lead.

MINJAK-LAQAM *v.* Oleo-resins.

MINJAK TENGKAWANG *v.* Borneo tallow.

MIRBANE, ESSENCE OF. A trade name for nitrobenzene as used in perfumery.

MISPICKEL, Arsenopyrite, or **Arsenical pyrites** (Ger. *Arsenikkies*). A mineral consisting of iron sulpharsenide of FeAsS, crystallising in the orthorhombic system. The crystals are usually quite simple in form, being bounded by a longer or shorter rhombic prism and terminated by dome faces. They are isomorphous with marcasite (*q.v.*). When not tarnished, the material is tin-white in colour with a brilliant metallic lustre. Sp.gr. 6·1; hardness 6. Granular and compact masses are frequent. A cobaltiferous variety (4–10 p.c. cobalt replacing iron) is known as *danaite*. The mineral is sometimes highly auriferous, and it is then a valuable ore of gold, as in New South Wales, California, and Alaska.

Mispickel occurs chiefly in mineral-veins. Large quantities are found in the silver-lead veins of Freiberg, Saxony, and in the tin veins of Cornwall and Devon. White arsenic is obtained as a by-product when these ores are roasted.

L. J. S.

MITIS GREEN. *Copper aceto-arsenate, Schweinfurth green v.* Arsenic.

MITTLER'S GREEN. Sny. with *Guignet's green*, art. Chromium.

MOCHA-STONE *v.* Agate.

MOIRÉE MÉTALLIQUE. The term given to the variegated arborescent or crystalline appearance given to the surface of tin plate produced by heating the plate and applying to it some dilute *aqua regia* for a few seconds, washing it with water, drying and coating it with lacquer.

MOLASSES *v.* Sugar.

MOLYBDENITE. A mineral consisting of molybdenum disulphide MoS_2, crystallising in the form of six-sided scales or short prisms, the system of crystallisation being possibly

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[1] The samples were deprived of their husks before analysis.

[2] A sample grown in South Africa, highly prized as food for ostriches.

hexagonal. There is a perfect cleavage parallel to the base, and the laminæ are very flexible but not elastic. The mineral is very soft (H.$=$1), sectile, and greasy to the touch, and it readily marks paper. The colour is lead-grey with a bluish tinge and a metallic lustre. Sp.gr. 4·7. In its scaly form and general appearance molybdenite bears a striking resemblance to graphite, differing from this, however, in the bluish tinge of its colour. It is, of course, readily distinguished from graphite by its greater density and by its chemical reactions. The name molybdenite (from μόλυβδος, lead or lead-ore) itself bears witness to the confusion between this mineral and black-lead or plumbago (graphite); and, indeed, the two minerals were not distinguished until Scheele in 1778 obtained molybdic acid from one of them.

As isolated scales disseminated through crystalline rocks of various kinds (granite, gneiss, marble, &c.), molybdenite is of wide distribution, though only in small amounts. It is also found in metalliferous veins and in quartz-veins. In small quantities it has been won by mining at Altenberg in Saxony, near Flekkefjord and Egersund in Norway, Kingsgate in New South Wales, the Hodgkinson mining district in north Queensland, in Canada, and in the State of Washington. It is used for the preparation of molybdenum compounds employed in the laboratory; for the preparation of a fine blue pigment for dyeing fabrics; and for the manufacture of ferro-molybdenum, which, combined with chrome-steel, gives a self-hardening product, especially suitable for tools.

L. J. S.

MOLYBDENUM. Sym. Mo. At.wt. 96·0 (Seubert and Pollard). This metal, the presence of which in molybdenite was first pointed out by Scheele in 1778, and which is said to have been isolated by Hjelm in 1790, is grouped under Mendeléeff's classification with chromium, tungsten, and uranium, but, from the technical point of view, it may be regarded as a member of a group of heavy metals, including columbium, tantalum, tungsten, uranium, vanadium, and titanium, which occur in the oldest plutonic rocks and schists, and are capable of imparting special properties to steel when added to it in extremely small proportions.

Molybdenum owes its name to the word *molybdaena*, under which title most minerals resembling lead in appearance were formerly known, and its nature and value are even now so little recognised that its principal source, the sulphide (MoS_2) is frequently passed over by the prospector as being merely graphite, which it closely resembles. The writer has, in fact, seen it employed as blacklead in the north of Newfoundland within the last 20 years.

Molybdenum occurs in *Molybdenite* MoS_2, *Wulfenite* $PbMoO_4$, and *Molybdic ochre* MoO_3 (usually containing a considerable amount of Fe_2O_3), and as the extremely rare minerals, *Powellite* $Ca(Mo{\cdot}W)O_4$, *Belonesite* $MgMoO_4$, and *Pateraite* $FeCo(Mo)O_4$. It also occurs in small quantities in other minerals containing the rare heavy metals of the same group, but is probably more an accidental occurrence than an essential constituent. The purest molybdenum metal is produced from wulfenite, but practically the whole of the world's supply of the metal and its compounds is obtained from molybdenite. Until within the last 5 years, most of this mineral was produced by hand-picking from pegmatite and other granitic rocks, and from schists in which it occurs as sparsely distributed flakes resembling high-grade graphite in appearance and general physical properties. It was only purchased when of high quality (90–95 p.c. of MoS_2 equivalent to 54–57 p.c. Mo), and commonly by inspection and not on assay. It is now, however, in increasing demand, and is purchased on the usual commercial basis of so much per unit per cent. of Mo or of its equivalent in MoO_3 with a guarantee of not more than so much per cent. of arsenic, phosphorus, antimony, or copper. The limit fixed for these objectionable metals is always subject to special agreement, and is becoming more elastic on account of the increasing demand and the small supply, and from the fact that in modern smelting methods, in which the electric furnace is employed, they are, to a great extent, eliminated. Lower-grade molybdenite concentrates are also obtained by the treatment of ores in which it occurs in small flakes to the extent of even less than 2 p.c., by ordinary washing plants or by electrostatic or oil flotation processes.

Metallic molybdenum may be prepared by reduction of molybdic acid MoO_3, or, preferably, of the less volatile dioxide MoO_2, with pure carbon or by the alumino-thermic process or by heating one of the oxides or chlorides in a current of hydrogen. It has a sp.gr. of about 9 (after melting), and, when pure and free from more than a trace of carbon, is softer than steel, malleable and capable of being forged and welded. Its fusing-point is about 2000°, slightly below that of tungsten. It is attacked by the halogens and by most acids and fused salts, and has not so far been applied to any practical use, except in alloy with other metals, and is prepared for the manufacture of such alloys, by direct reduction of the sulphide in the electric furnace under conditions which eliminate the bulk of the sulphur and other non-metallic impurities, partly through the high temperature obtained and partly by the use of basic materials in the furnace charge or linings. Similarly, ferro-molybdenum and other alloys are produced by the direct electric furnace reduction of molybdenite in admixture with oxide of iron, chromium, nickel, or tungsten, the only metals with which it is at present alloyed for technical use.

The addition of molybdenum to steel in the form of the pure metal or one of the above alloys, largely increases its tensile strength, toughness, and fineness of grain and its retention of magnetism. For the production of high-grade tool steel, it has a value similar to, but greater than, that of tungsten. At present, it is mainly employed in crucible steel, and, like many of the steels now being prepared for special purposes, molybdenum steels and molybdenum alloys must be regarded as still on trial as compared with others, although the fact that they are of great value is beyond doubt.

Molybdenum is now prepared for addition to steel, as 90–98 p.c. molybdenum powder or fused lump practically free from carbon, as ferro-molybdenum containing 10, 25, 50, and

80–85 p.c. molybdenum, and as an alloy with tungsten, chromium, or nickel.

The following are typical analyses of ferro-molybdenum as now made by the electric furnace:—

Mo . .	85·80	80·00	85·00	50·00
Fe . .	10·96	16·50	14·20	49·30
C . .	3·07	3·24	0·50	0·35
Si . .	0·11	0·21	0·25	0·30
S . .	0·05	0·02	0·03	0·03
P . .	0·01	0·03	0·02	0·02
	100·00	100·00	100·00	100·00

The two low-carbon alloys were probably produced by the refining of crude cast ferro-molybdenum by a modification of the process of Moissan, who removes the excess of carbon by heating the powdered metal with molybdenum dioxide or calcium molybdate, with the addition of alumina for production of slag.

Molybdenum combines with the halogens to form a large variety of compounds, including many double halogen salts and various oxy-salts. It forms compounds with phosphorus, boron, silicon, and sulphur, which are of no technical interest except in so far as their presence in molybdenum or ferro-molybdenum is objectionable. Similarly, molybdenum carbides can be produced, and one of the difficulties in obtaining metallic molybdenum and ferro-molybdenum by direct reduction of the oxide with carbon, is the fact that too large a proportion of the latter is commonly contained in them to permit of their use in steel making without further de-carburising treatment. G. T. H.

COMPOUNDS OF MOLYBDENUM.

Oxides. Molybdenum forms a series of oxides, which, during their formation in solution, often show changes of colour through various shades of blue to black or violet-black. The following are the best known oxides:—

The sesquioxide Mo_2O_3, formed when one of the higher oxides is treated with sodium amalgam or zinc, is a black powder, which forms black or dark grey salts. These salts give black or dark purple solutions when concentrated, but on dilution, the solutions become transparent and of a purple tint. They have a styptic taste, oxidise somewhat in the air, and are precipitated by alkalis forming the brownish-black hydroxide $Mo(OH)_3$ (Muthmann and Nagel, Ber. 1898, 31, 2009).

Molybdenum dioxide MoO_2 is formed by heating the sesquioxide in air or by heating the trioxide in a current of hydrogen at 470° and in other ways (Guichard, Compt. rend. 1899, 129, 722; *ibid.* 1900, 131, 998; Friedheim and Hoffmann, Ber. 1902, 35, 791; Chapman and Law, Analyst, 1907, 32, 250). It is a brown or violet-brown crystalline powder, which, like the other oxides, is reduced to metallic molybdenum when heated at 600° in hydrogen. It gives unstable salts, the concentrated solutions of which are black, but turn, successively, bluish-green, greenish-yellow, red and yellow on dilution. The hydroxide $Mo(OH)_4$ is dark red and forms a yellow or red colloidal solution in water.

Molybdenum trioxide MoO_3 is usually found with molybdenite and occurs as molybdic ochre, either as an earthy powder or incrustation, or in crystalline masses. It is obtained by roasting the powdered mineral with quartz sand, treating the mass with ammonia, and after removing impurities, converting the ammonium molybdate thus formed into the trioxide by decomposition and evaporation with nitric acid (Wöhler, Annalen, 1856, 100, 376; Muthmann, *ibid.* 1887, 238, 117; Eng. Pat. 5821, 1909). It is a white powder, which becomes yellow on heating, melts at 791° to a yellow liquid, and readily volatilises in the air (Groschuff, Zeitsch. anorg. Chem. 1908, 58, 113). Towards strong acids the trioxide acts as a base (Guichard, Compt. rend. 1906, 143, 744), but generally it behaves as an acid forming oxide.

Molybdic acid $H_4Mo_2O_5$ or $MoO_3{\cdot}2H_2O$ (Mylius, Ber. 1903, 36, 638; Rosenheim and Bertheim, Zeitsch. anorg. Chem. 1906, 50, 320; Graham, Journ. Franklin Inst. 1907, 163, 69) is obtained as yellow crusts, and forms colloidal, or, according to Wöhler and Engels (Zeitsch. Elektrochem. 1910, 16, 693) semi-colloidal solutions (Graham, Chem. Soc. Trans. 1864, 326: Sabanéeff, J. Russ. Phys. Chem. Soc. 21, 515). When reduced by metallic molybdenum, in neutral or faintly acid solution, the blue oxide or molybdenum molybdate is formed, but if the solution is strongly acid a brown oxide appears (Guichard, *l.c.*).

The normal molybdates are unstable and readily form polymolybdates by uniting with further molecules of the trioxide and also with other acidic oxides to form a large number of complex molybdates. A large number of alkaline and other molybdates are known, some of which are used for the production of pigments and dyes, in pottery glazes and in analytical work.

Molybdenum molybdate (molybdenum blue or molybdenum indigo) is obtained by reducing molybdic acid as above or with other reducing agents or by adding a cold dilute hydrochloric acid solution of molybdenum dioxide to a similar solution of ammonium molybdate and washing with sodium chloride (Guichard, Compt. rend. 1900, 131, 389, 419). Its solubility, and possibly its composition, depends on the mode of formation (Klason, Ber. 1901, 34, 158). It is said to form a useful, though somewhat expensive, pigment for india-rubber (Gummi Zeit. 1903, 17, 418).

Phosphomolybdic acid $H_3PO_4,12MoO_3$ is formed by treating its ammonium salt with *aqua regia* (Finkener, Ber. 1878, 11, 1638; Levi and Spelta, Gazz. chim. ital. 1903, 33, i. 207; Miolati, *ibid.* ii. 335) is employed as a reagent for alkaloids. Its ammonium salt $(NH_4)_3PO_4,12MoO_3$ is a canary-yellow crystalline powder almost insoluble in water and in dilute acids.

Permolybdic acid $H_2MoO_5xH_2O$ is an orange-red amorphous powder, formed by treating the trioxide with hydrogen peroxide (Muthmann and Nagel, *l.c.* 1836); a number of permolybdates have been prepared.

Sulphides. *Molybdenum sesquisulphide* M_2S_3 forms steel-grey needles of sp.gr. 5·9 at 15°, and is obtained by heating the disulphide in the electric furnace (Guichard, Compt. rend. 1900, 130, 137).

Molybdenum disulphide MoS_2 occurs native as *molybdenite* in foliated scales or in tabular hexagonal prisms, and can be obtained artificially by fusing the trioxide with sulphur or by heating it in sulphuretted hydrogen. It is very similar to graphite in appearance, possessing a metallic lustre and a lead-grey colour, but it is incombustible in the blowpipe. It is oxidised with evolution of sulphur dioxide when heated in the air, and when treated with nitric acid or *aqua regia*.

Molybdenum trisulphide MoS_3, obtained by the action of sulphuretted hydrogen on a concentrated molybdate solution, is a black-brown powder, which combines with basic sulphides to form thio molybdenum salts (Annalen, 1884, 225, 1; Hofmann, Zeitsch. anorg. Chem. 1896, 12, 55). Molybdenum tetra-sulphide and thiomolybdic acids are also known.

Halides and other compounds. Molybdenum forms a large number of halogen, mixed and double halogen, and oxyhalogen salts (Muthmann and Nagel, *l.c.*; Guichard, Compt. rend. 1896, 123, 821; Bull. Soc. chim. 1901, [iii.] 25, 188; Klason, *l.c.* 148; Nordenskjöld, Ber. 1901, 34, 1572; Ruff and Eisner, *ibid.* 1907, 40, 2926, 3931). Molybdenum combines with silicon to form silicides (Vigouroux, Compt. rend. 1899, 129, 1238; Defacqz, *ibid.* 1907, 144, 1424; Bull. Soc. chim. 1908, [iv.] 3577; Watts, Trans. Electro. J. 1906, 9, 105; Hönigschmid, Monatsh. 1907, 28, 1017); with boron to form borides (Tucker and Moody, Chem. Soc. Trans. 1902, 16; Binet du Jassonneix, Compt. rend. 1906, 143, 169); with carbon to form carbides (Moissan and Hoffmann, *ibid.* 1904, 138, 1558); and with carbon monoxide forming a carbonyl compound (Mond, Chem. Soc. Trans. 1910, 798).

Molybdenum cyanides and thiocyanates and their complex salts with a number of organic compounds have been prepared (Rosenheim, Zeitsch. anorg. Chem. 1906, 49, 148; *ibid.* 1907, 54, 97; Ber. 1908, 41, 2386; *ibid.* 1909, 42, 149, 2295; Sand and Maas, *ibid.* 1907, 40, 4504; *ibid.* 1908, 41, 1500, 1861, 3367; *ibid.* 1909, 42, 2642; Chilesotti, Gazz. chim. ital. 1904, 34, ii. 493). A number of salts of molybdenum with organic acids have also been prepared (Rosenheim, Ber. 1895, 26, 1191; Zeitsch. anorg. Chem. 1903, 34, 427; Grossman and Krämer, *ibid.* 1904, 41, 43; Ber. 1903, 34, 1606; Henderson and Barr, Chem. Soc. Trans. 1896, 1455; Orr and Whitehead, *ibid.* 1899, 546; Mazzucchelli, Atti. R. Acad. Lincei. 1909, [v.] 18, ii. 259).

Molybdamide $OH{\cdot}MoO_2{\cdot}NH_2$ is obtained by treating a chloroform solution of molybdic chloride with ammonia. A black precipitate of the diamide is obtained, which, when extracted with alcohol, is converted into the brownish-red amorphous monamide.

The *monoethylamide* $OH{\cdot}MoO_2\,HNEtH_2O$, a white powder and the *diethylamide*

$$MoO_2(NHEt)_2,$$

a reddish-brown powder are formed readily by the action of molybdenum chloride on ethylamine. The diamide reacts violently with nitric acid, and gives a deep blue solution with strong sulphuric acid (Fleck and Smith, Zeitsch. anorg. Chem. 1894, 7, 351).

Molybdenum tannate is of a deep yellow colour, soluble, and has a great affinity for vegetable fibre. It produces fast shades on leather, and in conjunction with logwood extracts a variety of shades may be obtained (Pozzi-Escot, Compt. rend. 1902, 135, 880).

Nicotine ammonium molybdate, prepared by the action of ammonium molybdate on nicotine in the presence of acetic acid is a white powder, sp.gr. 2·5407, and is intensely poisonous. On oxidation in acid solution it yields nicotinic acid, but in alkaline solution dipyridine is formed. (Meszlényi, Landw. Versuchs.-Stat., 1905, 61, 321).

MONAZITE. A mineral consisting essentially of phosphate of the cerium metals $(Ce,La,Di)PO_4$, crystallising in the monoclinic system. Several other elements (yttrium, silicon, iron, calcium, tin, &c.) are usually present in small amounts, and in particular thorium (ThO_2 1–11 p.c.). The commercial value of the mineral depends on its use as a source of thoria for the manufacture of mantles for incandescent gas-lighting (*q.v.*). Crystals of monazite are yellowish-brown and translucent, or dull brown and opaque, with a lustre inclining to resinous. Sp. gr. 4·9–5·3; hardness 5½. Monazite gives the absorption-spectrum characteristic of didymium salts, and this affords a ready means of detecting the mineral.

Dull crystals of monazite of fair size are found in the pegmatite-veins of the Ilmen mountains in the southern Urals, and at several places in the south of Norway. Small, brilliant crystals are occasionally met with in crevices in the gneissic rocks of the Alps. As small grains embedded in gneissic and granitic rocks monazite has a very wide distribution, though only in relatively very small amounts. With the weathering and breaking down of such rocks, the monazite is accumulated with the other heavy minerals in the beds of streams. Under these circumstances it is often met with in alluvial gold washings. The careful examination of the heavy residues of river sands rarely fails to reveal the presence of some grains of this mineral. Occurrences of this kind have been recorded from all parts of the world, but it is only in Brazil and in North and South Carolina that the deposits are sufficiently rich to be worked commercially.

In Brazil, monazite-bearing sands are found on the seashore at certain spots near Alcobaca and Prado in the south of the State of Bahia, and at various points along the coast of the States of Espirito Santo and Rio de Janeiro. The amount exported annually is about 5000 tons. In the Carolinas, alluvial deposits are worked in the valleys of the several streams draining the South Mountains, an eastern outlier of the Blue Ridge. These sands contain monazite in amounts reaching to 1–2 p.c., and they are concentrated by the washing methods of the gold miner. Magnetite and other ferriferous minerals are extracted by an electro-magnet, and the product contains 65–70 p.c. of monazite mixed with other heavy minerals, such as zircon, garnet, rutile, corundum, &c. This cleaned monazite-sand is fine in grain, and of a resinous yellow colour with darker specks of other minerals. The production amounts to about 200 tons per annum, but it is now decreasing. At the felspar quarries of the south of Norway the isolated crystals of monazite are picked out by hand, about a ton per annum being so collected.

References—H. B. C. Nitze (16th Ann. Rep. U. S. Geol. Survey, 1895, pt. iv. 667–693; G. P.

Merrill, The Non-metallic Minerals, 2nd ed. 1910; Bull. Imperial Inst. London, 1905, iii. 151, 233, 285; J. H. Pratt and D. B. Sterrett, Monazite and Monazite-Mining in the Carolinas, Trans. Amer. Inst. Mining Engin. 1910, 40, 313–340. On some of the Brazilian occurrences (*see* F. Freise, Zeitsch. prakt. Geol. 1909, 17, 514).

L. J. S.

MOND GAS *v.* Fuel.

MONEL METAL. An alloy of nickel and copper made from the nickel-copper ores of Ontario; contains, in addition to copper, about 68 p.c. of nickel and a slight amount of iron. Combines a strength approaching that of steel with the non-corrosive qualities of copper or brass: used for roof covering, pump-rods, marine propellers, &c. The cast metal has a tensile strength of 82,500 lbs. per square inch. Elastic limit 37,500 lbs. per square inch, and elongation 44 p.c. The modulus of elasticity is from 22,000,000 to 23,000,000 lbs. as against 30,000,000 lbs. for steel and 13,000,000 lbs. for manganese bronze; m.p. 1360°, sp.gr. (cast) 8·87. Electrical conductivity 4 (copper 100). An important characteristic is the retention of the mechanical properties at high temperatures, which has led to the adoption of the alloy for locomotive fire-boxes in Germany (J. E. Thompson, Eng. and Min. J. 1911, 91, 223; J. Soc. Chem. Ind. 1911, 30, 287).

MONOBROMO-CAMPHOR *v.* Camphors.

MONTANIN. Trade name for a solution of hydrofluosilicic acid; used as a disinfectant.

MONTAN WAX is a bituminous substance extracted by various solvents from *pyropissite*, obtained from the lignites of Saxony and Thuringia. The crude substance is hard and odourless, resembling ozokerite in appearance, and having m.p. 80°–90°. Montan wax comes into commerce as a white, high-melting candle-like material. It is not a paraffin, but consists of two compounds, *montanic acid*, $C_{29}H_{58}O_2$, m.p. 83°–84°, and an alcohol, m.p. 60° (*v.* Boyen, Zeitsch. angew. Chem. 1901, 14, 1110; *cf.* Marcusson, Chem. Rev. Fett- u. Harz. Ind. 1908, 15, 193; Eisenreich, *ibid.* 1909, 16, 211). Asher (D. R. P. 207488 of 1907) purifies the crude substance by heating twice with nitric acid of sp.gr. 1·2–1·4, then washing and melting it, whereby the asphaltic or resinous matter separates out. It may also be purified by dissolving in a suitable organic solvent and then heating with alcoholic alkali. After separation of the saponified matter, the wax is finally treated with concentrated sulphuric acid at 100° (D. R. P. 220050 of 1906). The aluminium salts of montanic acid have been prepared for use as impregnating materials (D. R. P. 221888 of 1908).

Similar waxes have been extracted from Irish peat, and are sold under the names of *montana wax* and *montanin wax* (Ryan and Dillon, Proc. Roy. Dublin Soc. 1909, 12, 202).

MOONSTONE *v.* Felspar.

MORDANT ROUGE. *Aluminium acetate v.* Acetic acid.

MORIN *v.* Old Fustic.

MORINDA CITRIFOLIA. The roots of *Morinda citrifolia* (Linn.) and *M. tinctoria* (Roxb.), known as 'Morinda Root,' are extensively employed in various parts of India under the general trade name of *Suranji*, more especially for dyeing reds, purples, and chocolates. These plants, the native names for which are *Aal, A'l, Ach,* or *Aich*, are to be met with in nearly all the provinces of India, either wild as in the jungles of Bengal, or cultivated in small patches in betelnut plantations, or near the homesteads of the dyers. In Bengal the plant is usually propagated by slips or cuttings, but in other parts it is raised from seed, as well as from cuttings. When the plants have attained a height of from 5 to 6 feet, that is, as a rule, about the end of the third year, the straight spindle-shaped roots which extend into the ground to a depth of 3 or 4 feet, are dug out and the upper portions of the plant are cut into slips to serve for the propagation of the next crop.

The colouring matter is found principally in the root bark, and is developed in greatest quantity at about the end of 3 or 4 years, depending upon the character of the soil. After this time the dyeing principle gradually disappears, and the matured trees, which eventually attain the height of a mango tree, contain hardly a trace of it. The thin roots are most valuable, roots thicker than half an inch being thrown away as worthless. They are mainly used for dyeing the thread or yarn from which the coloured borders of the cotton garments worn by the lower classes are woven, but they are also employed for dyeing the coarse cotton fabric called 'Khárva,' or for dyeing the silk thread, which forms the border of the silk fabric known as 'Endi cloth.' The colours given by A'l range from a reddish-yellow through pink and various shades of red to a dark brown red. The tint seems to depend primarily upon the age of the root, and upon the proportion of root-bark to stem which is employed. The root bark gives the best reds; the dye in the woody part of the root is yellow, and hence when the wood preponderates over the bark, the resulting dye is reddish-yellow.

About 1790 some of the powdered root under the name of 'aurtch' came into the hands of Dr. Bancroft, who found little or no difficulty in applying it to both wool and cotton. At that time he considered that it might be profitably imported into Europe.

In 1832 Schwartz and Koechlin also examined the root under the names 'Nona' and 'Hachrout,' and reported on its dyeing properties to the Industrial Society of Mulhouse. They referred to the fact that of all the Indian *rubiaceæ* examined by them, it contained the largest quantity of certain yellow principles of an acid character which not only necessitated the washing of the root with cold water before dyeing, but also made it requisite to add a certain proportion of sodium carbonate to the dyebath in order to have a perfectly neutral bath. Their conclusion was that since morinda root only possessed one-third the dyeing power of a medium quality of madder, it could never compete with the latter in the European market.

About 1848 some morinda root was submitted for trial to some of the most experienced and skilful calico printers of the Glasgow district, all of whom concurred in declaring it not to be a dye at all.

In 1848 Anderson (Annalen, 71, 216)

isolated from the root of the *M. citrifolia* by extraction with alcohol, a crystalline yellow substance which he named *Morindin*, and to which he assigned the formula $C_{28}H_{30}O_{15}$. This substance, when strongly heated, gave a crystalline sublimate *morindon*, and Anderson pointed out the great similarity, on the one hand, between morindin and ruberythric acid, and on the other between morindon and alizarin.

Rochleder (Annalen, 1852, 82, 205) gave it as his opinion that morindin and morindon were identical with the ruberythric acid and alizarin derived from madder, and Stokes (Chem. Soc. Trans. 2, [2] 333) by examining the absorption spectra of solutions of alizarin and morindon in sodium carbonate and in ether, came also to the conclusion that these two colouring matters consisted of one and the same substance. Stenhouse (J. 1864, 17, 543) formed a similar opinion, and pointed out that morindin not only gives morindon by heating, but also when digested with boiling dilute mineral acids.

On the other hand, Stein (J. 1866, 19, 645) found that the absorption spectra of alizarin and morindon are not identical, and that ruberythric acid and morindin are distinct substances, although the latter resemble each other in the respect that both are glucosides. The distinction between these compounds was rendered much clearer by the work of Thorpe and Greenall (Chem. Soc. Trans. 1887, 51, 52), and Thorpe and Smith (*ibid.* 1888, 53, 171), who showed that morindon possesses the formula $C_{15}H_{10}O_5$; on distillation with zinc dust it gave methylanthracene (m.p. 190°–191°), and was evidently a derivative of methylanthraquinone. To morindin, the glucoside, the formula $C_{26}H_{28}O_{14}$ was assigned.

Somewhat later Perkin and Hummel (Chem. Soc. Trans. 65, 851), during an examination of the *Morinda umbellata* (Linn.) (*see* below), proved that morindon contains three hydroxyl groups, and that Thorpe and Smith's hydrocarbon was β-methylanthracene.

Oesterle and Tisza (Arch. Pharm. 1907, 245, 534) consider that the true formula of morindin is $C_{27}H_{30}O_{15}$, and that its hydrolysis with acid can be expressed as follows:

$$C_{27}H_{30}O_{15}+2H_2O=2C_6H_{12}O_6+C_{15}H_{10}O_5.$$

The sugar thus formed is not fermented by yeast and yields an osazone melting at 197°.

Morindin crystallises from 70 p.c. alcohol in glistening yellow needles, which melt at 245°, and dissolve in alkaline solutions with a red colour. It does not dye mordanted fabrics.

Nono-cetylmorindin $C_{27}H_{21}O_{15}(COCH_3)_9$ (O. and T.), citron yellow needles, melts at 236°.

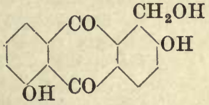
Nono-benzoylmorindin $C_{27}H_{21}O_{15}(CO{\cdot}C_6H_5)_9$ (O. and T.), yellow needles, melts at 186°.

Morindon, the colouring matter of *Morinda citrifolia*, which is obtained by the hydrolysis of morindin, and also exists as a rule to some extent in the free state in this root, consists of orange-red needles, melting at 271°–272°. It is soluble in alkaline liquids, with a blue-violet tint, somewhat bluer than the corresponding alizarin solutions, which, when treated with baryta water, give a cobalt-blue precipitate of the barium derivative. Its solution in sulphuric acid is blue-violet.

Triacetylmorindon $C_{15}H_7O_5(COCH_3)_3$ crystallises in citron-yellow needles, melting at 222°.

Morindon trimethyl ether $C_{15}H_7O_2(OCH_3)_3$ consists of a yellow crystalline powder, melting at 229°.

The exact constitution of morindon has not yet been determined, but it appears probable that if this compound contains in reality three phenolic hydroxyls, it is most likely to consist of a methyl anthragallol. If, on the other hand, as is quite probable, morindon contains an alcoholic group, which, according to Robinson and Simonsen, occurs in the isomeric emodin



then its constitution will be represented as alizarin in which one of the three β-positions is occupied by CH_2OH. Such a constitution would appear to harmonise well with the present known properties of morindon.

In many respects the *Morinda citrifolia* resembles chay-root and madder, for, in addition to morindin and morindon, it contains a large quantity of *chlorogenin*, and certain yellow non-tinctorial substances derivatives of anthraquinone. The preparation of morindon in quantity can be conveniently carried out by extraction with sulphurous acid, according to the details given in the articles on MADDER and CHAY ROOT, for the isolation of natural alizarin. The non-tinctorial yellow compounds, which are obtained as by-products by this method, have not yet been studied in the case of the *Morinda citrifolia*, but in the case of the *Morinda umbellata* have been partially investigated (*see* below).

From the alcoholic extract of the *Morinda citrifolia*, Oesterle (Arch. Pharm. 1907, 245, 287) has isolated a small quantity of a substance which has the constitution of a *monomethyl ether* of a *trihydroxymethylanthraquinone*. It consists of yellow crystals, melting at 216°, soluble in hot alkaline solutions, with a yellowish-red colour. It is not, as this author suggested, identical with the emodin methyl ether which exists in the *Ventilago maderaspatana* (A. G. Perkin, Chem. Soc. Trans. 1907, 2074).

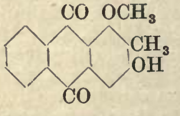
Dyeing properties.—In Dr. G. Watts' Dictionary of the Economic Products of India, Dr. J. Murray has written under the head of *Morinda*, not only a most complete account of the more important species, but full details of the native methods of dyeing with them. These methods of dyeing vary considerably in detail in different parts of India, but they are all similar in general principles, and are practically crude processes of the turkey-red dyeing known in Europe. An extended series of dyeing experiments in connection with morinda root have been carried out by Hummel and Perkin (J. Soc. Chem. Ind. 1894, 13, 346), who find that by adopting certain precautions this dyestuff possesses a dyeing power which is greater than madder itself.

To obtain good results it is necessary, as previously indicated by the work of Schwartz and Koechlin (*l.c.*), to neutralise, or better still to remove, the free acid which exists in considerable quantity in the roots. Experiments also with the powdered morinda root which had been allowed to ferment, or had been digested with boiling dilute acid, as in the preparation of 'garancine' from madder, showed that these preparations dyed exceedingly well when 1 p.c. of chalk was added to the dye-bath. It was found, for instance, that 7·5 grams of a sample of washed morinda root (equivalent to 10 grams of the unwashed root) had a dyeing power equal to 15 grams madder root of good quality.

The reds and pinks obtained on alumina mordant are yellower than the corresponding madder colours, the chocolate presents a similar difference in tone, and hence again appears fuller than a madder chocolate, whilst the lilac is distinctly redder. Oil prepared calico mordanted as for turkey-red gives a very bright orange-red or scarlet similar in shade to that given by flavopurpurin, and fast to clearing with soap and stannous chloride. Chromium mordant on similarly prepared calico gives a full rich chocolate, and iron mordant yields colours varying from dull purple to black, according to the intensity of the mordant. On wool and silk, mordanted according to the usual methods, good chocolate browns are obtained with chromium, orange-reds with alumina, bright orange with tin, and dark purple and black with iron mordant. All the colours referred to are as fast to soap as the corresponding madder colours. With respect to wool and silk in the unmordanted condition, these fibres may be readily dyed both with the washed and unwashed root, more or less rich orange or yellow colours, the brightness of which is enhanced by the addition of a little acetic acid to the dye-bath. These colours, however, which appear to originate from the glucoside morindin itself, are of a sensitive character towards alkalis, and of little value. A. G. P.

MORINDA LONGIFLORA, known as 'Ojuologbo' (woody vine) (Journal Society of Arts, 1905, 53, 1069), is a native of West Africa and considered to be one of the most valuable medicinal plants of that region. It is fully described in the Flora of Tropical Africa (1877, III. 192), where it is stated to be known under the native name of 'Mibogga.'

According to Barrowcliff and Tutin (Chem. Soc. Trans. 1907, 91, 1909) the root of the *M. longiflora* (G. Don) contains an hydroxymethoxymethyl anthraquinone and an alizarin-monomethyl ether, although morindin, the common constituent of the roots of the *M. citrifolia*, *M. tinctoria*, and *M. umbellata*, is absent. The *hydroxymethoxymethylanthraquinone* $C_{16}H_{12}O_4$, yellow needles, melts at 290°, and the *acetyl* derivative at 173°. Heated with 70 p.c. sulphuric acid it gives the 1 : 3-*dihydroxy*-2-*methylanthraquinone* of Schunck and Marchlewski (Chem. Soc. Trans. 1894, 65, 182). Accordingly it possesses one of the following formulæ—



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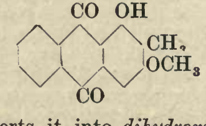
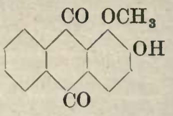


Hydriodic acid converts it into *dihydroxymethylanthranol* $C_{15}H_{12}O_3$ (m.p. 235°), and by methylation 1 : 3-*dimethoxy*-2-*methylanthraquinone* (m.p. 181°) is produced.

The *monomethyl ether of alizarin*.



is identical with the compound isolated by Perkin and Hummel (Chem. Soc. Trans. 1893, 63, 1174) from chay root (*Oldenlandia umbellata* [Linn.]).

The leaves of the *M. longiflora* also contain the above-mentioned hydroxymethoxymethylanthraquinone, and in addition a crystalline alcohol *morindanol* $C_{38}H_{62}O_4$, which melts at 278°, and has $[\alpha]_D + 65{\cdot}9°$. With sodium methoxide and methyl iodide it yields *methylmorindanol* $C_{38}H_{61}O_3{\cdot}OCH_3$ (m.p. 116°).

'Ojuologbo' does not appear to contain an alkaloid, and extracts of the leaves and root were not found to possess any pronounced physiological action (B. and T.). A. G. P.

MORINDA UMBELLATA or **MANG-KOUDU.** The dyeing material, variously named oung-koudou, jong-koutong, &c., is the root-bark of *Morinda umbellata* (Linn.), and is met with in Eastern commerce in the form of small, reddish-brown, irregular rolls of bark, much wrinkled in appearance. Its cost is about 6*d*. per lb. In Java it is largely used for producing the fast reds in the native calico prints, well known under the name of 'baticks.'

Although the shrub from which the root-bark is obtained is met with in Ceylon and the hilly regions of Eastern, Southern, and South-Western India, as well as in the Malay Peninsula and Java, the material does not appear to be considered as of any special importance by the Hindoo dyers, unless, indeed, as is very probable, they use the root as a whole under the general designation ál root, of which it must simply be regarded as a variety.

The following are a few of its Indian vernacular names: Âl (*Bomb.*); núna (*Tamil*); múlúghúdú (*Telugu*); mang-kudu (*Malay*).

The literature connected with mang-koudu is extremely limited, brief references to its dyeing properties only being found in the following publications: Philosophy of Permanent Colours (1813), Bancroft; Bulletin de la Société Industrielle de Mulhouse (1832), E. Schwartz and D. Koechlin; L'Art dela Teinture des Laines (1849), Gonfreville; Monograph on the Dye-stuffs and Tanning Matters of India, &c. (1878), T. Wardle; Watt's Dictionary of the Economic Products of India (1891), J. Murray.

The examination of this dyestuff by Perkin and Hummel (Chem. Soc. Trans. 65, 851) has indicated its close chemical resemblance to the *M. citrifolia.* It contains a glucoside of the nature of morindin, which yields by hydrolysis morindon, but which, according to Perkin (Chem. Soc. Proc. 1908, 24, 149), is best represented by the formula $C_{26}H_{28}O_{14}$, and is identical with that suggested by Thorpe and Greenall (Chem. Soc. Trans. 1887, 51, 52) for the morindin derived from the *M. citrifolia.* The acetyl derivative $C_{26}H_{20}O_{14}(C_2H_3O)_8$ is very sparingly soluble in alcohol, and melts at 246°–248°, and the sugar produced from the glucoside yields an osazone melting at 202°–203°, which is not readily dissolved by alcohol.

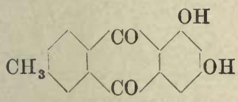
This root bark contains a considerable quantity of *chlorogenin* (*cp.* MADDER), together with a small amount of non-tinctorial yellow derivatives of anthraquinone. A quantitative extraction of 200 grams of the material with sulphurous acid (*cp.* MADDER) gave

9·47 grams of green precipitate, which yielded :

Crude chlororubin 8·075 grams = 4·03 p.c.
Pure morindon . 1·187 „ = 0·59 „
Yellow substances 0·208 „ = 0·104 „

These yellow substances proved to consist of a mixture of at least six distinct compounds. The main constituent isolated in yellow needles, melting at 171°–173°, possessed the formula $C_{16}H_{12}O_5$, and had properties in harmony with those required by a *monomethyl ether* of a *trihydroxymethylanthraquinone.* The *diacetyl* derivative $C_{16}H_{10}O_5(C_2H_3O)_2$ melts at 148°.

A second compound $C_{15}H_{10}O_4$, crystallised in yellow needles, melting at 269°, and was found to consist of the *methylpurpuroxanthin* prepared synthetically (Marchlewski, Chem. Soc. Trans. 1893, 63, 1142) by the condensation of metadihydroxybenzoic acid with paramethylbenzoic acid.



The remaining yellow substances (*a*) $C_{16}H_{12}O_6$, orange-red needles, m.p. 258°, (*b*) $C_{16}H_{10}O_5$, lemon-yellow needles, m.p. 198°–199° ; (*c*) $C_{16}H_{10}O_5$, needles, m.p. 208°, were isolated in such small amount that a determination of their constitution could not be attempted.

Dyeing properties.—This dyestuff is largely employed by the Javanese for producing the fast reds in their celebrated 'baticks.' The colours it yields are practically identical with those given by morinda root, but much fuller, a fact not to be wondered at, for it is well known that in ordinary morinda root the colouring principle is situated chiefly in the root bark. In its ordinary condition mangkudu is not useful in dyeing, but as in the case of *ál* root, a preliminary washing or steeping in water suffices to remove the deleterious acid principles present, and thus to transform it into a valuable red dyestuff. A. G. P.

MORINDIN *v.* MORINDA, and GLUCOSIDES.

MORITANNIC ACID *v.* OLD FUSTIC.

MORPHINE *v.* VEGETO-ALKALOIDS.

MORPHOSAN *v.* SYNTHETIC DRUGS.

MORTAR *v.* CEMENTS.

MORTAR, HYDRAULIC, *v.* CEMENTS.

MOSAIC GOLD. *Ormolu*, *v.* GOLD, MOSAIC.

MOTHER-LIQUOR. The liquid which remains after the crystallisation of a salt or other solid.

MOTHER-OF-PEARL. This is the nacreous lining of the shell of various molluscs, notably that of the large pearl-oyster *Meleagrina margaritifera* (Lam.). The nacre is secreted by the mantle of the mollusc, and consists mainly of calcium carbonate (the orthorhombic modification corresponding with the mineral aragonite) associated with organic matter (up to 12 p.c. of conchiolin). On digesting the nacre in a dilute acid, all the calcareous salt may be dissolved, leaving a coherent pellicle of connective tissue which retains the iridescence until disturbed by pressure. The iridescence is due to the interference of light reflected from the microscopic corrugated edges of the delicate layers of nacre. In consequence of its pleasing lustre, mother-of-pearl is largely employed for buttons, counters, card-cases, knife-handles, and a great variety of trivial ornaments. Large quantities are used by the manufacturers of Birmingham and Sheffield. An important use is that of inlaying papier-maché work, while it is also used in the ornamentation of Moorish and other Oriental furniture. Mother-of-pearl is sometimes decorated by engraving, especially by the Chinese, or by having a pattern etched upon it by means of acid. In trade three varieties of shell are recognised—namely, the white, the gold-edged, and the black-edged. Dark shells are known generally as 'smoked pearl.' The principal fisheries for pearl-shell are in Torres Straits, off the north-west coast of Western Australia, in the Sooloo Archipelago, in the Persian Gulf and Red Sea, and round Tahiti and some other islands of the South Pacific. The shell is commonly known in the market by the name of its place of shipment, such as 'Manila' and 'Egyptian' shells. In the Bay of California and the Gulf of Panama mother-of-pearl shell is obtained from the *Meleagrina californica* (Cpr.), and passes in trade as 'bullock shell.' The brilliant shells of the *Haliotis* and certain species of *Turbo* are also used for inlaid papier-maché and other ornamental purposes. *V.* W. H. Dall, Amer. Nat. 1883, 27, 579 ; and E. W. Streeter, Pearls and Pearling Life, London, 1886 ; G. F. Kunz and C. H. Stevenson, The Book of the Pearl, New York, 1908. L. J. S.

MOTTRAMITE *v.* VANADIUM.

MOULDS, fermentations produced by, *v.* FERMENTATION.

MOUNTAIN ASH, *Sorbus Aucuparia* (Linn.) or [*Pyrus Aucuparia* (Gaert.)] *Service tree, Rowan.* The fruit of this plant affords one of the best natural sources of malic acid (*q.v.*) and of sorbitol. A partial analysis of the berries by Kelhofer (Chem. Zeit. 1895, 19, 1835) shows them to contain 2·78 p.c. free malic acid, 0·49 p.c. tannin, and 6·27 p.c. of sugar. Sorbinose is not present in the juice of the ripe berries, but on dilution and keeping for some months, is produced by the oxidation of the sorbitol (Freund, Monatsh. 1891, 11, 560). This oxidation is effected by a specific bacterium (Bertrand, Compt. rend. 1898, 127, 124, and 728). H. I.

MOUNTAIN BLUE. Syn. with *Azurite* $Cu(HO)_2{\cdot}2CuCO_3$, *v.* COPPER.

MOUNTAIN CORK, FLAX, LEATHER, WOOD. See ASBESTOS.

MOUNTAIN GREEN. Syn. with *Malachite* (*q.v.*, also *v* COPPER). The term is also applied to a mixture of Schweinfurth green with gypsum or heavy spar ; *v.* ARSENIC.

MOUNTAIN SOAP. *Steatite v.* TALC.

MOWRAH SEED OIL *v.* BASSIA OIL.

MUCIC ACID *v.* CARBOHYDRATES.

MUCIC FERMENTATION GUM *v.* GUMS.

MUCILAGE. The older writers made a distinction generally between gums which, like arabic and tragacanth, are obtained as a solid exudate, and the gum which is almost a universal constituent of plants, especially of some seeds

and roots, and may be extracted by treatment with water (*cf.* Gm. 15, 209). The latter was termed *mucilage*, or *vegetable mucilage*, or *pflanzenschleim* (Ger.). Among the more important sources of this gum are marshmallow, salep, fleawort, linseed, and quince; *v.* Gums.
A. S.

MUKOGEN *v.* Synthetic drugs.

MULBERRY, *Morus* spp. The name of several varieties of trees, grown for fruit, ornament, timber, shade, or for the sake of the leaves, which form the best food for silkworms. Many species and varieties are known, the three best known types being *M. alba* (Linn.), *M. nigra* (Linn.), and *M. rubra* (Linn.). Fresenius (Annalen, 185, 101, 219) found in the fruit of black mulberries—

Water	Protein	Free acid	Invert sugar	Pectins	Seeds and fibre	Ash
84·71	0·39	1·86	9·19	2·03	1·16	0·65

The leaves contain from 62 to 73 p.c. of water, and the dry matter contains from 3·8 to 6·1 p.c. of nitrogen and from 7 to 8·5 p.c. of ash (Sestini, Versuchs. Stat. Organ. 15, 286). Alpe (Bied. Zentr. 1900, 29, 422) estimates that in Italy about 20 kilos. of wood and 25 kilos. of leaves are removed from each tree annually, and that this robs the soil of about 510 grammes of N, 172 grammes of P_2O_5, and 486 grammes of CaO, a loss which could be made good by about 100 kilos. of farm-yard manure to each tree. Menozzi (Chem. Soc. Abstr. 1899, ii. 682) found the dry matter of mulberry leaves to contain 5·0 p.c. of pentosans and 11·2 p.c. of cellulose.
H. I.

MULBERRY PAPER. The inner bark of *Broussonetia papyrifera* (Vent.) contains bast-fibres which are used in China and Japan for the preparation of a kind of paper, and in Polynesia for the manufacture of a fabric.

MULHOUSE BLUE *v.* Triphenylmethane colouring matters.

MUNDIC. The name given by the Cornish miners to iron pyrites. Similarly mispickel arsenical pyrites is known as 'arsenical mundic.'

MUNJEET or **MANJEET.** The *Rubia cordifolia* (Linn.) was formerly extensively cultivated in India, particularly in the mountainous districts, for the sake of the colouring matters contained in its stem or roots. In the Dárjéling district it occurs as a small climber common all over the hills, at elevations varying from 3000 to 7000 feet, but most abundant between 5000 and 6000 feet, and is found either creeping along the ground or climbing the trunks of trees in large festoons. In Bengal it would seem that the dye of munjeet is extracted mainly from the stem, and only occasionally from the root, as is the case in the North-Western Provinces and elsewhere in India. The munjeet of Bengal is apparently rather the *Rubia munjista* of Roxburgh than the *Rubia cordifolia.* This species of Roxburgh is, however, reduced to *Rubia cordifolia* in Hooker's Flora of British India. To prepare the dye the wood of the munjeet is first dried, then crushed and pounded, and then generally boiled with water, but sometimes merely left to steep in cold water. The solution obtained is of a deep red, and is used generally to dye coarse cotton fabrics, or the thread which is to be woven into such fabrics. Alum appears to be generally employed as a mordant, although myrabolans also are used in the Dárjéling district, and other astringents in the Maldah district. In the latter district munjeet is used in conjunction with iron salts to produce a deep purple, and in the Dárjéling district is mixed with indigo to form a maroon (McCann, Dyes and Tans of Bengal). The red and chocolates of East Indian chintzes were formerly entirely obtained from munjeet. The colours produced from munjeet are bright, but not so durable as those from ordinary madder, the inferiority being due, according to Stenhouse (Pharm. J. 13, 148), to the presence of purpurin and an orange dye munjistin (purpuroxanthin carboxylic acid). Runge, who examined the tinctorial power of munjeet, concluded that it contained twice as much available colouring matter as madder; but later experiments have shown that the colouring power is actually less. Stenhouse found that munjeet garancine has only half the colouring power of garancine made from Naples roots, but that munjeet yields (according to Higgin) from 52 to 55 p.c. of garancine, whereas madder yields only 30–33 p.c.

When madder was so much in vogue, munjeet was employed to some extent in this country, because it was considered that a good quality of this material contains as much colouring matter as madder, and could be applied by exactly the same methods.

The important colouring matter of munjeet is *purpurin*, and no alizarin is present in this root, and it is therefore interesting to note that whereas chay root contains alizarin, and munjeet purpurin, in madder both these substances exist together.

For the analysis of the phenolic constituents of munjeet, a modification of the method of Stenhouse, who first submitted this plant to examination, is to be recommended.

The ground dyestuff is digested with boiling alum solution for 5 hours, and the deep red extract treated with acid and allowed to cool. The red precipitate is collected, washed, and dried, and then extracted with boiling toluene (carbon disulphide was employed by Stenhouse), by which means the colouring matters pass into solution, and a resinous impurity remains undissolved. The colouring matters are now removed from the toluene by agitation with dilute potassium hydroxide solution, the alkaline liquid is acidified, and the precipitate collected, washed, and dried. In order to separate the constituents of this product it is extracted about 10 times with boiling dilute acetic acid, and the dark red residue consisting of *purpurin* is crystallised from alcohol.

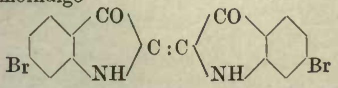
The earlier acetic acid extracts are mixed with hydrochloric acid, and the yellowish-red deposits are crystallised from alcohol. The product consists of orange-coloured leaflets, and is *purpuroxanthin carboxylic acid* or *munjistin*, as it was termed by Stenhouse, its discoverer, who first obtained it from munjeet. The properties of this compound have already been given in detail in the article upon Madder.

Munjeet has also been examined by Perkin and Hummel, who, in addition to the above constituents, detected the presence of a trace of *purpuroxanthin* (Chem. Soc. Trans. 1893, 63, 115).
A. G. P.

MUNTZ METAL *v.* Zinc.

MUREX *v.* Purple of the Ancients.

The Tyrian or antique purple was mainly obtained from shell-fish, especially from *Murex brandaris.* Friedländer (Monatsh. 1907, 28, 991; 29, 247) has isolated 1·4 grams of a pure purple dye from 12,000 specimens of *Murex brandaris*, and has shown that it is identical with 6:6′-dibromoindigo



(Sachs and Kempf, Ber. 1903, 36, 3303) *v.* Indigo, synthetic, and Punicin.

MUREXAN *v.* Uramil.

MUREXIDE, *ammonium hydrogen purpurate* $C_8H_8O_6N_6,H_2O$. The formation of a red residue when a solution of uric acid in nitric acid is evaporated to dryness, was first observed by Scheele in 1776, and forms the basis of the well-known *murexide test* for uric acid and compounds related thereto. In 1818 Prout (Ann. Chim. Phys. 11, 48) obtained the coloured principle in a crystalline form, and regarded it as the ammonium salt of a hitherto unknown acid, which he named *purpuric acid;* and by double decomposition prepared several other red purpurates. Liebig and Wöhler (Annalen, 1838, 26, 319) showed that the compound obtained by the action of mineral acids on ammonium purpurate, and regarded by Prout as the free acid, was in reality 'murexan' (afterwards identified by Beilstein with *uramil*), which, together with alloxan, form the chief products of decomposition of purpuric acid by mineral acids. These authors therefore gave the name of *murexide* to the compound, regarding it as having more of the nature of an acid amide than of a true ammonium salt. Subsequent work has, however, not justified this conclusion, since purpuric acid mixed with ammonium chloride can be obtained by the action of dry hydrogen chloride on murexide suspended in hot anhydrous acetic acid; it is an orange-red powder, and forms soluble salts with organic bases such as methylamine, ethylamine, pyridine, quinoline, and aniline (Möhlau and Litter, J. pr. Chem. 1906, [ii.] 73, 449).

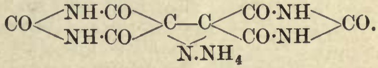
Preparation.—(1) From uric acid, by oxidising with nitric acid and subsequent treatment with ammonia or ammonium carbonate (Prout, *l.c.*; Liebig and Wöhler, *l.c.*; Kodweiss, Pogg. Ann. 19, 12; Fritzsche, Annalen, 1839, 32, 316).

(2) From alloxantin or alloxan by the action of ammonium salts in solution (Fritzsche, *l.c.*; Liebig, *l.c.*; Gregory, J. pr. Chem. [i.] 22, 374); or by passing dry ammonia over finely powdered alloxantin at 100° (Gmelin, Hand. f. Chem. 1856, iv. 195). According to Piloty and Finckh (Annalen, 1904, 333, 22), a yield of 80 p.c. of pure murexide can be obtained by adding 5 grams of alloxantin in 200 c.c. of water to a mixture of 25 grams of ammonium acetate in 100 c.c. water and 15 c.c. of 10 p.c. ammonia saturated with carbon dioxide; the solutions are mixed at 80° and the murexide crystallises out. The alloxantin may be replaced by a mixture of ammonium dialurate and alloxan. Hartley (Chem. Soc. Trans. 1905, 1791) prepared spectroscopically pure murexide by passing a stream of dry ammonia into finely-powdered alloxantin mixed with 100 times its weight of boiling absolute alcohol, for 3 hours or more. The precipitated anhydrous murexide is washed with absolute alcohol and dried at 100°, or in a vacuum.

(3) From uramil by oxidation with mercuric oxide in the presence of ammonia (Liebig and Wöhler, *l.c.*; Beilstein, Annalen, 1858, 107, 176); or by adding alloxan to a saturated solution of uramil in hot ammonia solution (Liebig).

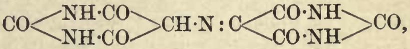
The formation of murexide by the interaction of aqueous solutions of alloxan and amino acids was first observed by Strecker (Annalen, 1862, 123, 363). The reaction has been more closely investigated by Piloty and Finckh (*ibid.* 1904, 333, 22), and by Hurtley and Wootton (Chem. Soc. Trans. 1910, 99, 288). According to the latter authors, the amino acid is oxidised by the alloxan to the next lower aldehyde with the elimination of carbon dioxide and ammonia; the alloxan is reduced to dialuric acid, which combines with the unchanged alloxan to form alloxantin, and this, with the ammonia, forms murexide. The red stain caused by alloxan on the skin is probably due to a similar reaction, and it is suggested that alloxan may prove a suitable reagent for the detection of amino acids.

Constitution.—Matignon (Ann. Chim. Phys. 1893, [vi.] 28, 347) regarded purpuric acid as the imino derivative of alloxantin and expressed the constitution of its ammonium salt, murexide, by the formula



$$\mathrm{CO}<\begin{matrix}\mathrm{NH{\cdot}CO}\\ \mathrm{NH{\cdot}CO}\end{matrix}>\underset{\mathrm{N.NH_4}}{\mathrm{C{-}C}}<\begin{matrix}\mathrm{CO{\cdot}NH}\\ \mathrm{CO{\cdot}NH}\end{matrix}>\mathrm{CO.}$$

Slimmer and Stieglitz (Amer. Chem. J. 1904, 31, 661) showed that the molecule of murexide could not have a symmetrical structure, since the ammonium dimethylpurpurates obtained by the condensation of 1:3-dimethyluramil and alloxan, and of uramil and 1:3-dimethylalloxan are isomerides and not identical as would be the case if Matignon's formula were correct. These authors therefore suggest that the constitution of purpuric acid is best expressed by the formula

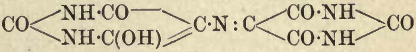


$$\mathrm{CO}<\begin{matrix}\mathrm{NH{\cdot}CO}\\ \mathrm{NH{\cdot}CO}\end{matrix}>\mathrm{CH{\cdot}N:C}<\begin{matrix}\mathrm{CO{\cdot}NH}\\ \mathrm{CO{\cdot}NH}\end{matrix}>\mathrm{CO,}$$

or in the hydrated form

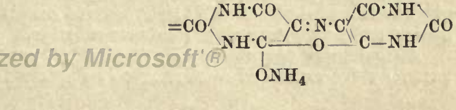
$$\mathrm{CO}<\begin{matrix}\mathrm{NH{\cdot}CO}\\ \mathrm{NH{\cdot}CO}\end{matrix}>\mathrm{CH{\cdot}NH{\cdot}C(OH)}<\begin{matrix}\mathrm{CO{\cdot}NH}\\ \mathrm{CO{\cdot}NH}\end{matrix}>\mathrm{CO,}$$

the salts being derived from the *pseudo* form of the acid

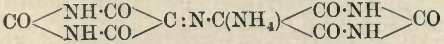


$$\mathrm{CO}<\begin{matrix}\mathrm{NH{\cdot}CO}\\ \mathrm{NH{\cdot}C(OH)}\end{matrix}>\mathrm{C{\cdot}N:C}<\begin{matrix}\mathrm{CO{\cdot}NH}\\ \mathrm{CO{\cdot}NH}\end{matrix}>\mathrm{CO.}$$

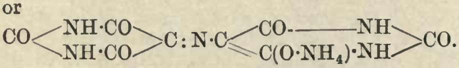
Piloty and Finckh (Annalen, 1904, 333, 22), having regard to the intense colour of murexide, assign to alloxan a quinonoid structure and to murexide that of a diureide oxazonium ammonium salt, and express its formation from uramil, alloxan, and ammonia by the following scheme



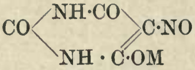
Möhlau and Litter (Ber. 1904, 37, 2686; J. pr. Chem. 1906, [ii.] 73, 449) represent murexide as a ketoimide having an unsymmetrical structure such as may be expressed by the formulæ



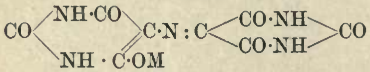
or



The second of these is identical with that proposed by Slimmer and Stieglitz (*l.c.*); and deduced by Hartley (Chem. Soc. Trans. 1905, 87, 1794) from a study of the action of alcoholic ammonia on alloxantin. Hantzsch and Robison (Ber. 1910, 43, 92) point out the correspondence between their formula for the coloured salts of violuric acid and the above formula for murexide



Violurate.



Purpurate.

the oxygen of the nitroso group of the violurate, being replaced by a malonylurea residue.

Murexide crystallises in short four-sided garnet-red prisms, with gold-green reflex. The anhydrous salt forms a brownish powder which assumes a green metallic lustre when rubbed. Its molecular heat of combustion is 736·7 cal. (Matignon, Ann. Chim. Phys. 1893, [vi.] 28, 346), it is sparingly soluble in cold, more readily so in hot water, insoluble in alcohol or ether. The absorption spectrum shows two absorption bands, one in the visible spectrum and one in the ultraviolet (Hartley, Chem. Soc. Trans. 1887, 199; 1905, 1805).

Solutions of murexide dye silk, wool, cotton, or leather red to purple shades in the presence of mercury salts, or orange to yellow shades in the presence of zinc salts, and at one time the compound was prepared on a commercial scale, as a dyestuff, from uric acid extracted from guano. The fugitiveness of the colours in the presence of even sulphurous acid, and the superiority of the aniline dyes have caused it to be entirely superseded.

In addition to murexide, the following salts of purpuric acid have been described: *sodium hydrogen salt* $C_8H_4NaO_6N_5$, dark brick-red solid; *potassium hydrogen salt* $C_8H_4KO_6N_5$, dark red microcrystalline solid, prepared like the other salts from murexide by double decomposition, also by oxidising dipotassium uramil with iodine in ethereal solution (Piloty and Finckh, Annalen, 1904, 333, 22); di-*potassium salt* $C_8H_3K_2O_6N_5$, dark blue solid, formed by dissolving the mono-potassium salt in potassium hydroxide (Fritzsche); *calcium salt* $C_8H_3CaO_6N_5$, dark green crystalline precipitate (Beilstein); *barium salt*

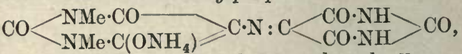
$$Ba(C_8H_4O_6N_5)_2,3H_2O,$$

dark green precipitate, very sparingly soluble in water (Fritzsche); *silver salt* $C_8H_4AgO_6N_5,1\frac{1}{2}H_2O$, bright purple powder; a solution of murexide gives a red precipitate with lead acetate and a bronze red precipitate with mercuric chloride.

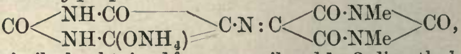
Methylamine purpurate $C_9H_{10}O_6N_6,H_2O$, prepared by the action of methylamine on alloxan and alloxantin, forms red microscopic rhombic crystals, loses H_2O at 110°, decomposes at 210°, and when heated with water yields 7-methyluramil, alloxantin, alloxan, and methylamine.

Ethylamine purpurate $C_{10}H_{12}O_6N_6,H_2O$ decomposes at 205° (Möhlau and Litter, J. pr. Chem. 1906, [ii.] 73 449).

Other derivatives of purpuric acid are: *ammonium*-1:3-*dimethylpurpurate*

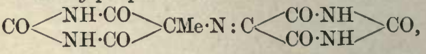


formed from 1:3-dimethyluramil and alloxan in the presence of ammonium carbonate, crystallises in small four-sided prisms, is slightly yellower in colour than murexide, and closely resembles its isomeride *ammonium* 1′:3′-*dimethylpurpurate*

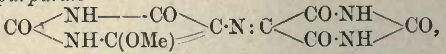


similarly obtained from uramil and 1:3-dimethyl alloxan.

5-*Methylpurpuric acid*



prepared from methyl iodide and anhydrous potassium purpurate; the isomeric O-4-*methylpurpurate*



obtained from methyliodide and silver purpurate is unstable (Slimmer and Stieglitz, Amer. Chem. J. 1904, 31, 661). M. A. W.

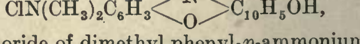
MUREXOÏN (*tetramethylmurexide ?*)

$$C_{12}H_{16}O_6N_6$$

is prepared by the action of air and ammonia on dry or moist amalic acid (tetramethylalloxantin) (Rochleder, J. 1850, 436; Brunn, Ber. 1888, 21, 514); or by treating desoxyamalic acid with bromine, and afterwards with ammonia (Fischer and Ach, Ber. 1895, 28, 2477). It forms cinnabar-red four-sided prisms reflecting a golden yellow light from two faces, it sublimes at 230°, and decomposes without previous fusion at a higher temperature. It is sparingly soluble in alcohol or water, forming deep purple-red solutions. It is decomposed on warming with hydrochloric acid, but the only product of the reaction that has been identified is dimethylparabanic acid (cholestrophan) (Brunn, *l.c.*). M. A. W.

MURIATIC ACID *v.* Chlorine.

MUSCARINE



the chloride of dimethyl phenyl-*p*-ammonium-β-hydroxynaphthoxazine obtained by the action of nitrosodimethylaniline hydrochloride on α-dihydroxyhaphthalene. A colouring matter introduced by Durand and Huguenin. Is a brownish-violet powder, sparingly soluble in cold water but readily soluble in hot water with a bluish-violet colour. Alkalis precipitate the base as a yellow-brown powder. Dyes cotton mordanted with tannin and tartar emetic a blue colour *v.* Oxazine colouring matters.

MUSCARINE *v.* Ptomaïnes.

MUSCOVADA. The unrefined brown or raw sugar of commerce *v.* Sugar.

MUSCOVITE or **MUSCOVY GLASS.** A term occasionally applied to mica (*q.v.*).

MUSHROOM, the name given to various species of edible fungi. Species of *Agaricus*, *Lactarius*, and *Coprinus*, and popularly even of *Boletus*, *Polyporus*, and *Morchella*, furnish most of the edible mushrooms, although some species of the same genera are poisonous. The following analyses, chiefly from König, are of edible fungi :—

	Water	Protein	Fat	Mannitol	Glucose	Other N-free extract	Crude fibre	Ash
Psalliota (Agaricus) campestris (Quél.) . . .	89·7	4·9	0·2	0·4	0·7	2·5	0·8	0·8
Cantharellus cibarius (Fries.)	91·4	2·6	0·4	0·7	0·3	2·8	1·0	0·7
Boletus edulis (Bull.) .	87·1	5·4	0·4	0·4	2·2	2·6	1·0	1·0
,, *luteus* (Linn.) .	92·6	1·5	0·3	2·0		2·0	1·2	0·5
Lactarius deliciosus (Fries.)	88·8	3·1	0·7	2·2		0·9	3·6	0·7
(?) *Polyporus ovinus* (Schäff.)	91·6	1·0	0·6	2·6		1·7	1·8	0·7
Morchella esculenta (Pers.)	90·0	3·3	0·4	0·7	0·1	3·7	0·8	1·0
Coprinus comatus (Pers.)	94·3	2·0	0·1	2·9			0·2	0·5

Mushrooms are liable to considerable variation in composition according to the age at which they are gathered and to the character of the soil or other medium on which they are grown. The nitrogenous matter and crude fibre are the most variable constituents. Owing to the very large proportion of nitrogenous substances in the dry matter, mushrooms are usually considered to be highly nutritious, but, according to the investigations of Saltet (1885), Uffelmann, Strohmer (1886), and Mendel (1898), the nitrogenous matter has a low digestibility, about 33 p.c. of the pure proteids usually being indigestible. Of the total nitrogen, from 60–80 p.c. exists as proteid, 6–13 p.c. as amino acids, 11–17 p.c. as acid amides, and about 0·2 p.c. as ammonia. Choline occurs to the extent of 0·01 p.c. in *Cantharellus cibarius*, 0·015 p.c. in *Psalliota campestris*, and 0·0056 p.c. in *Boletus edulis* (Polstorff, Chem. Zentr. 1909, ii. 2014).

Lietz (Zeitsch. Nahrungm. Unters. Hygiene u. Waarenk. 1893, 7, 223) found that 19 varieties of mushrooms contained, in the dry matter, from 0·08 to 1·64 p.c. lecithin, and from 0·11 to 3·08 p.c. of combined phosphorus pentoxide.

Gilson (Compt. rend. 1895, 120, 1000) obtained from various species, a substance identical with chitin, the horny external covering of insects. The fat consists of phytosterol and a dark brown oil, about half of which consists of free fatty acids, the remainder being neutral fat (Opitz, Arch. Pharm. 1895, 229, 290).

The non-nitrogenous extract of mushrooms consists chiefly of mannitol, trehalose (or mycose), inulin and pentosans. According to Bourquelot (Compt. rend. 108, 568) mannitol is largely produced from the trehalose during the after-ripening and drying, whilst the trehalose itself is formed from some dextrin-like carbohydrate, which constitutes the tissue of the fungus. The proportion of pentosans is small; Wittmann found about 0·1 p.c., whilst Menozzi (Chem. Soc. Abstr. 1899, ii. 683) found, in the dry matter of *Boletus edulis*, 1·9 p.c.

The ash varies in amount and composition; it forms from 5 to 9 p.c. of the dry matter, and usually contains about 50 p.c. K_2O, 30 p.c. P_2O_5, with smaller quantities of lime, magnesia, soda, silica, and chlorine. Alumina is often present, in some cases to the extent of 5–7 p.c. A poisonous fungus, *Amanita muscaria* (Pers.), contains an isomeride of betaine, *muscarine* $CH(OH)_2CH_2{\cdot}N(CH_3)_3OH$, which acts like a ptomaine. One of the edible fungi *Gyromitra* (*Helvella*) *esculenta* (Fries.) in the fresh state, contains a poisonous constituent, helvellic acid $C_{12}H_{20}O_7$ (Böhm and Külz, Archiv. experimentelle Path. 19, 403). H. I.

MUSK. *Moschus.* (*Musc*, Fr.; *Moschus*, Ger.) Musk consists of the dried secretion of the preputial follicles of the musk deer, *Moschus moschiferus* (Linn.), which inhabits the mountainous districts of Central Asia. *Cf.* Pereira (Mat. Med. [iii.] 2, 2251). An analysis by Geiger and Reimann, quoted by Gmelin (Handb. Chem 2, 1449), shows that it contains cholesterol together with fatty, waxy, and albuminous substances. The well-known odour of musk is due to the presence of a ketone *muskone*. When distilled with steam crude musk yields 1·4 p.c. of a dark brown oil, about half of which distils at 200°–210° under 9 mm. pressure. Muskone $C_{15}H_{28}O$ or $C_{16}H_{30}O$ is obtained by treating the distillate with alcoholic potassium hydroxide and distilling the product at 160°–164° under 7 mm. pressure. It is a colourless, viscid oil, boils at 142°–143° under 2 mm., or with slight decomposition at 327°–330° under 752 mm. pressure. It is sparingly soluble in water, readily so in alcohol. The *oxime* melts at 46°. The *semicarbazone* melts at 133°–134°, and is odourless, but gives an odour of musk when heated with dilute sulphuric acid. The fraction of the oil boiling at 65°–106° under 7 mm. pressure obtained in the preparation of muskone has an unpleasant odour and gives the pine-wood reaction for pyrrole (Walbaum, J. pr. Chem. [ii.] 73, 488). Besides its use as a perfume, musk is employed in medicine as a nervous stimulant.

Compounds having the odour of musk have been prepared synthetically, but such substances have an entirely different chemical structure. These are, however, not poisonous, and are largely substituted in the cheaper forms of perfumery for the expensive natural product. The musk substitutes at present known are trinitro-*meta*-tertiarybutyltoluene and the corresponding compounds obtained from the homologues of toluene, and the dinitro derivatives of the ketones which are formed by the interaction of acyl chlorides on butyl derivatives of toluene and homologues (Baur, Compt. rend. 111, 238; Ber. 24, 2832; *ibid.* 31, 1344). A. S.

MUSK, ARTIFICIAL *v.* Butyl.

MUSK-ROOT *v.* Oleo-resins.

MUSTARD. Mustard is derived from the seed of an annual cruciferous plant which grows wild or is cultivated in Great Britain, and throughout Europe, the United States, and many other countries. It grows to a height of from 3 to 6 feet, has yellow flowers and lyrate leaves.

Two varieties are commonly used, *Sinapis alba* (Linn.) or white mustard, and *Brassica nigra* (Koch) or black mustard. These only are recognised by the British Pharmacopœia. The seeds of the former are spherical, 2 to 3 mm. in diameter, of a buff colour outside, with a finely granular surface. Those of black mustard are from 1 to 1·5 mm. in diameter, have a dark brown reticulated surface but are yellow within. Indian mustard is *Brassica juncea* (Coss.), and the Russian sarepta mustard is *B. Besseriana* (Andr.). The Dakota (wild) mustard or Charlock is *B. sinapistrum* (Boiss) (or *Sinapis arvensis* (Linn.)).

Preparation.—The ground farina is usually a mixture of the two varieties, and is prepared by crushing the seeds, winnowing out the husks, which form an obstacle to fine grinding, and sifting. A large proportion of the fixed oil is very generally removed by hydraulic pressure.

Composition.—The main constituent of the seed is the fixed oil, which is tasteless and nearly odourless, and is employed for mixing with other illuminating oils and sometimes for culinary purposes. This occurs in both varieties of the seed. The valuable and characteristic properties of mustard are due to the volatile oil, allyl *iso*-thiocyanate C_3H_5NCS, which, however, is not present in the mustard as such, but is formed by the action of water and an enzyme, *myrosin*, which is present in both kinds of seed, on a glucoside, potassium myronate $KC_{10}H_{18}NS_2O_{10}$, which is only found in the black variety. White mustard also contains a glucoside, *sinalbin* ($C_{30}H_{42}N_2S_2O_{15}$), which on hydrolysis forms an acrid pungent oil, *acrinyl iso-thiocyanate* (C_7H_7ONCS), which, however, is only slightly volatile with steam. Mustard seeds contain mucilage but no starch.

Fairly complete analyses by Piesse and Stansell gave the following results—

TABLE I.

—	Whole seed		Farina	
	White	Brown	White	Brown
Moisture . .	8·66	8·52	6·04	4·83
Fat . . .	26·53	25·54	35·16	37·05
Cellulose . .	9·69	9·01	5·79	2·80
Sulphur . .	0·96	1·28	1·27	1·43
Nitrogen . .	4·51	4·38	4·73	4·75
Proteins . .	28·21	26·50	29·56	28·71
Myrosin & albumin	4·91	5·24	6·70	6·46
Soluble matter .	26·83	24·22	33·94	31·94
Volatile oil . .	0·07	0·47	0·03	1·44
Ash, total . .	4·63	4·98	4·28	4·93
Ash, soluble . .	0·65	1·11	0·44	0·92
Potassium myronate	—	1·69	—	5·15

Mustard is chiefly used as a condiment, but is also employed in medicine internally as an emetic and externally as a rubefacient and counter-irritant. The volatile oil is also official in the British Pharmacopœia, and is a powerful vesicant.

Adulteration.—Practically the only adulteration to which mustard is subject in this country is the addition of foreign starches, accompanied not unfrequently by turmeric or aniline dyes to restore the colour. Cayenne pepper is also said to be added to increase the pungency.

The addition of starch is defended on the ground that it confers better keeping properties on the preparation and prevents it caking. Provided the addition is notified and the amount moderate there is no objection; but in England, at all events, it is quite unnecessary.

In inferior grades traces of starch may be present owing to the accidental admixture of starch-bearing seeds during the gathering of the crop.

The removal of the fixed oil has been regarded by some as an adulteration, and at least one successful prosecution has been recorded in this country (British Food Journal, 1903, 278). The practice, however, is very general, especially on the Continent, and little can be said against it. The fixed oil adds nothing to the flavour, and is certainly liable to become rancid.

The admixture of ground hulls in excessive proportion has also been recorded.

In order to comply with the British Pharmacopœia definition both the black and the white varieties of mustard should be present, though no directions are laid down as to the proportions of each. The judicious mixture of the two kinds is advantageous in that, while the volatile oil, to which the characteristic aroma is mainly due, is only yielded by the black mustard, the latter is somewhat deficient in myrosin, and this deficiency is supplied by the white variety.

Detection of adulteration.—Added starch is detected by the microscope. If much is present the addition of iodine solution will stain the sample blue. As, however, the volatile oil absorbs iodine rapidly, it is desirable in the case of small quantities of starch, to prevent the formation of the volatile oil by previously boiling with potassium iodide (Amer. J. Pharm. 1898, 70, 433). The determination of the starch may be effected approximately by microscopical comparison of the sample with mixtures of mustard containing known weights of the particular starch ascertained to be present.

Methods based on the conversions of the starch into sugar and the estimation of the reducing power are not very satisfactory, owing to the presence of other reducing substances not derived from the starch. To obviate this as far as possible the conversion should be by diastase, and should be preceded by extraction with ether and 10 p.c. alcohol.

A method in which the starch is weighed as such is that of Kreis (Chem. Zeit. 1910, 1021), in which the substance is digested with alcoholic potash, the insoluble matter, after washing with alcohol, is heated with dilute sodium hydroxide, and the solution diluted and filtered and a portion of the filtrate treated with an equal volume of 95 p.c. alcohol. The precipitate is allowed to settle (aided by a centrifuge), filtered off, washed with 50 p.c., then with 95 p.c. alcohol, finally with ether and dried and weighed. An allowance of 3 p.c. should be made for non-starchy substances in the precipitate.

The proportion of added starch may also be calculated, in the absence of other adulterants, from the reduction in the percentage of nitrogen in the fat and water free sample. Methods based on the determination of the fixed oil are obviously unreliable.

Turmeric is detected by the microscope or by soaking a strip of filter paper in an alcoholic extract of the sample, then in a solution of borax, and finally acidifying with dilute (2 p.c.) hydrochloric acid. When dry the paper will assume a rose-red colour, which turns deep blue with ammonia or olive-green with dilute caustic potash.

The presence of an undue proportion of the hulls is at once apparent on microscopic examination, the most characteristic structures being the cellular epidermal layer with its mucilage, the sub-epidermal cells with their thickened angles in the case of white mustard; also the palisade cells, yellow and not reticulate in white mustard, and brown and reticulated in the black variety. As will be seen from Table II. the indications of the microscope may be confirmed by chemical analysis, the total nitrogen, fibre, and copper reducing power, after treatment with diastase, being the most useful determinations.

Table II.—Analysis of Mustard (Leach).

—	Flour					Hulls						Seeds				
	Black			White		Black		White				Black		White		
	English	Californian	German	German	Californian	English		English		Californian	German	Bari	Californian	English	Dutch	German
Moisture . .	5·55	7·23	9·50	7·47	5·09	6·83	8·67	6·46	5·36	9·12	8·46	5·88	6·49	6·43	5·93	6·69
Total ash . .	5·58	4·90	5·25	4·73	4·69	5·03	4·43	4·56	4·65	4·59	4·66	4·07	3·84	4·37	4·83	4·34
Water soluble ash	0·27	0·23	0·09	0·18	0·22	0·95	1·26	2·33	1·91	1·78	1·80	0·46	0·45	0·52	0·73	0·63
Ash insol. HCl .	0·08	0·13	0·50	0·35	0·29	0·14	0·23	0·05	0·22	0·05	0·04	0·22	0·21	0·16	0·33	0·56
Fat (ether extract)	17·46	20·64	16·28	12·65	25·95	13·81	10·51	7·03	6·63	7·79	6·17	37·81	35·39	27·45	30·84	27·19
Volatile oil .	3·98	4·67	3·09	0·00	0·00	2·26	1·83	0·00	0·00	0·00	0·00	2·76	2·91	0·00	0·00	0·00
Alcohol extract .	25·31	19·22	21·98	24·21	20·78	14·21	14·15	11·07	10·46	8·51	8·07	13·70	14·26	16·31	14·98	17·75
Total nitrogen .	6·37	6·75	7·13	7·44	6·21	3·89	4·04	3·03	3·22	3·60	2·90	4·10	4·49	3·96	4·12	5·09
Crude fibre .	3·28	2·27	2·45	1·87	2·21	10·90	11·34	16·46	17·69	16·08	18·95	4·41	4·21	4·95	6·53	4·87
Reducing matters (acid conversion)	11·89	4·87	5·63	6·12	5·75	9·90	14·05	20·40	20·00	19·90	17·35	7·34	6·94	8·42	10·06	9·35
Reducing matters (diastase method)	0·71	0·23	0·22	0·23	0·00	1·20	3·56	6·11	4·21	3·74	2·91	1·76	1·78	0·92	1·82	1·45

Cayenne pepper may be detected by the pungent taste of the residue obtained by evaporating the alcoholic extract on the water-bath, and the acrid fumes which it yields on gentle ignition.

The presence of unofficial species of mustard which are more likely to occur in foreign brands is almost entirely a matter of microscopical examination (*v.* Winton, Microscopy of Vegetable Foods; also Pammel, Amer. Monthly Micr. Journal, 17, 206, and 213; Pharm. J. 1905, [74] 719).

As the efficiency of mustard for medicinal purposes depends on the proportion of volatile mustard oil, its determination is of some importance. Roeser's method (J. Pharm. Chim. 1902, 361) is carried out as follows: 5 grammes of the sample are mixed with 60 c.c. of water and 15 c.c. of 60 p.c. alcohol, allowed to stand for 2 hours and distilled into 10 c.c. of ammonia until two-thirds of the liquid has passed over; 10 c.c. of N/10 silver nitrate are added, and after standing for 24 hours the solution is diluted to 100 c.c. To 50 c.c. of the filtered solution are added 5 c.c. of N/10 potassium cyanide, and the excess of cyanide determined by titration with standard silver nitrate, using slightly ammoniacal 5 p.c. potassium iodide as indicator. The percentage of volatile oil is obtained by multiplying the number of c.c. of silver nitrate used up by the oil by 0·6274 (*v.* also German Pharmacopœia). (For proportion of volatile oil yielded by various kinds of mustard oil, *see* Ann. Falsi. 1909, 2, 215, and 12, 372.)

Standards.—United States Dept. of Agriculture. Mustard seeds should be those of *S. Alba*, *B. Nigra*, and *B. Juncea*. Ground mustard should consist of powdered mustard seeds with or without a portion of the hulls having been removed and from which a portion of the fixed oil has been expressed. Standard ground mustard is mustard yielding not more than 2·5 p.c. of starch by the diastase method and not more than 8 p.c. of ash. Leach (J. Amer. Chem. Soc. 1904, 26, 1210) suggests ash and starch as above, crude fibre not exceeding 5 p.c., nitrogen not less than 8 p.c. C. H. C.

MUSTARD OIL *v.* Oils, Essential.

MYCOSE, TREHALOSE, *v.* Carbohydrates.

MYDROL. Trade name for iodomethylphenyl pyrazolone. A white, odourless powder, with a bitter taste, soluble in water (*v.* Synthetic drugs).

MYOSIN *v.* Proteins.

MYRICA WAX (MEXICAN) *v.* Waxes.

MYRICA NAGI (Thunb.). This is an evergreen tree belonging to the *Myricaceæ* met with in the sub-tropical Himalaya from the Ravi eastwards, also in the Khasia mountains, the Malay Islands, China, and Japan. It is the box-myrtle or *yangmae* of China, and is synonymous with *M. sapida* (Wall.), *M. rubra* (Sieb. and Zucc.), and *M. integrifolia* (Roxb.). The bark is occasionally used as a tanning agent, and is said to have been exported from the North-West Provinces to other parts of India to the extent of about 50 tons per annum. In Bombay it is met with under the name of *kaiphal*, and in Japan as *shibuki*.

Myricetin $C_{15}H_{10}O_8,H_2O$, the colouring matter can be isolated from an aqueous extract of the plant by a similar method to that which is serviceable for the preparation of fisetin (see article Young Fustic) but is more readily obtained in quantity from the Japanese commercial 'shibuki' extract (Perkin and Hummel, Chem. Soc. Trans. 1896, 69, 1287; and Perkin, *ibid.* 1902, 81, 204).

The extract is treated with ten times its weight of hot water to remove tannin, and when cold the clear liquid is decanted off, the residue washed twice in a similar manner, and well drained. The product is extracted with boiling alcohol, and the solution evaporated until crystals commence to separate. On cooling these are collected (the filtrate A being reserved), and washed first with strong and then with dilute alcohol. A complete purification is best effected by converting the colouring matter into its acetyl derivative, and when pure hydrolysing this in the usual manner. Myricetin crystallises in yellow needles, melting at about 357°, and closely resembles quercetin in appearance. Dilute potassium hydroxide solution dissolves myricetin with a green colouration, which, on standing in air, becomes first blue, then violet, and eventually brown coloured. Alcoholic lead acetate gives an orange-red precipitate, and ferric chloride a brown-black colouration.

With mineral acids in the presence of acetic acid the following compounds which crystallise in orange-red needles have been prepared:

Myricetin sulphate $C_{15}H_{10}O_8 \cdot H_2SO_4$, *myricetin hydrochloride* $C_{15}H_{10}O_8 \cdot HCl$, *myricetin hydrobromide* $C_{15}H_{10}O_8 \cdot HBr$, and *myricetin hydriodide* $C_{15}H_{10}O_8 \cdot HI$. Alcoholic potassium acetate yields monopotassium myricetin $C_{15}H_9O_8K$. Bromination in the presence of alcohol gives *tetrabrom-myricetin ethyl ether* $C_{15}H_5O_8Br_4Et$, colourless needles, m.p. about 146° (Perkin and Phipps, *ibid.* 1904, 85, 62), and this is analogous to the behaviour of morin under similar circumstances. By the action of bromine in acetic acid *tetrabrom-myricetin* $C_{15}H_6O_8Br_4$, brown-red needles, m.p. 235°–240° is produced.

When fused with alkali myricetin gives *phloroglucinol* and *gallic acid. Hexa-acetyl myricetin* $C_{15}H_4O_8(C_2H_3O)_6$, colourless needles, m.p. 211°–212°; *hexabenzoyl myricetin*

$$C_{15}H_4O_8(C_7H_5O)_6,$$

colourless needles; *myricetin pentamethyl ether* $C_{15}H_5O_3(OCH_3)_5$, pale yellow needles, m.p. 138°–139°; *acetylmyricetin pentamethyl ether* $C_{15}H_4O_3(OCH_3)_5C_2H_3O$, colourless needles, m.p. 167°–170°; *myricetin hexamethyl ether,*

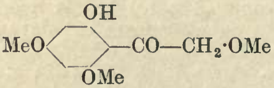
$$C_{15}H_4O_2(OCH_3)_6,$$

colourless needles, m.p. 154–156; and *myricetin hexaethyl ether* $C_{15}H_4O_2(OC_2H_5)_6$, almost colourless needles, m.p. 149°–151°, have been prepared.

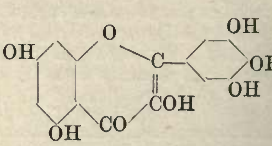
Myricetin dyes mordanted woollen cloth the following shades, which are practically identical with those given by quercetin:

Chromium.	*Aluminium.*	*Tin.*	*Iron.*
Red-brown.	Brown orange.	Bright red orange.	Olive black.

On digestion with alcoholic potash at 170° myricetin pentamethyl ether, gives *gallic acid trimethyl ether* and *phloroglucinol monomethyl ether*, whereas myricetin hexaethyl ether gives *gallic acid triethyl ether* and *phloroglucinol diethyl ether.* With boiling alcoholic potash myricetin hexamethyl ether gives gallic acid trimethyl ether and 2-*hydroxy-fisetol trimethyl ether* (Perkin, Chem. Soc. Trans. 1911, 100, 1721)



Myricetin hexaethyl ether behaves similarly with production of gallic acid triethyl ether and 2-*hydroxy-fisetol triethyl ether,* prismatic needles, m.p. 96°–97° (Perkin and Wilkinson, *ibid.* 1902, 81, 590). Myricetin is therefore a *hydroxyquercetin,* and possesses the following constitution:



Myricitrin $C_{21}H_{22}O_{13},H_2O$, the glucoside, is present in the alcoholic filtrate A, from the crude myricetin, from which it separates on standing. The crystals are collected, washed first with alcohol, then with dilute alcohol, crystallised from water, from alcohol, and finally from water. Myricitrin forms pale yellow, almost colourless, leaflets, melting at 199°–200°, and is soluble in alkalis with a pale yellow tint. Aqueous lead acetate gives an orange-yellow precipitate, and alcoholic ferric chloride a deep greenish-black colouration. In appearance it cannot be distinguished from quercetin and the shades given by the two substances on mordanted woollen cloth are practically identical.

Chromium.	*Aluminium.*	*Tin.*	*Iron.*
Full brown yellow.	Full golden yellow.	Lemon yellow.	Brown olive.

When hydrolysed with dilute sulphuric acid myricitrin yields rhamnose and myricetin, according to the equation

$$C_{21}H_{22}O_{13}+H_2O=C_{15}H_{10}O_8+C_6H_{14}O_6$$

and is analogous to quercitrin which in a similar manner gives rhamnose and quercetin. In addition to myricetin the *Myrica nagi* contains a trace of a glucoside of second colouring matter, which is probably *quercetin.*

The dyeing properties of myrica bark are generally similar to those of other yellow mordant dyestuffs. On wool with chromium mordant it gives a deep olive-yellow, and with aluminium a dull yellow, similar to the colours obtained from quercitron bark, but much fuller; with tin mordant it gives a bright red-orange, redder in hue than that given by quercitron bark; with iron mordant it gives a dark greenish olive like that obtained from quercitron bark but again fuller.

On cotton with aluminium and iron mordants it dyes colours which are more similar to those obtained from old fustic than from quercitron bark. Some specimens of myrica bark are exceedingly rich in colouring matter, and a sample examined by Hummel and Perkin (J. Soc. Chem. Ind. 1895, 14, 458) possessed much stronger dyeing power than old fustic.

OTHER SOURCES OF MYRICETIN.

Sicilian sumach the leaves of the *Rhus Coriaria* (Linn) contain myricetin, probably as glucoside (Perkin and Allen, *ibid.* 69, 1299). This colouring matter also exists in Venetian sumach *R. cotinus* and this is interesting, because the wood of this tree constitutes 'young fustic,' and contains fisetin. Among other plants myricetin has been isolated from the *Myrica Gale* (Linn), the leaves of *Pistacia Lentiscus* (Linn.), the leaves of the logwood tree *Hæmatoxylon campechianum* (Linn), and in conjunction with quercetin in the leaves of the *Coriaria myrtifolia* (Linn.), and the *Rhus Metopium* (Linn.).

MYRICIN. The more difficultly soluble portion of beeswax, consisting mainly of myricyl palmitate *v.* WAXES.

MYRICYL ALCOHOL *v.* WAXES.

MYRISTIC ACID $C_{13}H_{27}\cdot COOH$, discovered by Playfair in nutmeg butter, from *Myristica moschata* (Annalen, 37, 155); is found also in otoba fat from *M. otoba* (Görgey, *ibid.* 66, 314); in Dika bread (Oudemans, J. 1860, 322); in cocoa-nut oil; in butter; in the oil from quince seeds (Hermann, Arch. Pharm. 237, 367), and in wool fat (Darmstädter and Lifschütz, Ber. 1896, 620; 1898, 97), and may be obtained by melting stearolic acid with potash. It crystallises in needles, m.p. 53·8°, b.p. 121°–122° (0 mm.) and 250·5° (100 mm.), sp.gr. 0·8622 at 53·8°/4°.

Trimyristin or *trimyristil glyceride*

$$C_3H_5(C_{14}H_{27}O_2)_3$$

in which form myristic acid occurs in the various *Myristica* fats, crystallises from ether in needles, m.p. 55°.

MYRISTICA FATS comprise a number of fats belonging to the family of *Myristicaceæ.* They are all characterised by a preponderant proportion of myristin and hence by high saponification values. Some of these fats, like ochoco fat, consist almost entirely of myristin. The following fats—arranged, as far as is possible at present, in the order of the iodine values—include the better known members of this group: (*a*) nutmeg butter, mace butter; (*b*) Papua nutmeg butter; (*c*) fat from *Myristica malabarica*; (*d*) Kombo fat; (*e*) fat from *Myristica canarica*; (*f*) fat from *Myristica guatemalensis*, 13·8 p.c.; (*g*) Ucuhuba fat, Bicuhyba fat; (*h*) Ochoco fat.

In addition to the foregoing members there must be also included in this group the fats from: (1) *Myristica otoba* (Humb. and Bonp.), which yields the commercial otoba fat or otoba wax; (2) *Virola sebifera* (Aubl.), a fat used in Guiana in the manufacture of soaps and candles; (3) *Myristica ocuba* (Humb. and Bonp.), known commercially as ocuba wax, used in Para as a candle-making material; (4) *Virola Micheli* (Heckel), occurring in French Guiana; (5) *Staudtia kamerunensis* (Warb.).

(*a*) **Nutmeg butter,** mace butter, is obtained from the seeds of *Myristica officinalis* (Linn.) (*S. moschata* [Thunb.]. *S. fragrans* [Houtt.]), a tree growing wild on the islands of the Indian Archipelago, notably Celebes, Sumatra, Java, Molucca, and the Banda Islands. The tree (or at least varieties thereof) is also cultivated in Ceylon, in the West Indies, Brazil, and Guiana. The pericarp of the seed yields the arillus (mace) which is used in pharmacy, as a condiment for culinary purposes, and for the preparation of the ethereal oil contained in it. Formerly the small, as also the worm-eaten, rejected nuts which could not be exported were worked up for mace butter on the islands of the Indian Archipelago. The nuts were ground to a coarse meal, filled into sacks, and steamed for about 6 hours over boiling-pots. The sacks were then placed in a strong press and subjected to pressure. The butter so obtained represented a brownish mass. This was exported in the shape of bars (resembling soap bars) wrapped in cocoa-nut tree leaves (hence these bars were termed 'soap of Banda'). At present mace butter is chiefly obtained in European works (Holland, Germany) where the nuts are powdered and expressed when hot. The fat is also prepared in small quantities by extraction with light petroleum or common ether, in pharmaceutical laboratories.

The world's annual production of nutmegs does not exceed 1500 tons. Only a small quantity is used in the manufacture of nutmeg butter, so that the price of the fat is somewhat high. The seeds contain 38–40 p.c. of fat. Nutmeg butter has the consistence of soft tallow, is of a yellowish colour, and has the strong taste and odour of nutmegs.

The commercial fat varies considerably in composition. It contains from 4 to 10 p.c. of an ethereal oil (hence its saponification value does not exceed 190, and falls to as low a figure as 154) and contains chiefly trimyristin, in addition to a liquid fat and free fatty acids.

Cold alcohol dissolves the liquid fat, the free fatty acids, and the ethereal oil (unsaponifiable matter), leaving about 45 p.c. undissolved. The undissolved portion yields, on crystallisation from ether, pure trimyristin, melting at 55°.

Boiling alcohol dissolves nutmeg butter almost completely. The solubility in alcohol is not only due to the high percentage of free fatty acids contained in the commercial samples, but also to the ready solubility of myristin itself in alcohol.

Investigation of genuine mace butter obtained from Ceylon nutmegs by Power and Salway (Chem. Soc. Trans. 1907, 1653) afforded the following composition of the specimen examined:

Essential oil	12·5 p.c.
Trimyristin	73·0 ,,
Oleic acid, as glyceride . .	3·0 ,,
Linolenic acid, as glyceride .	0·5 ,,
Formic, acetic, and cerotic acids (very small amounts) . .	—
Unsaponifiable matter . .	8·5 ,,
Resinous material . . .	2·0 ,,
	99·5 ,,

The unsaponifiable matter consisted of a substance of the formula $C_{18}H_{22}O_5$ (amounting to about 5 p.c. of the expressed oil) and some myristicin $C_{11}H_{12}O_3$ and a very small amount of alcohol $C_{20}H_{34}O$, melting at 134°–135°. This alcohol is described as a 'phytosterol;' it differs from the ordinary phytosterol (sitosterol) by its different chemical composition, although it has the same melting-point.

Owing to the proportion of ethereal oil, which the genuine mace butter contains, the refractive index is very high. Various specimens examined in the butyro-refractometer indicated from 77·5 to 85 scale divisions. The iodine value varied from 77 to 80, the Reichert-Meissl value was 4·1–4·2, and the melting point only 25°–26°.

(*b*) **Papua nutmeg butter.** In consequence of the large demand for mace butter (nutmeg butter), this butter is frequently substituted by fats from other species of *Myristica*. Recently Papua nutmeg butter, the fat from *Myristica argentea* (Warb.) from the so-called 'Papua nutmeg,' which grows wild in Dutch New Guinea is substituted for genuine mace butter. Papua butter chiefly differs from genuine mace butter in that it contains no ethereal oil.

(*c*) **Fat from Myristica malabarica** (Lam.) is obtained from the seeds of *Myristica malabarica*, a tall evergreen tree growing in the forests of Konkan, Kanara, Malabar, and Travancore. The seeds contain 32 p.c. of shells, and yield 40·76 p.c. of fat and resins. The mace from these seeds differs entirely from that of the genuine mace in that it contains no ethereal oil. These seeds, sold as 'Bombay seeds' ('Kaiphal') have been frequently confounded with the genuine seeds from *Myristica officinalis*. The fat from the kernels of 'Bombay seeds' differs entirely from the fat from *Myristica officinalis*, for its saponification value is about 190; it melts at 31°, has an iodine value of 50·4, and a Reichert-Meissl value of 1·1 only. In the butyro-refractometer it only indicates 48–49 scale divisions at 30°.

(*d*) **Kombo fat, kombo butter** is obtained from the seeds of *Myristica angolensis* (Welw.), *Pycnanthus Kombo* [Baillon] (Warb.). This tree is widely distributed in the Gaboon (known there as 'arbre à suif du Gabon,') in the Congo, Angola, and in Southern and Northern Nigeria. The fruit breaks up easily into two thick hard pieces of husk and an inner nut covered with a false arillus; hence the seeds which are frequently mistaken for nutmegs can be easily differentiated from official nutmegs. The saponification value of a specimen (determined in the Imperial Institute) was 183, the iodine value 33·7. The numbers refer to a fat refined from crude fat by treatment with alkali in order to remove the fatty acids. The original crude fat had the iodine value 65·4, and the saponification value 275, in the presence of about 14 p.c. of fatty acids.

(*e*) The seeds of **Myristica canarica** are derived from the 'candle nut tree,' growing in India on the Western Ghats, from the Konkan southwards. The entire seeds yield 49·4 p.c. of fat; the mace, 54·6 p.c. of fat; the kernels separated from the shells furnish 64·76 p.c. of fat. The fat examined by D. Hooper (Agric. Ledger, 1907, No. 3) was light brown and crystalline, and gave, in the cold, with strong sulphuric acid a carmine-red colour. The saponification value was 215·02, the iodine value 26·64. The proportion of myristic acid amongst the fatty acids is stated to be about 70 p.c. Possibly identical with the fat last named is the fat from *Myristica surinamensis* (Roland) (*Virola surinamensis* [Warb.]), and perhaps also the fat from *Virola guatemalensis* (Warb.), obtained from 'wild nutmegs,' which do not contain an ethereal oil. These are occasionally imported into this country under the name 'oil nuts,' from Africa, as also from South America. The iodine value of a specimen of fat from *V. guatemalensis* ('African oil nut') examined by Grimme was 13·8, and its saponification value 244, and the proportion of unsaponifiable matter 1·13 p.c.

(*g*) **Ucuhuba fat, Urucaba fat, Bicubyba fat** is obtained from the nuts of *Myristica* (*Virola*) *bicuhyba* (Humb.). It is stated that the fat from *Virola bicuhyba* is usually mixed in Brazil with that from *Myristica officinalis*, but genuine specimens submitted to the author do not bear this out. Owing to the crude method employed in its preparation, the fat brought into the market is yellowish-brown, and has an aromatic odour (due to a small quantity of an ethereal oil), recalling that of coco-nut oil. Ucuhuba fat consists of myristin and olein (about 20 p.c.), small quantities of an ethereal oil, of a resinous substance, and of a wax-like compound: The resinous substance is soluble in ether, hot alcohol, light petroleum and chloroform. Genuine specimens examined in the author's laboratory melted from 35°–44·7°, had the saponification value 218·8, the iodine value 18·5, Reichert-Meissl value 2·68, lactones 3·15 p.c., unsaponifiable matter 3·05 p.c., and insoluble fatty acids 89·37 p.c..

(*h*) **Ochoco fat** is contained in the seeds of *Scyphocephalium ochocoa* (Warb.), a tree indigenous to the west coast of Africa. From a description published by Pierre it appears that the nuts have no arillus, and that they are non-dehiscent. The specimens examined by the author were identified by the Kew authorities as the kernels of *Scyphocephalium ochocoa* The average weight of the kernels is 10 grams; the smallest weighing 5 grams, and the largest 12·5 grams. The kernels, together with the thin husks surrounding the endocarp, yield 58·8 p.c. of fat. By whatever process the fat is prepared, a dark brown colouring matter is at the same time extracted, which is so tenaciously retained by the fat, that the author has hitherto been unable to remove this colouring matter. Similar difficulties were met with by Heckel and his collaborators. This dark colouring matter is not only contained in the husks, but also in the membranous extension of the husk (spermoderm) which passes through the whole of the endosperm, in the form of irregular lamellæ radiating from the chalaza. As the examination of the dark fat offered some difficulties, the only way to obtain a fat free from colouring matter was to cut out the white endosperm carefully by hand. The amount of endosperm so obtained formed 84·7 p.c. of the kernels. These 84·7 p.c. contained 69·4 p.c. of fat.

The white endosperm, on being extracted in the usual manner, yielded a perfectly white fat of the saponification value 238·5, the iodine value 1·72, and Reichert-Meissl value 0·65. The fat may therefore be considered as consisting of practically pure myristin, or at most of 98 p.c. of myristin and 2 p.c. of olein.

The natives apply the name 'ochoco' indiscriminately to several edible fruits, such as the fruits from *Lophira alata* (Banks.) ('niam fat'). J. L.

MYRISTICA SURINAMENSIS. The fruit of the *Myristica surinamensis* (Roland), is imported into Germany under the name of 'oil nut.' The nuts have the size and form of a cherry, with a dark-grey brittle shell inclosing a hard kernel. The kernels freed from shell, ground to powder, and extracted with ether, give 73 p.c. of fatty extract. The crude fat contains resin and a free acid. 100 parts of crude fat contain therefore 87 parts of pure substance. The pure fat has the formula $C_{45}H_{86}O_6$, which agrees with that of trimyristin. Like tristearin and tripalmitin, this body exists in different modifications with different melting-points. The trimyristin, saponified with alcoholic potash, yields myristic acid $C_{14}H_{28}O_2$. No other glycerides exist in this fat. The free acid in the crude fat was found to be myristic acid. Owing to the purity of the fat, and the absence of other glycerides, Reimer and Will recommend it as a source of pure myristic acid (J. Soc. Chem. Ind. 4, 746).

MYRISTICOL *v* CAMPHORS.

MYROBALANS *v* TANNINS.

MYRRH, MYRRHIN, MYRRHOL *v.* GUM RESINS.

MYRTLE BERRY WAX *v.* Waxes.

MYRTLE OIL and **MYRTOL** (Umney, Imp. Inst. Jour. Scient. & Tech. Research Dept. 1896, 302; Schimmel. Chem. Zentr. 1910, i. 1719). This oil as used medicinally begins to boil at 160° and about 80 p.c. distils over up to 240°. The residue consists of high-boiling terpenes, partly resinised and partly polymerised. From the portion boiling between 160°–240° by repeated fractional distillation the following constituents can be separated :—

A terpene $C_{10}H_{16}$ boiling between 158° and 160°, and having a specific rotation $[\alpha]_D = +36{\cdot}8^\circ$. According to Bartolotti (Gazz. chim. ital. 21, 276) the b.p. is 154°–155°, $[\alpha]_D + 59{\cdot}3^\circ$. Its properties led Jahns to believe it to be right-handed pinene.

Cineol $C_{10}H_{18}O$, which, purified by Wallach's method, boiled constantly at 176°.

A camphor probably of the formula $C_{10}H_{16}O$, in small quantity, boiling at 195°–200°, $[\alpha]_D$ 24·8° (Bartolotti, *l.c*). The therapeutic value of the myrtle oil is dependent on the amount of cineol present in it, the latter substance being identical with cajeputol and eucalyptol (E. Jahns, Arch. Pharm. 27, [iii.] 174; J. Soc. Chem. Ind. 8, 721).

According to Semmler and Bartelt (Ber. 1907, 40, 1363), myrtle oil contains in its high boiling fraction the ester of an alcohol $C_{10}H_{16}O$, which is called *myrtenol* and has b.p. 222°–224°/760 mm., sp.gr. 0·9763 at 20°, $[n]_D$ 1·49668 and $[\alpha]_D$ (in 100 mm. tube) $+ 45^\circ\ 45'$ (according to Soden and Elze b.p. 220°–221°, $[\alpha]_D$ 49°25′). With phosphorus pentachloride it yields *myrtenyl chloride* $C_{10}H_{15}Cl$, b.p. 90°/12 mm., and on reduction with sodium, *d*-pinene is formed. On oxidation with chromic acid myrtenol yields an aldehyde *myrtenal* $C_{10}H_{14}O$, b.p. 87°–90°/10 mm., which yields an oxime, m.p. 71°–72° and a nitrile, b.p. 100°–102°/10 mm. On hydrolysing the nitrile *myrtenic acid* $C_{10}H_{14}O_2$, b.p. 148°/9 mm., m.p. 45°, is produced. By reduction of the acid *dihydromyrtenic acid* $C_{10}H_{16}O_2$, b.p. 142°–144°/8 mm. is formed. When oxidised with alkaline permanganate myrtenol yields *d*-pinic acid $C_9H_{14}O_4$, b.p. 212°–216°/10 mm.

The characteristic odour of myrtle oil is due chiefly to the ester in the fraction of the oil boiling at 160°–180° (von Soden and Elze, Chem. Zeit. 1905, 29, 1031; Bartolotti, *l.c.*).

Myrtle seed oil forms a yellow oil of characteristic flavour, is readily soluble in ether and turpentine, but less so in alcohol. It contains glycerides of oleic, linoleic, myristic, and palmitic acids (Scusti and Perciabosco, Gazz. Chim. ital. 1907, 37, 483).

MYRTLE WAX (*Laurel wax, Bayberry tallow*) is obtained from the berries of various species of *Myrica*. In North America where the *Myrica* shrubs are common along the Atlantic seacoast, the myrtle wax is obtained from *Myrica cerifera* (Linn.) and *Myrica carolinensis* (Willd.). In South America, notably in New Granada and Venezuela, it is obtained from *Myrica arguta* (Kunth), and *Myrica caracassana* (Humb., Bonpl. et K.), and in South Africa (Cape Colony) from *Myrica quercifolia* (Linn.), *Myrica cordifolia* (Linn.), *Myrica laciniata* (Willd.), and *Myrica serrata* (Lam.). In Abyssinia, myrtle wax is obtained from *M. ethiopica* (Linn.)

The myrica fruits are of the size of a pea, and are covered with a snow-white crust of fat, which is permeated with brown or black spots.

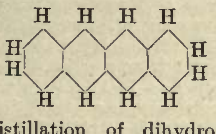
Myrtle wax is a glyceride and consists chiefly of palmitin with small quantities only of olein (Smith and Wade, Amer. Chem. J. 1903, 629). The iodine value of commercial samples varies between 2 and 4.

Myrtle wax worked up by itself does not yield useful candles; it can, however, be employed in the proportion of 20–25 p.c. as an addition to other candle material. In the United States 'beeswax' candles are made which contain a notable amount of myrtle wax. J. L.

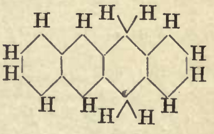
N.

NAGYAGITE. Native lead and gold telluride, containing more or less sulphur, and occasionally antimony (*v.* Tellurium).

NAPHTHA. This term was originally applied to a number of volatile, more or less mobile, inflammable liquids, usually ethers obtained by distillation, e.g., *Naphtha vitrioli* (ethyl ether), *N. nitri* (nitrous ether), *N. aceti* (acetic ether). The term was subsequently restricted to the naturally occurring liquid hydrocarbons, but was afterwards extended to other hydrocarbons obtained by the destructive distillation of shale, coal, bone, &c.

NAPHTHACENE  is obtained by the distillation of dihydroxynaphthacene quinone (*iso*ethine diphthalide) with zinc-dust (Gabriel and Leupold, Ber. 1898, 31, 1272; Fr. Pat. 320327, 1902; J. Soc. Chem. Ind. 1903, 22).

It forms orange-yellow to red-yellow leaflets, m.p. about 335°, which sublime forming a greenish-yellow vapour. It gives a green solution with sulphuric acid, and is insoluble in benzene. When treated with fuming nitric acid it yields naphthacenequinone.

Dihydronaphthacene  is formed by the distillation of naphthacene or of dihydroxynaphthacene quinone over zinc-dust; or by heating dihydroxy- or dichloronaphthacene quinone with hydrogen iodide and phosphorus (Gabriel and Leupold, *l.c.*). It forms flat needles, m.p. 206°–207°, b.p. about 400°. It gives a green solution in sulphuric acid with evolution of sulphur dioxide; is sparingly soluble in boiling alcohol, but more readily so in benzene, glacial acetic acid, and other organic solvents. It is oxidised by chromic acid, forming naphthacenequinone, whilst with concentrated nitric acid it yields a nitronaphthacenequinone.

NAPHTHACENEQUINONE *v.* Quinones.

NAPHTHALENE $C_{10}H_8$.[1]

History.—The production of naphthalene in the manufacture of coal-gas seems to have been noticed first by Clegg (*cf.* Brande, Quart. Journ. Sci. 1820, 8, 287); the discovery of its presence in coal-tar, however, was made simultaneously in 1819 by Garden (Annals Phil. 1820, 15, 74) and Brande (*l.c.*), the latter regarding it as a hydrocarbon (*cf.* Thomson, Schweig. J. 47, 337). It was further examined by Kidd, who named it 'naphthaline' (Phil. Trans. 1821, 209), by Ure (*ibid.* 1822, 473), and by Chamberlain (Annals Phil. 1823, [2] 6, 135); but its composition was determined first by Faraday in the course of his investigation of its isomeric monosulphonic acids (Phil. Trans. 1826, 159) and later by Laurent (Annalen, 1832, 3, 11). A bibliography of the early history of the subject is given in Gmelin (Eng. ed. 14, 1).

Formation and sources.—Naphthalene is almost invariably a constituent of the products obtained when organic substances are heated at a comparatively high temperature. For example, it is formed in small quantity, with other aromatic hydrocarbons, when marsh gas or acetylene (Berthelot, Bull. Soc. chim. 1867, [2] 7, 306), or the vapour of alcohol, acetic acid (Berthelot, Ann. Chim. Phys. 1850, [2] 33, 295), toluene, xylene, or cumene, or of a mixture of benzene, styrene or anthracene, with ethylene (Berthelot, Compt. rend. 1871, 63, 790, 834; Bull. Soc. chim. 1866, [2] 6, 268; 1867, 7, 218, 278, 285), is passed through porcelain tubes filled with pumice and heated to redness. It is present in small quantity in oil gas tar (Armstrong and Miller, Chem. Soc. Trans. 1886, 49, 80), and is produced when the vapour of toluene, or ethylbenzene, or of a mixture of toluene and ethylene is passed through a red-hot tube (Ferko, Ber. 1887, 20, 660). Berthelot's results have not been confirmed in every instance by later investigators (*cf.* Graebe, Ber. 1874, 7, 49; Lorenz, *ibid.* 1097; Carnelley, Chem. Soc. Trans. 1880, 37, 705; Ferko, *l.c.*), but this lack of confirmation may have been due to a difference in the conditions employed. Naphthalene is a constituent of brown coal tar (Heusler, Ber. 1897, 30, 2744); also of the tar produced when turpentine vapour is led through a red-hot iron tube (Schultz, *ibid.* 1877, 10, 116), and is formed when colophony or gum benzoin is distilled with zinc-dust (Ciamician, *ibid.* 1878, 11, 269).

With the object, primarily, of obtaining benzene, toluene, and anthracene, petroleum residues and the high-boiling oils of wood tar and brown coal tar have been passed, as in Berthelot's experiments, through red-hot tubes filled with charcoal, pumice, &c. The tars formed under these conditions from the residues of Baku petroleum (Letny, Ber. 1878, 11, 1210; Dingl. poly. J. 1878, 229, 355; Lissenko, Ber. 1878, 11, 342; Rudnew, Dingl. poly. J. 1881, 239, 72), and from the high-boiling oils of brown coal tar (Liebermann and Burg, Ber. 1878, 11, 723; Salzmann and Wichelhaus, *ibid.* 1431), and pinewood tar (Atterberg, *ibid.* 1222) contain considerable quantities of naphthalene, and in general resemble coal tar. Nevertheless, the production of valuable aromatic hydrocarbons on the large scale from petroleum residues, either under these conditions (Greiff, Chem. Ind. 1879, 2, 185; Liebermann, Dingl. poly. J. 1882, 246, 429; Redwood, J. Soc. Chem. Ind. 1885, 4, 79) or by the later methods patented by Hlawaty (D. R.-P. 51553 of 1888; Eng. Pat. 2242 of 1890), and Nikiforoff (D. R.-P. 143549; Eng. Pat. 21874 of 1901; Eng. Pat. 17450 of 1907; *cf.* Oglobine, Zeitsch. angew. Chem. 1905, 18, 406) is more costly than their isolation from coal tar, and at present of no commercial value.

Naphthalene is a constituent of the principal varieties of tar produced from coal in the manufacture of gas and coke; it is also present in coal gas, although the amount is kept as small as possible, to avoid blocking of the service pipes during cold weather (*cf.* Smith, J. Soc. Chem. Ind. 1889, 8, 949; Young, *ibid.* 1899, 18, 1109; 19, 813; Irwin, *ibid.* 19, 314; also, art. Gas, Coal). The proportion in gas tar varies considerably with the different kinds of coal employed (*cf.* Smith, J. Soc. Chem. Ind. 1889, 8, 951), and is greater the higher the temperature used during carbonisation (Smith, *ibid.* 1884, 3, 64), amounting usually to 4–6 p.c. (*ibid.* 1890, 9, 446), but in some cases to as much as 10 p.c. (Lewis, J. Gas Lighting, 47, 1248). In coke-oven tars, the proportion of naphthalene, as of other aromatic hydrocarbons, depends on the type of oven used (*cf.* Smith, J. Soc. Chem. Ind. 1883, 2, 404). With closed ovens, the tars do not differ greatly from gas tar, thus Watson Smith found from 1 to 10·17 p.c. in tars from Simon-Carvès ovens working with different kinds of coal (*ibid.* 2, 500; 3, 104, 508; J. Iron and Steel Inst. 1885, 103), and 'an equal amount to that contained in gas tar' in the tar from an Otto oven

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[1] The following abbreviations are employed for the names of firms to which frequent reference is made in the text of this article:—

Aktienges.	Aktiengesellschaft für Anilinfabrikation in Berlin.
Badische	Badische Anilin- und Soda-Fabrik in Ludwigshafen a. Rh.
Bayer	Farbenfabriken vorm. F. Bayer & Co. in Elberfeld.
Bindschedler	Basler chemische Fabrik, vorm. Basler chem. Fabrik Bindschedler in Basel.
Brönner	Farbfabrik vorm. Brönner in Frankfurt a. M.
Cassella	Anilinfarbenfabrik von L. Cassella & Co. in Frankfurt a. M.
Dahl	Dahl & Co. in Barmen.
Geigy	Anilinfarben- und Extrakt-Fabriken vorm. J. R. Geigy in Basel.
Gesellsch.	Gesellschaft für chemische Industrie in Basel.
Griesheim	Chemische Fabrik Griesheim-Elektron in Frankfurt a. M.
Heyden	Chemische Fabrik von Heyden, Aktiengesellschaft in Radebeul bei Dresden.
Höchst	Farbwerke vorm. Meister, Lucius & Brüning in Höchst a. M.
Kalle	Kalle & Co., Aktiengesellschaft in Biebrich a. Rh.
Landshoff	Chemische Fabrik Grünau, Landshoff und Meyer.
Leonhardt	Farbwerk Mülheim, vorm. A. Leonhardt & Co., in Mülheim bei Frankfurt.
Sandoz	Chemische Fabrik vorm. Sandoz in Basel.
Schöllkopf	Schöllkopf Aniline and Chemical Co., Buffalo (U.S.A.).
Verein	Verein chemischer Fabriken in Mannheim.

(J. Soc. Chem. Ind. 1884, 3, 508); Knublauch obtained from 4·27 to 5·27 p.c. in tars from Otto-Hoffmann ovens (Dingl. poly. J. 1884, 254, 37); whilst Lunge found 7·69 p.c. of the crude hydrocarbon in tars from Otto-Hoffmann ovens, and 6·7 p.c. of the crude hydrocarbon in tars from Otto-Hilgenstock ovens, as against 7·4 p.c. in gas tar from the same coal (J. Soc. Chem. Ind. 1887, 6, 583). Blast-furnace tar contains only a very small proportion of naphthalene (Smith, *ibid.* 1883, 2, 495), and it could not be detected in Sutherland gas-producer tar (Smith, *ibid.* 3, 10).

Synthetical methods of preparing naphthalene have been described by Aronheim (Ber. 1873, 6, 67), Wreden and Znatowicz (*ibid.* 1876, 9, 1606), Brunner and Brandenburg (*ibid.* 1878, 11, 698), and Baeyer and Perkin (*ibid.* 1884, 17, 448). It has also been obtained by heating barium carbide with barium hydroxide at 800°–1000° (Bradley and Jacobs, D. R.-P. 125936; Eng. Pat. 26061 of 1898).

Isolation and purification (Lunge, Coal Tar and Ammonia, 4th ed. 1909, 643 *et seq.*).—Naphthalene occurs in the coal tar fraction boiling at 180°–250°, and is present, therefore, in the 'light oil' (b.p. 110°–210°), and 'creosote oil' (b.p. 240°–270°), but most abundantly in the 'carbolic oil' (b.p. 210°–240°) of the tar distiller. From the carbolic oil the crude hydrocarbon crystallises out to a large extent on cooling, and can be freed from the accompanying oil by draining and subsequent hot-pressing. It is then stirred for some time with hot caustic soda solution of convenient strength to remove phenolic constituents; and, after the alkaline liquor has been run off, is washed with hot water. Next, it is heated for about an hour with 5–10 p.c. of concentrated sulphuric acid (sp.gr. 1·7–1·84)[1] at about 100°, to remove both basic substances and residual phenols as soluble sulphonic acids. It is then washed several times with hot water, afterwards with weak alkali, and again with hot water, and finally is either sublimed or preferably distilled, pure naphthalene being collected between 210° and 235°, or so long as a sample solidifies on cooling, and gives only a faintly-coloured solution when dissolved in hot sulphuric acid.

Properties.—Purified naphthalene is usually found in commerce in white crystalline masses or thin scales. It crystallises from alcohol in scales or monoclinic prisms (Groth, Ber. 1870, 3, 453), melts at 79°, solidifies at 79·6°–79·8° (Weger, Zeitsch. angew. Chem. 1909, 22, 341), and boils at 217·5° at 750·5 mm., or 218·5° at 767·6 mm. (Crafts, Bull. Soc. chim. 1883 [2], 39, 282). Its sp.gr. is 1·1517 at 18·75° (Vohl, J. pr. Chem. 1867, 102, 30), or 0·9774 in the liquid state at 79·2° (Kopp, Annalen, 1855, 95, 335; *cf.* Schiff, *ibid.* 1884, 223, 261). Naphthalene has a characteristic, penetrating, tarry odour, a pungent taste, and burns with a very smoky flame. It is only sparingly soluble in light petroleum, but very soluble in benzene or ether, and miscible in all proportions with hot toluene or absolute alcohol. According to Bechi (Ber. 1879, 12, 1978), 100 parts of toluene dissolve 31·94 parts of naphthalene at 16·5°, and 100 parts of absolute alcohol dissolve 5·29 parts at 15°; according to Smith 100 parts of benzene, toluene, 'xylene,' and 'cumene' dissolve 45·8, 32·0, 31·5, and 30·1 parts of naphthalene respectively at 15° (J. Soc. Chem. Ind. 1902, 21, 1225). Naphthalene volatilises at temperatures considerably below its boiling-point, and is readily volatile with steam, alcohol vapour, or the vapour of tar oils of low boiling-point. Naumann (Ber. 1877, 10, 2016; 11, 33) has determined the vapour-tension of naphthalene to be 2 mm. at 15°, 9 mm. at 78°, and 20·5 mm. at 100°, and finds that when steam is passed into it naphthalene distils with water in the following ratios:—

Barometer (cor.)	Temperature of liquid	Temperature of vapour	Ratio of naphthalene to water in distillate
mm.			
759·5	97·8°	99·2°	100 : 520
757·0	97·7°	99·1°	100 : 570
733·0	—	98·2°	100 : 555

Reactions.—(1) When heated with amorphous phosphorus and hydriodic acid, naphthalene yields a *tetra-*, *hexa-*, *octo-*, or *deka- hydride* (*cf.* Graebe and Guye, Ber. 1883, 16, 3028); with sodium and ethyl alcohol a *dihydride* (Bamberger and Lodter, Annalen, 1895, 288, 75); and with sodium and amyl alcohol a *tetrahydride* (Bamberger and Kitschelt, Ber. 1890, 23, 1561).

(2) On oxidation with potassium permanganate in aqueous solution (Tscherniac, D. R.-P. 79693 of 1894; Procházka, Ber. 1897, 30, 3109; Graebe and Trümpy, *ibid.* 1898, 31, 369; Daly, J. Physical Chem. 1907, 11, 93) or, better, with potassium manganate (Tscherniac D. R.-P. 86914 of 1895) naphthalene is converted into *phthalonic acid* with only a small proportion of *phthalic acid* (*cf.* Lossen, Annalen, 1867, 144, 71), but with acidified permanganate into *phthalic acid* (Tscherniac, *l.c.*). With dilute nitric acid (of sp.gr. 1·15) at 130°, *phthalic acid* is the product (Beilstein and Kurbatow, Annalen, 1880, 202, 215; *cf.* Boswell, J. Physical Chem. 1907, 11, 129); with chromic acid mixture, *phthalic acid* (Lossen, *l.c.*) in 32 p.c. yield (Heller, Ber. 1912, 45, 674, footnote); but with chromic acid in acetic acid solution, [α-]*naphthaquinone* (Groves, Chem. Soc. J. 1873, 26, 209) and *phthalic acid* (Beilstein and Kurbatow, *l.c.*). Oxidation in acid solution with ceric salts (Höchst, D. R.-P. 158609 of 1902) or electrolytic oxidation (de Bottens, Zeitsch. Electrochem. 1902, 8, 673) in presence of cerous salts (Höchst, D. R.-P. 152063; Eng. Pat., 19178 of 1902) also converts it into [α-]-*naphthaquinone* and *phthalic acid.* It is oxidised also, when heated with 15 times its weight of 100 p.c. sulphuric acid (monohydrate) and half its weight of mercuric sulphate at 200°, yielding *phthalic acid* in large amount, mixed with some *sulphophthalic acid* (Badische, D. R.-P. 91202; Eng. Pat. 18221 of 1896).

(3) With chlorine, *naphthalene dichloride* (Fischer, Ber. 1878, 11, 735, 1411), and *tetrachloride* (*q.v.*) are formed, which, by elimination of hydrogen chloride are converted into mono- and di-chloronaphthalenes (Faust and Saame,

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[1] To obtain naphthalene which will remain permanently white an oxidising agent—for example, about 5 p.c. of finely-ground pyrolusite, or of Weldon-mud—may be used with the acid (Lunge, Ber. 1881, 14, 1756; Chem. News, 1881, 44, 65).

Annalen, 1871, 160, 66; Krafft and Becker, Ber. 1876, 9, 1088; Widmann, *ibid.* 1882, 15, 2162; Armstrong and Wynne, Chem. Soc. Proc. 1890, 6, 85). With bromine, it forms a *tetrabromide*, but only at low temperatures (Orndorff and Moyer, Amer. Chem. J. 1897, 19, 262), and under ordinary conditions gives rise to substitution derivatives (Laurent, Ann. Chim. Phys. 1835, [ii.] 59, 216; Glaser, Annalen, 1865, 135, 40; Guareschi, *ibid.* 1884, 222, 265; Armstrong and Wynne, *l.c.*).

(4) Fuming nitric acid, or a mixture of nitric and sulphuric acids, converts naphthalene into *mono-*, *di-*, *tri-*, or *tetra-nitro-* derivatives; with sulphuric acid, according to the quantity, concentration, or temperature employed, *mono-*, *di-*, *tri-*, or *tetra- sulphonic acids*, or *sulphones*, are formed.

(5) When its vapour is passed through a red-hot iron tube, naphthalene yields about 15 p.c. of $\beta\beta$-dinaphthyl, and, when mixed with ethylene, gives in addition a very small quantity of acenaphthene and phenanthrene (Ferko, Ber. 1887, 20, 662).

(6) Naphthalene combines with trinitro-derivatives of benzene (Hepp, Annalen, 1882, 215, 380), toluene (Hepp, *l.c.*), aniline (Liebermann and Palm, Ber. 1875, 8, 377), phenol (Henriques, Annalen, 1882, 215, 332), or cresol (Noelting, Ber. 1882, 15, 1862; 17, 271), forming crystalline molecular compounds of varying stability. Of these, the *compound* with picric acid, $C_{10}H_8+C_6H_2(NO_2)_3{\cdot}OH$, crystallises in golden-yellow needles, m.p. 149°, and dissolves in alcohol, ether, or benzene without decomposition (Fritzsche, Jahresb. Chem. 1857, 456).

Tests.—Commercial naphthalene should melt at 79°,[1] boil at 217°–218° at 760 mm., volatilise without leaving a residue, and be white and free from phenols or quinoline bases. When heated with concentrated sulphuric acid at 170°–200° it should at most colour the acid grey (Witt, Chem. Ind., 1887, 10, 216), or faintly purple, and when left in contact with nitric acid (sp.gr. 1·42) should remain white for at least half an hour (Lunge, Coal Tar and Ammonia, *l.c.*).

The presence of phenols can be detected by boiling the sample with dilute caustic soda solution, cooling, filtering, and adding to the filtrate bromine water and hydrochloric acid, when any phenols present will be precipitated in the form of brominated compounds. Quinoline bases are detected by dissolving the sample in warm concentrated sulphuric acid, pouring the solution into water, filtering, rendering the filtrate alkaline and distilling, when any quinoline bases present will pass over with the steam, and will be recognised by their characteristic odour (Lunge, *l.c.*).

Estimation.—The proportion of naphthalene in commercial samples can be determined in many cases by sublimation. According to Küster (Ber. 1894, 27, 1101) an acidimetric method, based on the formation of the insoluble picrate, can be used for determining naphthalene. In this process a saturated solution of picric acid is employed, the excess of which is afterwards found by titration with standard baryta, using lacmoid as indicator; but as acenaphthene, chrysene, and the naphthols, also form insoluble compounds with picric acid, the method is valueless if they are present in the sample. In modified forms Küster's method has been employed for estimating the amount of naphthalene in coal gas by Colman and Smith (J. Soc. Chem. Ind. 1900, 19, 128) and by Gair (*ibid.* 1905, 24, 1279; 26, 1263).

Uses.—Until the discovery of the eosins about 1874, and of the azo- dyes about 1876, naphthalene had but a limited use, and was either employed as a fuel, or burned for soot. Now a large proportion of the output is utilised in the manufacture of (*a*) the phthalic acid required in the production of dyestuffs of the phthaleïn group and of indigo, (*b*) the naphthylamines and naphthols used in the azo- dye industry.

To a limited extent it finds employment as a disinfectant and insecticide, and in the enrichment of gaseous fuels, but its use as a carburettor for coal gas in the albo-carbon burner, with the object of increasing the illuminating power, has been much restricted, if not abandoned, as a consequence of the introduction of incandescent lighting (*cf. inter alia* Livesey and Kidd, Eng. Pat. 244; D. R.-P. 2075 of 1878; Kidd and Vale, Eng. Pat. 2135 of 1880; Vale, D. R.-P. 32255 of 1884; Lunge, *l.c.*).

CONSTITUTION OF NAPHTHALENE AND NAPHTHALENE DERIVATIVES.

The naphthalene compounds of greatest technical importance in connection with the manufacture of azo dyes are the naphthylamines, naphthols, aminonaphthols, and the derived isomeric sulphonic acids. These substances are by no means equally valuable as sources of dyes; some, for example, do not couple with diazotised bases, or form only aminoazo compounds, others yield azo dyes which are not fast to soap, or are valueless on account of their shade, insolubility, or instability,[2] and only a comparatively small number form azo dyes which answer all the requirements of the dyer so far as fastness, tinctorial power, and delicacy of shade are concerned. A knowledge of the constitution of the naphthalene derivatives employed in the colour industry is thus a question of much importance, as may be judged from the frequent references in this article to Patent specifications where no inconsiderable amount of the chemistry of naphthalene is to be found.

Constitution of naphthalene.—The Erlenmeyer-Graebe formula for naphthalene, proposed by Erlenmeyer (Annalen, 1865, 137, 346 (footnote)), but first made probable on the basis of experimental evidence by Graebe (*ibid.* 1869,

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[1] In practice, the temperature at which the sample solidifies is preferred to the melting point, the determination, if made in Shukoff's apparatus, being accurate to 0·1° (Chem. Zeit. 1901, 25, 1111).

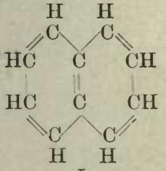
[2] For example: each of the following acids (2 mols.) coupled with diazotised benzidine (tetrazodiphenyl), gives worthless azo-dyes of the shades indicated:—

(*a*) β-Naphthylaminesulphonic acids:—5-[γ-] acid, sparingly soluble orange yellow; 6- [β-] acid, insoluble reddish brown; 7- [δ- or F-] acid, red changing to brown by action of atmospheric carbon dioxide; 8- [α-] none, but a yellow diazoamino- compound;

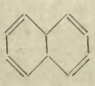
(*b*) β-Naphthylaminedisulphonic acids:—3 : 6- (amino-R-] acid, red of little tinctorial power; 6 : 8- [γ-, or amino-G-] acid, yellow and fugitive.

On the other hand, β-naphthylamine-3 : 7-disulphonic acid gives a red dye, remarkably fast towards light and acids (Cassella, D. R.-P. 46711 of 1888).

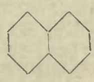
149, 22), represents the molecule as composed of two six-membered rings having two carbon atoms in common. This arrangement is shown in formula I, with which formula II, or, conventionally, when the object is merely to show the relative position of substituents in the molecule, formula III is equivalent :—



I

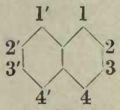


II

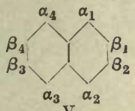


III

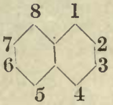
To save the labour of writing the symbol each time it is desired to indicate the orientation of a substituent, several methods for distinguishing the positions have been devised, of which three are shown in the symbols IV–VI :—



IV



V

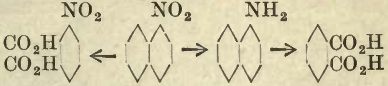


VI

Of these the last (VI), originally proposed by Graebe in 1869, and adopted by the Geneva Congress on Nomenclature in 1892 (Chem. News. 65, 280), is the only one now in use.[1]

With one exception (Wreden, Ber. 1876, 9, 950) all the formulæ proposed for naphthalene[2] show two six-membered rings in the same plane,[3] but differ from one another, and from the Erlenmeyer-Graebe symbol, in the mode of distribution of the fourth valency of each carbon atom, on which the unsaturation of the molecule, and the properties distinguishing naphthalene compounds from those of benzene probably depend. These six-membered rings have been termed benzene or benzenoid rings, but under a misapprehension : neither ring has the properties of benzene until the unsaturation of the other has been destroyed.

That naphthalene contains one six-membered ring is shown by its synthesis from benzene derivatives ; that it contains two, having two carbon atoms in common is demonstrated most convincingly, perhaps, by the production of 3-nitrophthalic acid from α-nitronaphthalene (Beilstein and Kurbatow, Annalen, 1888, 202, 217) and of phthalic acid from α-naphthylamine (Monnet, Reverdin and Noelting, Ber. 1879, 12, 2306) by the use of the same oxidising agent.



Incidentally, the production of 3-nitrophthalic acid fixes the α-position[4] relatively to the central carbon atoms in the formula (Reverdin and Noelting, Ber. 1880, 13, 36). As phthalic acid and nitrophthalic acid are benzene derivatives, it is evident that each six-membered ring of naphthalene becomes a benzene ring on disruption of the other by oxidation. Bamberger has shown that a similar result follows from the saturation of either ring by hydrogen.

The problem of the internal structure of the naphthalene molecule—in other words, the distribution of the fourth valency of each carbon atom—has been attacked both by chemical and physical methods with results which suggest that a complete solution has not yet been found. To be satisfactory on chemical grounds, the naphthalene formula must account for :—

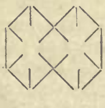
(i.) The symmetry of the molecule, in the sense that its two halves are alike as shown, for example, by the existence of four similar α- and four similar β- positions ;[5]

(ii.) The reduction, effected easily, of naphthalene derivatives to homonucleal tetrahydro-compounds with the loss of the properties distinguishing them from benzene derivatives ;

(iii.) The occurrence of substitution and of reduction initially in α- positions ;

(iv.) The difference between the four contiguous αβ- positions [1 : 2, 3 : 4, 5 : 6, 7 : 8] and the two contiguous ββ- positions [2 : 3, 6 : 7] of which the former alone have properties corresponding with those associated with the *ortho-* position in benzene. Only one 2 : 3-derivative, namely 3-hydroxy-β-naphthoic acid, is known to be formed by substitution from a β-mono- derivative, and the number formed in other ways is relatively very small.

Two formulæ, proposed respectively by Bamberger (*l.c.*) and by Thiele (*l.c.*), are of interest as designed to exhibit or account for some, if not all, of these requirements. Bamberger's formula (VII), based on Armstrong's centric formula for benzene, satisfies requirements (i.) and (ii.), and Thiele's formula (VIII), developed from his benzene formula with its conjugated double linkings, accounts also for requirements iii. and iv. by reference to the residual valencies shown in α- positions.



VII

VIII

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[1] To distinguish the relative positions in disubstitution derivatives otherwise than by the use of numbers, Erdmann (Annalen, 1893, 275, 188) has proposed the adoption of the italicised prefixes in addition to those (shown in Roman type) which were previously in use :

1 : 4 para-	1 : 2 ortho-	1 : 7 *kata-*
1 : 5 *ana-*	1 : 3 meta-	2 : 6 *amphi-*
1 : 8 peri-	1 : 6 *epi-*	2 : 7 *pros-*

The suggestion was made by him that 2 : 3-derivatives should also be distinguished as *ortho-*, but as they are essentially different in properties from 1 : 2-compounds, confusion would arise from its adoption.

[2] *Cf.* Berthelot, Compt. rend. 1866, 73, 788, 834 ; Wichelhaus, Ber. 1868, 2, 107 ; Wreden (second formula), *l.c.* ; Claus, Ber. 1882, 15, 1827 ; Bamberger, Annalen, 1890, 257, 44 ; Armstrong, Chem. Soc. Proc., 1890, 6, 102 ; Thiele, Annalen 1899, 306, 138 ; Knoevenagel, *ibid.* 1900, 311, 194 ; Hartley, Chem. Soc. Trans. 1905, 87 ; Baly and Tuck, *ibid.* 1908, 93, 1905 ; Willstätter and Waser, Ber. 1911, 44, 3423 ; *cf. ibid.* 1912, 45, 1481.

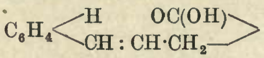
[3] Kaufler (Annalen, 1907, 351, 154) has proposed a formula with the two rings in different planes.

[4] The use of the terms α and β for the isomeric naphthalenemonosulphonic acids was introduced by Merz (Zeitsch. Chem. 1868, [ii.] 4, 394) without reference to the naphthalene symbol.

[5] The existence of these two sets of interequivalent positions follows from the recognition of three isomeric αα-dichloronaphthalenes (Atterberg, Ber. 1877, 10, 547), and of three isomeric ββ-dichloronaphthalenes (Armstrong and Wynne, Chem. Soc. Proc. 1890, 6, 83). For the interequivalence of the 2 : 7-position, compare Beschke (Annalen, 1909, 369, 157).

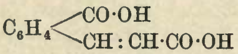
As against these and other theories of the structure of the naphthalene molecule, the Erlenmeyer-Graebe formula still commands the largest measure of assent. It contains the five double linkings, the presence of which is probable on physical grounds (*cf.* Brühl, Ber. 1887, 20, 2307); it shows clearly the difference between $\alpha\beta$- and $\beta\beta$- positions in the same nucleus; and, in common with Bamberger's or Thiele's formula, it accounts for the assumption of benzenoid properties when one of the two rings is saturated by hydrogen. It is also the formula which agrees best with the conclusions to be drawn from (*a*) the synthesis of α-naphthol by heating phenyl*iso*crotonic acid (Fittig and Erdmann (Annalen, 1885, 227, 242):

(*a*)



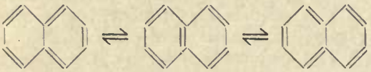
and (*b*) the production of carboxy-*o*-cinnamic acid from β-naphthol by oxidation (Ehrlich and Benedikt, Monatsh. 1888, 9, 527):

(*b*)



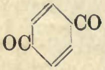
as in both of these compounds an $\alpha\beta$- double linking is present in the side chain.

Oscillation formulæ of the type suggested by Kekulé for benzene have been proposed also for naphthalene (*cf.* Erdmann, Annalen, 1893, 275, 191; Hartley, Chem. Soc. Trans. 1905, 87, 1828):—



but they would predicate a similarity in the properties of contiguous $\alpha\beta$- and $\beta\beta$- positions which does not exist. On the contrary, evidence from the chemical side (*cf.* Marckwald, Annalen, 1893, 274, 373; 1894, 279, 5) points to fixity of structure,[1] which finds its expression in the central double linking of the Erlenmeyer-Graebe formula.

That the internal structure of the naphthalene molecule can undergo modification under some conditions, just as that of benzene does, is clear from the existence of 2 : 6-naphthaquinone (Willstätter and Parnas, Ber. 1907, 40, 1406, 3971)

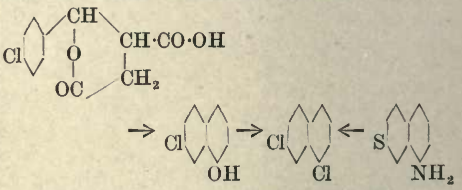


but this change—of much interest on other grounds—has no obvious connection with the question of a fixed or oscillatory structure for either hydrocarbon.

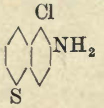
The mono-, di-, and tri-chloronaphthalenes furnish an argument in support of the symbol, for the investigation of all the substances described as di- and tri-chloro- derivatives has shown that the number is ten for the one and fourteen for the other[2] in agreement with the number of isomerides predicted from the formula. In no other series of tri-derivatives have all the possible isomerides been isolated, and as, by well-known reactions, it is not difficult in most cases to connect a naphthalene derivative under investigation with one or other of the chloronaphthalenes, this group of substances serves as a standard to which the orientation of other di- and tri- derivatives is referred.

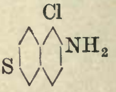
The constitution of the chloronaphthalenes has been ascertained mainly by two independent methods of investigation,[3] of which only an outline can be given here.

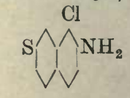
In one of them the isomeric sulphonic acids of α-naphthylamine (Erdmann, Annalen, 1888, 247, 306; 1893, 275, 192; Erdmann and Süvern, *ibid.* 275, 230) and α-nitronaphthalene were converted into dichloronaphthalenes, and the constitution of these determined by comparison with heteronucleal dichloronaphthalenes obtained synthetically from chlorophenylparaconic acids (Erdmann and Kirchhoff, Annalen, 1888, 247, 366; Erdmann, *ibid.* 1893, 275, 255)



In the other method use was made of 1-chloro-β-naphthylamine and its three heteronucleal sulphonic acids. Each of these acids was converted respectively into a chloro- and an amino-naphthalenesulphonic acid by eliminating (*a*) the NH_2-radicle, (*b*) the chlorine atom, and these in turn into dichloronaphthalenes. These dichloronaphthalenes, five in number and necessarily heteronucleal, contained each a chlorine atom derived from, and occupying the same position as either the Cl or the NH_2 radicle of 1-chloro-β-naphthylamine, and two isomerides were obtained from each acid. Thus their constitution was ascertainable, and that of the acids shown to be (S being used for SO_3H):—







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[1] That part of Marckwald's objection to oscillation formulæ which is based on the assumed impossibility of preparing 2 : 3-naphthaquinone, seems no longer to be valid owing to the isolation of the 2 : 3-quinone of 1-methylnaphthalene in the form of a halogen derivative (Fries and Empson, Ber. 1909, 42, 3375). But the argument drawn from the impossibility of coupling β-naphthol with diazotised bases in the contiguous β-position still remains, and is supported, for example, by the results of experiments on the etherification of β-naphthol derivatives (Davis, Chem. Soc. Trans., 1900, 77, 44).

[2] When the substituents are not alike the number of isomerides is greater; thus the existence of 14 naphtholsulphonic acids, of 42 naphtholdisulphonic acids, and of 84 aminonaphtholsulphonic acids is deducible from the naphthalene symbol, and Ray has calculated the total number of substitution derivatives of which it allows to be 10,766,600 (Ber. 1900, 33, 1910; *cf.* Kauffmann, *ibid*, 2131).

[3] The agreement between the conclusions reached by these methods excludes the possibility that intramolecular change may have occurred at any stage of the work, and strengthens the evidence derived from many sources, that high temperature reactions which, in the case of benzene, are untrustworthy for the purpose of ascertaining structure, give with naphthalene derivatives consistent results. For example, the SO_3H radicle of naphthalene-, naphthylamine-, and naphtholsulphonic acids can be exchanged for OH by fusion of the acids with caustic alkali (*cf.* Erdmann, Annalen, 1889, 247, 308), and by distillation of hydroxy- or nitro- or sulphonic derivatives with phosphorus pentachloride, OH, or NO_2, or SO_2Cl radicles can be exchanged for Cl without any change in orientation.

(Armstrong and Wynne, Chem. Soc. Proc. 1889, 5, 34, 48; 6, 77). By an extension of this method the constitution of the fourteen trichloronaphthalenes also was ascertained (*ibid.*, Chem. Soc. Proc. 1895, 11, 84).

Reference to the following tables shows that in several instances di- and tri-chloronaphthalenes respectively have nearly the same melting points, and as they cannot easily be identified by their crystalline form, other means of characterising them are necessary. By sulphonating the dichloronaphthalenes with chlorosulphonic acid, and the trichloronaphthalenes with 10 p.c. anhydrosulphuric acid, sulphonic acids are formed, of which the chlorides and amides, each with a definite melting point, differ sufficiently among themselves to render identification complete (Armstrong and Wynne, Chem. Soc. Proc. 1890, 6, 77; 1895, 11, 84).

Dichloronaphthalenes.

Trivial name	Constitution	Melting point	Character of crystallisation from alcohol
—	1:2	35°	Prisms.
—	1:3	61°	Long, flat needles.
[β-]	1:4	67·5°	Long, flat needles.
[γ-]	1:5	107°	Short, flat needles.
[η-]	1:6	48°	Long, flat needles.
[θ-]	1:7	62·5°	Small aggregates.
[ξ-]	1:8	82°	Rhombohedra.
[ι-]	2:3	119·5°	Thin, lustrous scales.
[ε-]	2:6	135°	Long, flat needles.
[δ-]	2:7	114°	Thin laminæ.

Trichloronaphthalenes.

Trivial name	Constitution	Melting point	Character of crystallisation from alcohol
[α-]	1:2:3	81°	Groups of long needles.
—	1:2:4	92°	Tufts of flat needles.
—	1:2:5	78·5°	Short, flat needles.
—	1:2:6	92·5°	Slender needles.
—	1:2:7	88° and 84°	Microscopic needles.
—	1:2:8	83·5°	Long slender needles.
[γ-]	1:3:5	103°	Long, flat needles.
[θ-]	1:3:6	80·5°	Tufts of thin needles.
[η-]	1:3:7	113°	Short, thin needles.
[β-]	1:3:8	89·5° and 85°	Large, flat prisms.
[δ-]	1:4:5	131°	Very long needles.
[ε-] and [ξ-]	1:4:6	66° and 56°	Needles, becoming opaque.
—	2:3:5	109°	Long, thin needles.
—	2:3:6	91°	Minute plates.

Throughout this article the constitution of a substance is indicated by numerals, except in those cases where the use of α- and β-, as equivalent to the 1- and 2- positions, is commonly employed, *e.g.* α-naphthol instead of the less familiar 1-hydroxynaphthalene. When it has been necessary to use the letters α, β-, γ- . . . to distinguish isomerides, of which the constitution is unknown, the plan adopted by Ladenburg (Handwörterbuch, art. NAPHTALIN) of placing the letters in brackets (*e.g.* [α-]) to indicate that they bear no reference to the constitution of the compounds, has been followed.

SUBSTITUTION IN THE NAPHTHALENE SERIES.

A full discussion of the laws of substitution in the naphthalene series, and of the theories which have been proposed to account for or explain them, lies outside the scope of this article, but a summary of what is known or surmised in connection with nitration and sulphonation may be attempted in view of the importance of these processes in the manufacture of naphthalene derivatives for use in the colour industry.

The existence of two series of mono- substitution derivatives in the naphthalene series, and the fact that substitution tends to occur mainly in the α- position have long been recognised. For example, by chlorination, bromination, or nitration, naphthalene yields α-chloro-, α-bromo- or α-nitro-naphthalene; whilst, by nitration, α-chloronaphthalene yields three, α-nitronaphthalene two, naphthalene-α-sulphonic acid three, and naphthalene-β-sulphonic acid three α-nitro- derivatives. Owing to the very small proportion in which the β-isomeride is formed, the separation of β-chloro-, β-bromo-, or β-nitronaphthalene from the respective mono- substitution products was not achieved until recently, and the only recorded attempt to increase this proportion, by nitrating naphthalene at 200°–300° instead of at the ordinary temperature, led to negative results (Nägeli, Bull. Soc. chim. 1899, [iii.] 21, 786).

With sulphuric acid as the agent very different results are obtained, as β-isomerides can be prepared easily and in large amount. Faraday, who was the first to study the action of sulphuric acid on naphthalene, isolated the barium salts of the two monosulphonic acids, known now as the α- and β- acids, and later investigations have not only confirmed his discovery, but shown that the β- compound increases in amount as the temperature of sulphonation is raised until at 160° it constitutes almost the sole product (*v. Naphthalene-α-sulphonic acid*). This increase in the amount of the β-, accompanied by a corresponding diminution in that of the α- acid is shown clearly by the following numbers, obtained with many others by Euwes (Rec. trav. chim. 1909, 28, 298) in a quantitative study of the molecular reaction expressed by the equation:—

$$C_{10}H_8 + H_2SO_4 \rightarrow C_{10}H_7 \cdot SO_3H + H_2O$$

t°	P.c. $C_{10}H_8$ recovered [1]	P.c. in product		Disulphonic acid	Sulphone
		α-acid	β-acid		
80°	27·0	96·4	3·6	—	—
100°	20·0	83·2	16·8	—	—
129°	10·0	44·4	55·6	—	1·0
138·5°	8·6	28·4	71·6	—	(?)
150° [2]	6·4	18·3	81·7	—	3·2

According to Euwes, when equilibrium is attained, the relative proportion of α- and β-acid is fixed for any given temperature; thus

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[1] It should be noted that this decrease in the amount of naphthalene recovered at the higher temperatures does not harmonise with Merz and Weith's results (*v. Naphthalene-α-sulphonic acid*).

[2] At temperatures above 160°, disulphonic acid was formed, but the data given do not show to what extent, if any, the consequent increase in dilution of the sulphuric acid influenced the relative proportion of α- and β-monosulphonic acids.

with 90 p.c., 96 p.c., and 100 p.c. sulphuric acid at 129°, the proportion of α-acid in the product was 44·6–44·4 p.c., the recovered naphthalene being 32 p.c., 23 p.c., and 10 p.c. respectively.

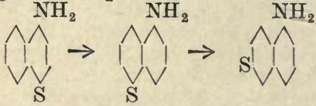
It has long been known that sulphonation is a reversible process, and, in the naphthalene series that α-sulphonic acids are hydrolysed at lower temperatures than β-sulphonic acids under conditions otherwise comparable. To Noelting is due the suggestion that naphthalene, regenerated by hydrolysis of its α-sulphonic acid at the high temperature is at this high temperature resulphonated, but in the β-, not the α-position (Ber. 1875, 8, 1095). This explanation, which does not account for the presence of β-acid at the lowest temperature of sulphonation, or for its progressive increase as the temperature rises, seems to have been accepted (*cf.* Weinberg, Ber. 1887, 20, 3354; Bender, *ibid.* 1889, 22, 994) until Erdmann published the first detailed study of an example of sulphonation.

Briefly, Erdmann's results, which were obtained with α-naphthylamine, showed that:—

(i.) When heated with 5 times its weight of 95–96 p.c. sulphuric acid at 130°, the base was rapidly converted into the 4-acid, with a small amount of the 5-acid, and traces of the 6-acid.

(ii.) The product at the end of 20 minutes was soluble in water, but contained some α-naphthylamine;

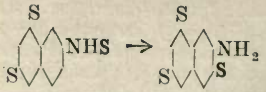
(iii.) The amount of naphthylamine increased, with simultaneous formation of the 4:7-disulphonic acid, as the heating at 130° was prolonged, the 5-acid, and afterwards the 6-acid, becoming the chief product:

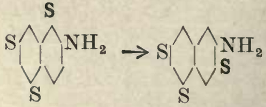


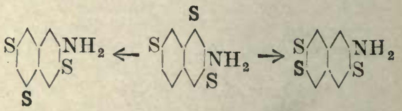
To explain these facts, Erdmann modified Noelting's view by the assumption that the 4-, 5-, and 6-acids are produced simultaneously but in widely differing amounts. The formation of water by the further sulphonation of the 4-acid $NH_2{\cdot}C_{10}H_6{\cdot}SO_3H + H_2SO_4 = NH_2{\cdot}C_{10}H_5(SO_3H)_2 + H_2O$ disturbs the equilibrium which otherwise would be attained, and brings about the hydrolysis first of the 4-acid, and then of the 5-acid. Thus he accounted for the increase in the amount of α-naphthylamine; of the 5-acid; and finally of the 6-acid—the least easily hydrolysed of the three acids—in the product.

While this view accounts for the phenomena observed by Erdmann, and evidently implies that the introduction of a sulphonic group, like other processes of substitution, takes place mainly in α- and only to a small extent in β-positions at whatever temperature it may be effected—the subsequent change in the proportion of the isomerides being due to hydrolysis mainly of α-acid and resulphonation—it does not furnish a general theory of sulphonation. For example, it leaves unexplained:

(*a*) The transference of the SO_3H radicle S to a β- position under the influence of 30–40 p.c. anhydrosulphuric acid at 130°–180° in cases such as the following [1]—

I. 

II. 

III. 

(*b*) The rare occurrence of acids in which two SO_3H radicles occupy contiguous positions, and the non-occurrence of acids in which they occupy relatively 1:4- or 1:8- positions, even when on general grounds the occurrence of such acids in the sulphonation melt might be expected.[2]

The acids, five in number, in which two SO_3H radicles occupy contiguous positions, are each obtained by the aid of 40 p.c. anhydrosulphuric acid at 130°. Four of them are the β-naphthylamine- and β-naphthol- sulphonic acids of the orientation [R being NH_2 or OH]:

and the fifth is an α-naphthasultamtrisulphonic acid, in which contiguity occurs either in a ββ- or in a αβ- position.

If, with so great a wealth of material as is indicated—at least in part—in this article, the absence of a comprehensive theory of sulphonation should invite comment, the difficulties of separating the mixtures of soluble acids or salts, and of recognising the presence or demonstrating the absence in a melt of those small amounts of isomeric acids on which the validity of any theory must ultimately rest, should not be forgotten. These difficulties, as all experience would suggest, may not be insuperable, but until they have been overcome the prospect of more adequate views on the mechanism of this highly important industrial process seems to be remote.

Laws of Substitution in the Naphthalene Series.

Reference has been made to the fact that monosubstitution occurs mainly in the α-position. When a second radicle enters the

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[1] Until their nature and the operative conditions are better understood, changes of this type can be classified only as intramolecular or isomeric. Apart from the many cases of "isomeric change" among sulphonic acids, two others are sufficiently remarkable to merit reference, viz. the conversion of naphthalene-α-sulphohydroxamic acid $C_{10}H_7{\cdot}SO_2{\cdot}NH{\cdot}OH$ into naphthalene-β-sulphinic acid and of dinaphthalene-α-sulphohydroxamic acid $(C_{10}H_7{\cdot}SO_2)_2N{\cdot}OH$ into the β-compound by dilute alkali solutions at the ordinary temperature (Angeli, Angelico and Scurti, Gazz. chim. ital. 1903, 33, ii. 296).

[2] The existence of 1:2-, 1:4-, and 1:8-naphthalenedisulphonic acids, prepared by indirect methods, makes the "invincible objection" of sulphonic groups to assume, or to remain in, these positions during sulphonation the more remarkable (Armstrong and Wynne, Chem. Soc. Proc. 1890, 6, 133; 1893, 9, 166). With nitric acid, no such difficulty is encountered (*v. Di-* and *tri-nitronaphthalenes*). The similarity in the orientating effect of the NO_2 and SO_3H radicles in benzene does not extend without modification to naphthalene.

molecule it may do so in the same ring as the first—homonucleally—or in the other ring—heteronucleally. As in the case of benzene, it is possible to indicate in general terms the directing influence of the radicle already present on the position taken up by the entering substituent, but a comparison of the laws of the two series, benzene and naphthalene, shows important differences. Summarised with reference only to the naphthalene derivatives which find a place in this article, the laws are as follows :—

Homonucleal substitution in position 4, or in positions 2 and 4 occurs—

(i.) When Cl, OH, or NHAc [1] is already present in the *α*- position;

but in position 1, or in positions 1 and 4—

(ii.) When OH or NHAc is already present in the *β*- position.

Heteronucleal substitution in position 5, or in positions 5 and 8, occurs—

(i.) When NO_2 or SO_3H is already present in either the *α*- or the *β*- position.

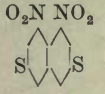
(ii.) When Cl or NH_2 is already present in the *β*- position.

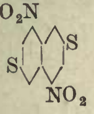
Tri-substitution. The evidence of directing influence obtained in the course of the production of tri- from di-substitution derivatives does not admit, at present, of broad generalisation, but from the facts accumulated about nitration and sulphonation, two deductions can be drawn :—

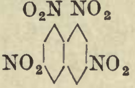
(i.) The non-existence of derivatives in which SO_3H groups occupy relatively the 1 : 2-,[2] 1 : 4-, or 1 : 8- position, has its counterpart in the rare occurrence of nitro- compounds containing NO_2 groups relatively in the 1 : 2- or 1 : 4- position. The analogy does not extend to the 1 : 8- position, many 1 : 8- dinitro-derivatives being known.

(ii.) The inhibition of 1 : 2-disulphonation and largely of 1 : 2- dinitration extends to the sulphonation of nitro- compounds, and to the nitration of sulphonic acids. No case is known in which a NO_2 and a SO_3H group occupy relatively the 1 : 2- or the 2 : 1- position.

As an illustration of the effect of these restrictions on the orientation of nitration products, the constitution of the following substances, said to be the only dinitration products of naphthalene-2 : 6-, and -2 : 7-disulphonic acids, and of 1 : 8-dinitronaphthalene, may be quoted :



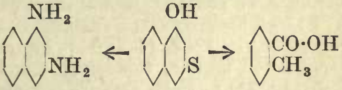




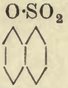
Properties peculiar to 1 : 3- *and* 1 : 8- *Derivatives.*

While the properties of the 1 : 2- and 1 : 4-derivatives of naphthalene resemble, in the main, those of the corresponding *ortho*- and *para*- derivatives of benzene, there is no such agreement between the properties of 1 : 3-derivatives in the two series. For this reason the use of the prefix *meta*- for naphthalene compounds of this orientation is apt to be misleading. Moreover, from the point of view of substitution, it is evident (*v. supra*) that the 5- and 8- positions, more nearly than the 3-position, in naphthalene have the functions of the *meta*- position in benzene.

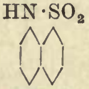
As examples of properties peculiar to di- (and tri-) derivatives of naphthalene containing the radicles OH, NH_2, or SO_3H relatively in the 1 : 2- position, reference may be made to the conversion of *α*-naphthol- or *α*-naphthylamine-3-sulphonic acid [3] into 1 : 3-diaminonaphthalene by interaction with ammonia, and into *o*-toluic acid by fusion with caustic potash.



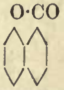
Turning to 1 : 8- or *peri*- derivatives, certain of these furnish internal condensation products, *e.g.* naphthalic anhydride, recalling the behaviour of some 1 : 2- or *ortho*- derivatives under similar conditions. But, as condensation in each of these positions is dependent on the possibility of a 5- or 6- membered ring being formed, many of the products arise from reactions applicable only to the one series or the other, but not to both. For example, among the well-known *ortho*- condensation products, anhydrides of the following types obtained with *peri*-derivatives are not represented :



Sultone.



Sultam.



Lactone.

DEVELOPMENT OF NAPHTHALENE CHEMISTRY SINCE 1890.

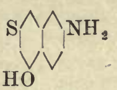
During the interval since the publication of the first edition of this Dictionary, the chemistry of naphthalene has been explored with a degree of completeness which seems to suggest that little of technical importance remains to be discovered. Most of the work dealing with the production of substances of possible or actual value in the manufacture of azo- dyes is to be found in Patents published before the end of last century, and much of it has been accomplished by applications or variations of well-known processes to which reference is not necessary in this place. But there are three subjects sufficiently remarkable in themselves to call for more extended notice than is possible in the summaries prefacing the various sections of this article, namely :—

(i.) 2-Amino-5-naphthol-7-sulphonic or J- acid as a source of direct cotton dyes;

(ii.) The bisulphite reaction, confined almost entirely to naphthalene derivatives;

(iii.) The naphthazarin reaction, elucidated first in connection with compounds of the hydroxyanthraquinone series.

2-Amino-5-naphthol-7-sulphonic acid. Among isomeric aminonaphtholsulphonic acids, the chief interest attaches to the 2 : 5 : 7- or J- acid, which, unlike all other aminonaphthol derivatives, resembles *para*diamines (benzidine, &c.) and sulphur bases (dehydrothiotoluidine, primuline, &c.) in endowing most of the azo dyes of



J- acid.

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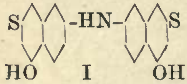
[1] Reference to *α*-naphthylamine derivatives will show that a summary of the directing influence of the NH_2 radicle in *α*-compounds cannot easily be made.

[2] *α*-Naphthasultamtrisulphonic acid (*q.v.*) is a possible exception.

[3] The *β*-naphthol- and *β*-naphthylamine-4-sulphonic acids yield the toluic acid but not the diamine.

which it is a component with the valuable property of dyeing unmordanted cotton.[1] This fact was recognised first of all[2] in disazo-dyes containing the N-ethyl derivative of J-acid as end component (*cf.* Leonhardt, D. R.-P. 95624; Eng. Pat. 10699 of 1895), then in those from its N-phenyl derivative, from J-acid itself (*ibid.* D. R.-P. 114248 of 1896), and also from 2-amino-5-naphthol-7 : 1-disulphonic acid (*ibid.* D. R.-P. 117950 of 1896). Nevertheless, the utilisation of this discovery seems to date from the introduction of direct cotton dyes produced from 5 : 5′-dihydroxy-2 : 2′-dinaphthylamine-7 : 7′-disulphonic acid (I *infra*) by coupling with diazotised aniline, toluidine, &c. (Bayer, D. R.-P. 114841; Eng. Pat. 24296 of 1899), followed by a series of direct cotton monoazo dyes (*ibid.* D. R.-P. 122905; Eng. Pat. 2683 of 1900), disazo dyes (*ibid.* D. R.-P. 129494 of 1900; Gesellsch., D. R.-P. 126802 of 1901), and trisazo dyes (Bayer, D. R.-P. 121867; Eng. Pat. 3673 of 1900) obtained from J-acid itself.

Experience showed that the affinity for unmordanted cotton was increased by the substitution of acyl radicles in the amino- group of J-acid,[3] and, of the many derivatives examined, the azo dyes from the substituted ureas (II) gave, perhaps, the best results in this respect.



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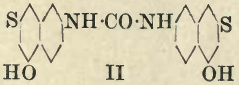
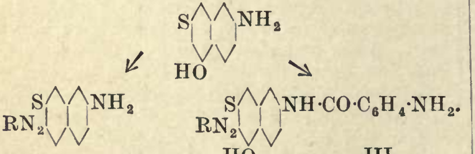


II

But these dyes, although pure in shade and fast to acids, were less fast to alkalis. By transference of the diazotisable amino- group in the monoazo dyes of J-acid from the naphthalene nucleus to a benzene ring present in the acyl radicle (III), fastness to alkalis also was secured (*cf.* Gesellsch., D. R.-P. 151017; Eng. Pat. 13778 of 1902; D. R.-P. 170045; Eng. Pat. 24936 of 1903).



III

These aminoarylacyl-2-amino-5-naphthol-7-sulphonic acids when coupled in alkaline solution give monoazo- dyes which can be diazotised on the fibre, and, without any essential alteration in shade, developed with β-naphthol and thereby rendered fast to washing.[4] By appropriate substitution, therefore, it is possible to obtain from J-acid direct cotton dyes of any desired degree of intensity, purity of shade, or fastness.

The bisulphite reaction.—For more than forty years Piria's discovery of the reduction of α-nitronaphthalene to α-naphthylaminesulphamic (thionaphthamic) acid and naphthionic acid by aqueous alcoholic ammonium sulphite (Annalen, 1851, 78, 31), remained an isolated fact. The interest attaching to the reaction is nevertheless considerable, as the conversion of α-naphthylamine into naphthionic acid by the usual method requires both concentrated sulphuric acid and a high temperature.

From the patents of Fischesser & Co. (D. R.-P. 76438 of 1893; 79577 of 1894), it is evident that the method is of restricted application, but can be used for the simultaneous reduction and sulphonation of α-nitronaphthalene-3 : 8-disulphonic acid, and of 1 : 5-dinitro- or (*cf.* Höchst, D. R.-P. 215338 of 1908) of 1 : 8-dinitro-naphthalene by the aid of sodium bisulphite solution. Further, α-nitronaphthalene with a large excess of bisulphite yields not Piria's compounds, but α-naphthylamine-2 : 4-disulphonic acid[5] (Höchst, D. R.-P. 92082 of 1895).

In none of these cases is the nitrogen atom eliminated from the molecule as the result of the interaction with bisulphite, but in the last recorded application of the process—conversion of 1 : 8-dinitronaphthalene-3 : 6-disulphonic acid into 1-amino-8-naphthol-3 : 6-disulphonic acid (Bayer, D. R.-P. 113944 of 1899; *cf.* Bucherer, J. pr. Chem. 1904, [2] 70, 349), replacement of a NO_2 (or NH_2) group by OH was observed, and a new field for investigation opened up.

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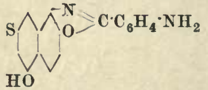
[1] Certain disazo dyes, with J-acid as middle component and nitro-*o*-diazophenols as end components are unsuitable for dyeing unmordanted cotton (Oehler, D. R.-P. 151332; Eng. Pat. 8575 of 1903).

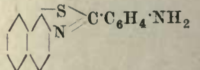
[2] J-acid, obtained from Armstrong and Wynne's β-naphthylamine-5 : 7-disulphonic acid (Badische, D. R.-P. 75469; Eng. Pat. 2614 of 1893), was employed originally for the production of direct cotton dyes by coupling with diazotised *para*diamines (*ibid.*), or dehydrothiotoluidine (*cf.* Bayer, D. R.-P. 88846, 92708; Eng. Pat. 10629 of 1894), its specific cotton fixing capacity being thereby obscured.

[3] The following acyl and other derivatives have been studied in this connection, R being J-acid in the amino- group of which substitution has occurred:
CH_3·CO·R (Bayer, D. R.-P. 119828; Eng. Pat. 2683 of 1900).
C_6H_5·CO·R (*ibid*, D. R.-P. 127141 of 1900).
R·C(NH)·R (*ibid.* D. R.-P. 129417, 132537; Eng. Pat. 18939 of 1900).
R·CH_2·CO·R (*ibid.* D. R.-P. 126443, 128195; Eng. Pat. 18939 of 1900).
R·CH_2·CH_2·R (*ibid.* D. R.-P. 129478, 126801; Eng. Pat. 18939 of 1900).
R·CS·R (*ibid.* D. R.-P. 116201, 122286, 126133 of 1899; Eng. Pat. 3615 of 1900).
R·CO·R (*ibid.* D. R.-P. 116200, 122904 of 1899; Eng. Pat. 3615 of 1900).

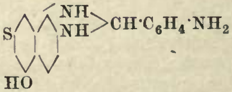
[4] In the other naphthalene derivatives which have been found to give cotton dyeing powers to azo dyes of which they are components, this method of securing fastness to alkalis without alteration in shade, is also used. Compare, for example:—



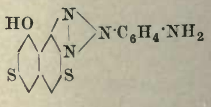
(Bayer, D. R.-P. 165102 of 1904; Eng. Pat. 1675 of 1905).



(Bayer, D. R.-P. 166903: Eng. Pat. 27843 of 1905).



(Cassella, D. R.-P. 209110 of 1907).



(Gesellsch., D. R.-P 146375 of 1902).

[5] Bucherer (J. pr. Chem. 1904, [2] 69, 50) makes the interesting statement that occasionally a small quantity of α-naphthol-4-sulphonic acid is formed in this reaction.

Two nitroso-compounds, α-nitroso-β-naphthol and β-nitroso-α-naphthol, also undergo this type of change with sodium bisulphite solution, furnishing the corresponding aminonaphtholsulphonic acids (Böniger, Ber. 1894, 27, 23).

Slightly earlier in date than this patent of Bayer & Co., is one in which it is shown that the conversion of α-naphthylamine- into α-naphthol- derivatives can be achieved under the influence of sodium bisulphite solution in open vessels at the boiling-point (Bayer, D. R.-P. 109102 of 1899). With β-naphthylamine derivatives, unless a large excess of bisulphite is used (Badische, D. R.-P. 134401 of 1899; *cf.* Bucherer and Stohmann, J. pr. Chem. 1905, [2] 71, 436), condensation to ββ′-dinaphthylamine derivatives occurs (Bayer, D. R.-P. 121094 of 1900).

The clue to these results was supplied by the discovery that in this reaction a highly soluble intermediate compound is formed, which, although stable towards acids, is decomposed by alkalis with the production of ammonia and the naphthol.[1] This intermediate compound is a sulphite (Badische, D. R.-P. 126136 of 1899), identified as a naphthyl sulphite, as it does not couple with diazotised bases, and can be obtained from the corresponding naphthol derivative by interaction with bisulphite (Badische, D. R.-P. 115335 of 1899).

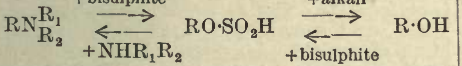
I. $R\cdot NH_2+2NaSO_3H\rightarrow RO\cdot SO_2H+Na_2SO_3+NH_3$
II. $R\cdot OH+2NaSO_3H\rightarrow RO\cdot SO_2H+Na_2SO_3+H_2O$

The naphthyl sulphite, which by alkalis is hydrolysed forming the naphthol, regenerates the naphthylamine by interaction with ammonia; the reversal of the reaction discovered by Bayer & Co. can therefore be effected (Badische, D. R. P. 117471 of 1899)—

III. $RO\cdot SO_2H+3NH_3\rightarrow R\cdot NH_2+(NH_4)_2SO_3$.

Usually ammonium sulphite replaces sodium bisulphite in the first stage (II), and the conversion of the naphthol into naphthylamine derivative is conducted at 100° in pressure vessels (to prevent escape of ammonia), the yield being almost quantitative, as against 30–65 p.c. when the naphthol derivative is heated with ammonia and ammonium chloride at a high temperature.

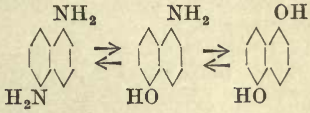
By the use of methylamine, aniline or their homologues in place of ammonia in reaction III, alkylated α- and β-naphthylamines (Badische, D. R.-P. 121683 of 1900) and arylated β-naphthylamines (Badische, D. R.-P. 122570 of 1900) can be obtained. In the Patent literature and in the papers published by Bucherer (J. pr. Chem. 1904, [ii.] 69, 47; 70, 345; 1905, [ii.] 71, 433), to whom the detailed study of the reaction is due, a convenient expression for the bisulphite reaction is given, which shows clearly the reversible nature of the change:—



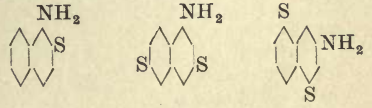
$$RN\begin{matrix}R_1\\R_2\end{matrix}\ \underset{+NHR_1R_2}{\overset{+\text{bisulphite}}{\rightleftarrows}}\ RO\cdot SO_2H\ \underset{+\text{bisulphite}}{\overset{+\text{alkali}}{\rightleftarrows}}\ R\cdot OH$$

in which R is a naphthyl radicle and R_1R_2 are hydrogen, alkyl, or (for β- compounds only) aryl radicals.

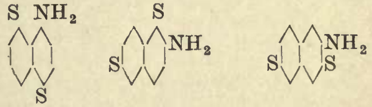
With the exception of derivatives of *m*-dihydroxy- and *m*-diamino-benzene the bisulphite reaction is confined to the naphthalene series, and it is dependent on the use of a large excess (3–5 mols.) of the reagent. It is applicable to diaminonaphthalene, aminonaphthol and dihydroxynaphthalene derivatives as well as to the naphthylamines and naphthols,



its technical importance being therefore evident. But it is subject to restrictions; for example, it does not succeed with α- derivatives in which a substituent is present in the 2- or 3- position, or with β- derivatives in which a substituent is present in the 4- position, such as the acids:

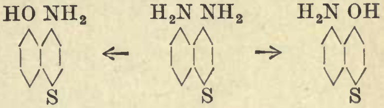


although it takes place easily with acids in which these respective positions are not occupied:

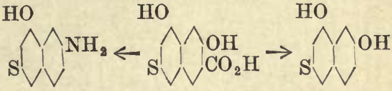


Many interesting applications of the reaction are to be found in the literature, from which two may be taken by way of illustration:

(*a*) 1:8-Diaminonaphthalene-4-sulphonic acid will furnish either the 4- or the 5-sulphonic acid of 1-amino-8-naphthol according as the process is conducted in the presence or absence of acetone (Badische, D. R.-P. 120016 of 1900):—



(*b*) Two formulæ are possible for the aminonaphtholsulphonic acid, and two for the dihydroxynaphthalenesulphonic acid obtained respectively by fusing β-naphthylamine- and β-naphthol-6:8-disulphonic acids with caustic potash. That these acids have the formulæ I and II, and not the alternative formulæ,



I Nigrotic acid. II

is established by the fact that they can be formed from nigrotic acid by interaction with sodium bisulphite and with ammonium sulphite respectively (Bucherer, J. pr. Chem. 1907, [2] 75, 287).

The naphthazarin reaction. Naphthazarin is formed when a solution of 1:5-dinitronaphthalene in sulphuric acid or anhydro-acid is heated with a reducing agent, such as sulphur or zinc, and the blue solution formed by pouring the product into water is boiled until the colour has changed to red. Although the constitution of naphthazarin was determined finally in 1895 to be 5:6-dihydroxy[α]-naphthaquinone (Will, Ber. 1895,

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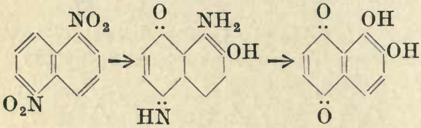
[1] This process differs essentially from that in which the exchange of NH_2 for OH is effected at high temperatures under the influence of water or mineral acids. The end products of the two reactions are usually the same, but differences between them are not unknown, *e.g.* naphthionic acid is converted almost quantitatively by the bisulphite method into α-naphthol-4-sulphonic acid, but by the acid method into α-naphthol.

28, 2234) by production of the substance from 1 : 2 : 5 : 8-tetranitronaphthalene, that of the 'intermediate product' which dissolves in water with the blue colour first observed by Aguiar (Ber. 1871, 4, 439) has not been established by direct experiment. As reference to naphthazarin (p. 656) will show, the numerous patents of the Badische Company and of other firms taken out in 1896–1900, together with the investigations of Graebe (Ber. 1899, 32, 2876; *cf.* Graebe and Oeser, Annalen, 1904, 335, 153; Badische, D. R.-P. 91391 of 1896) and of Friedlaender (Ber. 1899, 32, 3528) on the nitronitrosonaphthols isolated from the naphthazarin melt, suggest a close resemblance to the reaction between 1 : 5-dinitroanthraquinone, anhydrosulphuric acid and sulphur at 50° which leads to the formation of a soluble bluish 'intermediate' product identified as 1-nitro-5-nitroso-8-hydroxyanthraquinone (Bayer, D. R.-P. 104282 of 1898; *cf.* 105567 of 1897). By analogy, the naphthazarin reaction therefore is represented by the formulæ:



I II

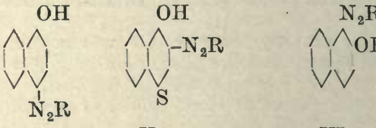
The 1-nitro-5-nitroso-8-hydroxynaphthalene (nitronitrosonaphthol) is formed at relatively low temperatures, but the 'intermediate product' (I) at higher temperatures, passing when boiled with dilute acids into naphthazarin (II), with elimination of the NH_2 radicle as ammonia.

Diazo and Azo Compounds.

Without exception, diazotised bases couple homonucleally with naphthols, naphthylamines, or their sulphonic acids,[1] and in the formation of azo dyes from the β- compounds, the remarkable difference between contiguous homonuclear αβ- and ββ- positions, to which reference has been made (p. 563), is constantly in evidence. For example:

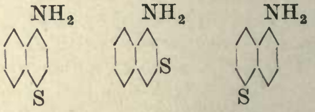
α-Naphthol will couple in the 4- position, and its derivatives in this position also if it be not occupied (I), otherwise they couple in the 2- position (II); but

β-Naphthol and its derivatives will couple only in the contiguous 1- position (III):

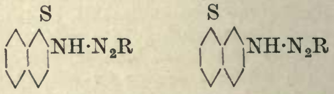


I II III

To this generalisation there are exceptions, due probably to steric hindrance, among amino- and hydroxy-naphthalenesulphonic acids of certain configurations. Thus the α-naphthylamine- or α-naphthol-sulphonic acids of the formulæ:



couple in the 2- position, although in one of them only is the 4- position occupied; and β-naphthylamine-8-sulphonic acid and its derivatives, like the 1-sulphonic acids, furnish diazo amino- compounds instead of azo derivatives:



Other examples of this deviation from the general rule will be found among sulphonic acids of the diaminonaphthalenes, aminonaphthols, and dihydroxynaphthalenes.

The position of the azo group in azo dyes can be determined either by reduction, *e.g.* with stannous chloride (Witt, Ber. 1888, 21, 3471), or with sodium hypo- ('hydro-') sulphite (Grandmougin, *ibid.* 1906, 39, 2494, 3561, 3929), whereby the base used for diazotisation and an amino derivative of the second component are obtained; or by fission with cold fuming nitric acid (Schmidt, *ibid.* 1905, 38, 3202; *cf.* Meldola and Hanes, Chem. Soc. Trans. 1894, 65, 841), whereby the diazo compound used and nitro derivative of the second component are formed. The former of these processes has found some application in the preparation of aminonaphthalene derivatives (*v. Diaminonaphthalene-* and *aminonaphthol-sulphonic acids*).

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[1] The following trivial names are given to sulphonic acids employed in the manufacture of azo dyes:—

Naphthylaminesulphonic acids [$NH_2 : SO_3H$]
[1 : 4] Naphthionic [2 : 6] Brönner
[1 : 5] Laurent [2 : 7] F-acid
[1 : 8] S or Schöllkopf [2 : 8] Badische

Naphthylaminedisulphonic acids [$NH_2 : SO_3H : SO_3H$]
[1 : 3 : 8] ε-disulpho. [2 : 3 : 6] Amino-R
[1 : 4 : 8] Disulpho. S [2 : 3 : 7] Disulpho. F
[2 : 4 : 8] Disulpho. C
[2 : 6 : 8] Amino-G

Naphtholsulphonic acids [$OH : SO_3H$]
[1 : 4] Nevile & Winther [2 : 6] Schaeffer
[1 : 5] L-acid [2 : 7] F-acid
[1 : 8] S-acid [2 : 8] Croceïc-acid

Naphtholdisulphonic acids [$OH : SO_3H : SO_3H$]
[1 : 3 : 8] Disulpho. E [2 : 3 : 6] R-acid
[1 : 4 : 8] Disulpho. S [2 : 3 : 7] F-acid
[2 : 4 : 8] C-acid
[2 : 6 : 8] G-acid

Aminonaphtholsulphonic acids [$NH_2 : OH : SO_3H$]
[1 : 5 : 7] M-acid [2 : 3 : 6] R-acid
[1 : 7 : 3] B-acid [2 : 5 : 7] J-acid
[1 : 8 : 3] H-monosulpho. [2 : 7 : 3] F-acid
[1 : 8 : 4] S-acid [2 : 8 : 6] G-acid
[2 : 8 : ?] V-acid

Aminonaphtholdisulphonic acids [$NH_2 : OH : SO_3H : SO_3H$]
[1 : 8 : 2 : 4] S-acid [1 : 8 : 4 : 6] K-acid
[1 : 8 : (2) : ?] L-acid [1 : 8 : (5) : ?] D-acid
[1 : 8 : 3 : 5] B-acid
[1 : 8 : 3 : 6] H-acid [2 : 8 : 3 : 6] 2 R-acid

Dihydroxynaphthalenesulphonic acids [$OH : OH : SO_3H$]
[1 : 5 : 2] C-acid [2 : 3 : 6] R-acid
[1 : 7 : 3] G-acid [2 : 7 : 3] F-acid
[1 : 8 : 3] ε-acid
[1 : 8 : 4] S-acid

Dihydroxynaphthalenedisulphonic acids [$OH : OH : SO_3H : SO_3H$]
[1 : 3 : 5 : 7] Yellow acid (Gelbsäure)
[1 : 5 : 3 : 7] Red acid (Rotsäure)
[1 : 7 : 3 : 6] A-acid
[1 : 8 : 2 : 4] S-acid [1 : 8 : ? : ?] I-, G-, and R-acids
[1 : 8 : 3 : 5] K-acid [2 : 3 : 6 : 8] B-acid
[1 : 8 : 3 : 6] Chromotrope acid

Dihydroxynaphthalenecarboxylic acids [$OH : OH : CO_2H$]
[1 : 7 : 6] S-acid [2 : 6 : 3] L-acid

Carbodihydroxynaphthalenesulphonic acid [$OH : OH : CO_2H : SO_3H = 1 : 7 : 6 : 3$] Nigrotic acid.

Reference is made in the article Azo- colouring matters (*q.v.*) to the differing capacity of isomeric naphthylamine- and naphthol-sulphonic acids for combination with diazotised bases. This property can be utilised in appropriate cases for the separation of isomeric sulphonic acids. For example:

(i.) The sulphonation product of β-naphthol at 50°–60° contains Schaeffer's and croceïc acids, of which the latter only is of value for the manufacture of croceïn-scarlet. Schaeffer's acid couples with diazotised benzidine, whereas croceïc acid does not; hence by fractional precipitation (as a disazo compound) the former can be removed, leaving the latter in a state of purity (Bayer, D. R.-P. 30007; Eng. Pat. 8495 of 1884).

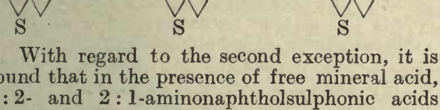
(ii.) β-Naphthylamine-3:6-disulphonic acid, obtained by heating β-naphthol-3:6-disulphonic acid (R-acid) with ammonia under pressure, can be freed from any unchanged hydroxy acid (which spoils the shade of azo- dyes formed from the amino- acid) by fractional treatment with diazobenzene or diazoxylene (Cain, *priv. comm.*).

Diazo-oxides.—The formation of diazo compounds by interaction of naphthylamine- or aminonaphthol-sulphonic acids with nitrous acid proceeds normally except with:—

(*a*) Naphthylaminesulphonic acids containing one SO_3H group in the ortho- (1- or 2-) position relatively to the amino- radicle;

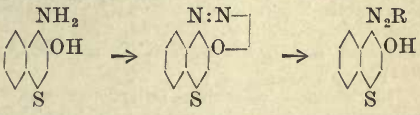
(*b*) 1:2- and 2:1-aminonaphtholsulphonic acids or their derivatives.

With respect to the first exception, it is found that when warmed with solutions of alkali carbonates or acetates, to remove free mineral acid, diazotised α- or β-naphthylamine-*ortho*-sulphonic acids (Badische, D. R.-P. 145906; Eng. Pat. 6615 of 1902; D. R.-P. 156440; Eng. Pat. 27372 of 1903; 160536; Eng. Pat. 4997 of 1904; 162009; Eng. Pat. 21638 of 1904; Höchst, D. P. Anm. F. 16863; Eng. Pat. 23993 of 1902), also diazotised 1-chloro-β-naphthylaminesulphonic acids (Badische, D. R.-P. 145906; 148882 of 1902), and 2:4-dichloro-α-naphthylaminesulphonic acid (Badische, D. R.-P. 153298; Eng. Pat. 16995 of 1903), furnish anhydrides (diazo oxides) of hydroxydiazonaphthalenesulphonic acids, *e.g.* for β- compounds:



With regard to the second exception, it is found that in the presence of free mineral acid, 1:2- and 2:1-aminonaphtholsulphonic acids are not diazotised by nitrous acid (Witt, Ber. 1888, 21, 3475), but oxidised to [β-]naphthaquinonesulphonic acids (Böniger, *ibid.* 1894, 27, 24; *cf.* Badische, D. R.-P. 153298; Eng. Pat. 16995 of 1903). By removal of free mineral acid, diazotisation of these aminonaphthols to diazo oxides has been rendered possible (Weiler-ter Meer, D. R.-P. 155083 of 1903; Badische, D. R.-P. 157325 of 1903), and almost quantitative in the presence of cupric and ferric salts (Geigy, D. R.-P. 171024; Eng. Pat. 10235 of 1904; D. R.-P. 172446 of 1904), zinc salts (Kalle, D. R.-P. 175593; Eng. Pat. 23034 of 1904), nickel salts (*ibid.*, D. R.-P. 178621 of 1905), or mercuric salts (*ibid.*, D. R.-P. 178936 of 1905). But as these salts are found to spoil the brightness and solubility of the derived azo dyes, they may with advantage be replaced by salts of the alkali or alkaline earth metals (Badische, D. R.-P. 189179; Eng. Pat. 10323 of 1906).

The diazo oxides form non-explosive, yellow, crystalline powders (Geigy, D. R.-P. 171024; Eng. Pat. 10235 of 1904); they can be chlorinated (Kalle, D. R.-P. 246574 of 1911); brominated (Sandoz, D. R.-P. 236656 of 1910); nitrated by nitrosulphuric acid without decomposition (Geigy, D. R.-P. 164655; Eng. Pat. 15418 of 1904; Kalle, D. R.-P. 176619 of 1905); and sulphonated by anhydrosulphuric acid (*ibid.* D. R.-P. 176618, 176620 of 1905). Their coupling capacity, probably as the result of their structure:



is not pronounced, except for resorcinol (Badische, D. R.-P. 148881 of 1902); the derived *ortho*-hydroxyazo-dyes give fast bluish black shades on chromed wool.

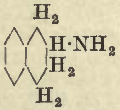
Tetrahydronaphthalene Derivatives.

On reduction in boiling amyl alcohol solution with sodium, naphthalene (Bamberger and Kitschelt, Ber. 1890, 23, 1561) and the naphthylamines and naphthols (Bamberger, Annalen, 1890, 257, 2) are converted into tetrahydro-derivatives, of which two types exist:—

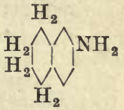
(1) Those termed *alicyclic* (or *ac.*-) derivatives, in which both the substituent and the four added hydrogen atoms are in the same ring.

(2) Those termed *aromatic* (or *ar.*-) derivatives, in which the substituent is in one and the four added hydrogen atoms in the other ring.

With α-naphthylamine and α-naphthol, 'aromatic' derivatives are exclusively formed, but with β-naphthylamine and β-naphthol both types of derivative are obtained, the 'alicyclic' compound forming about 95 p.c. of the product:



(*ac.*-derivative.)



(*ar.*-derivative.)

The specific properties which distinguish corresponding derivatives of naphthalene and benzene are suppressed in the tetrahydronaphthalene derivatives, and, in connection with the naphthalene theory, it may be noted that 'alicyclic' compounds display the characters of the secondary amines and alcohols of the fatty series, whereas 'aromatic' compounds show a close analogy in properties with the *o*-xylidines and *o*-xylenols of the benzene series. Physiologically *ac.*-tetrahydro-β-naphthylamine ('Thermine,' *cf.* J. Soc. Chem. Ind. 1890, 9, 888) and its alkyl-derivatives are interesting on account of their powerful mydriatic properties (Bamberger and Filehne, Ber. 1889, 22, 777).

I. Chloro-Derivatives.

Introductory.—Naphthalene derivatives, in which chlorine is associated with the carbon atoms of the nucleus, are of two kinds: additive compounds (*e.g.* naphthalene dichloride and tetrachloride) and those in which substitution of chlorine for hydrogen has taken place, viz. the chloronaphthalenes.

The formation of chloronaphthalenes can be achieved by the following methods:

(1) By chlorination of naphthalene or chloronaphthalenes (*cf.* Faust and Saame, Annalen, 1871, 160, 65; E. Fischer, Ber. 1878, 11, 735; Widman, *ibid.* 1882, 15, 2160; Armstrong and Wynne, Chem. Soc. Proc. 1890, 6, 85; Badische, D. R.-P. 234912 of 1910).

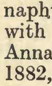
(2) From aminonaphthalenes by diazotisation and the Sandmeyer reaction (*cf.* Friedlaender and Szymanski, Ber. 1892, 25, 2081; Chattaway and Lewis, Chem. Soc. Trans. 1894, 65, 877).

(3) From nitro-, amino-, or hydroxynaphthalenesulphonic acids by conversion into chlorosulphonic acids and subsequent hydrolysis (*cf.* Cleve, Ber. 1892, 25, 2487).

(4) From naphthalenesulphonyl, or chloronaphthalenesulphonyl chlorides, by heating them with phosphorus pentachloride (*cf.* Carius, Annalen, 1860, 114, 145; Armstrong, Ber. 1882, 15, 205), or alone (*cf.* Armstrong and Wynne, Chem. Soc. Proc. 1895, 11, 80, 83; 1897, 13, 152).

(5) From nitronaphthalene (de Koninck and Marquart, Ber. 1872, 5, 11), and from nitronaphthalenesulphonyl chlorides (Erdmann and Süvern, Annalen, 1893, 275, 232, 252) by distillation with phosphorus pentachloride.

Allusion has been made to the complete series of mono-, di- and tri-chloronaphthalenes and to their use as reference compounds (p. 565). As sources of naphthol or naphthylamine derivatives certain of the α-chloronaphthalenesulphonic acids, viz. the 4- and 5- mono-, the 4 : 7-di- and the 2 : 4 : 7-tri- sulphonic acids (the last most readily) or 4-chloro- α-nitronaphthalene can be used, as in them the halogen can be exchanged for NH_2 or OH by digestion with caustic alkali or ammonia.



α-Chloronaphthalene is obtained when chlorine is passed into boiling naphthalene (Rymarenko) in the presence of ferric chloride (Oehler, D. P. Anm. O. 1921 of 1893) until the calculated increase in weight has been attained; when naphthalene dichloride is decomposed by heat or by alcoholic potash (Faust and Saame, Annalen, 1871, 160, 68; Armstrong and Wynne, Chem. Soc. Proc. 1890, 6, 85); or when diazotised α-naphthylamine hydrochloride is warmed with hydrochloric acid (Gasiorowski and Wayss, Ber. 1885, 18, 1940), or cuprous chloride solution (Atterberg, Bull. Soc. chim. 1894, [iii.] 65, 877). It boils at 263°, and has the sp.gr. 1·2025 at 15°.

Reactions.—(1) On nitration, it is converted into 4-*chloro-α-nitronaphthalene* (Atterberg, Ber. 1876, 9, 927), mixed with the 5- and 8- derivatives in small quantity (Griesheim, D. R.-P. 120585 of 1900).

(2) By sulphonation, it yields the 4-, 5-, 6-, and 7-*monosulphonic*, the 4 : 7- and a second *disulphonic* and the 2 : 4 : 7-*trisulphonic acids* (*v. infra*).

Dichloronaphthalenes. A mixture of 1 : 4- and 1 : 5- dichloronaphthalenes is obtained when naphthalene, with a carrier (ferric chloride, iodine, etc.), is chlorinated in carbon tetrachloride solution at −10° to 0°; the product contains small amounts of the 1 : 2- and 1 : 7-derivatives, which can be removed as sulphonic acids by sulphuric acid in the cold (Badische, D. R.-P. 234912 of 1910).

Perchloronaphthalene $C_{10}Cl_8$ is formed by exhaustive chlorination of naphthalene, finally in the presence of antimony trichloride (Berthelot and Jungfleisch, Bull. Soc. chim. 1868, [ii.] 9, 446). It crystallises in long needles, m.p. 203°, is moderately soluble in benzene or light petroleum, and when heated with 70 p.c. anhydro- acid at 50° is converted into a red dyestuff of unknown composition (Badische, D. R.-P. 66611 of 1892).

Naphthalene tetrachloride $C_{10}H_8Cl_4$ is formed together with oily impurities containing, according to the conditions employed, varying quantities of naphthalene dichloride, α-chloronaphthalene tetrachloride, and a dichloronaphthalene tetrachloride, by the action either of chlorine (Faust and Saame, Annalen, 1871, 160, 67), or of potassium chlorate and hydrochloric acid (E. Fischer, Ber. 1878, 11, 735) on naphthalene. According to Leeds and Everhart (J. Amer. Chem. Soc. 1880, 2, 208), the best yield (45 p.c.) is obtained by leaving naphthalene in thin layers in an atmosphere of chlorine until absorption is complete. Extraction of the product with light petroleum, to remove dichloride, and with alcohol, leaves the tetrachloride in a pure state. It crystallises from chloroform in large rhombohedra, m.p. 182°.

Reaction.—When heated at 100° with 8·7 times its weight of nitric acid (sp.gr. 1·45), it yields 2 : 3-*dichloro*-[*α*-]*naphthaquinone* (Helbig, Ber. 1895, 28, 505), or, boiled with ten times its weight, *phthalic acid* (Fischer, *l.c.*); but with chromic acid at 90° it gives 3 : 4-*dichloro-α-naphthol* (Helbig. *l.c.*).

α-Chloronaphthalenesulphonic Acids.

Introductory.—α-Chloronaphthalenesulphonic acids can be obtained by three methods:

(1) From the corresponding α-naphthylaminesulphonic acids by diazotisation and interaction with cuprous chloride solution.

(2) From α-chloronaphthalene by sulphonation, the products with sulphuric acid being successively the 4-, the 5-, and a mixture of the 6- and 7-monosulphonic acids as the temperature is raised gradually to 160°–170°, and the 4 : 7- (possibly also the 2 : 7-) disulphonic acid at 180°–190°.

(3) From sodium naphthalene-α- or β-sulphonate by chlorination.

When prepared by the last two methods, these acids can be used for the production of α-naphthylaminesulphonic acids, but the process has no technical importance.

(i.) α-**Chloronaphthalene-4-sulphonic acid** is the chief product when α-chloronaphthalene is sulphonated with chlorosulphonic acid in the cold (Armstrong and Wynne, Chem. Soc. Proc. 1900, 6, 86). Its *chloride* forms triclinic prisms, m.p. 95° (Cleve, Ber. 1887, 20, 73).

Reactions.—(1) When heated with 25 p.c. ammonia solution under pressure at 200°–210°, it is converted into *naphthionic acid* (Oehler, D. R.-P. 72336 of 1893).

(2) By digestion with 25 p.c. caustic soda solution under pressure at 200°–220°, it yields α-*naphthol*-4-*sulphonic acid* (Oehler, D. R.-P. 77446 of 1893).

(ii.) α-**Chloronaphthalene-5-sulphonic acid**, formed in small quantity when α-chloronaphthalene is sulphonated with chlorosulphonic acid in the cold, becomes almost the sole product when the sulphonation mixture is heated at 150° (Armstrong and Wynne, Chem. Soc. Proc. 1900, 6, 87). It can be obtained by chlorinating sodium naphthalene-α-sulphonate with a mixture of sodium chlorate and hydrochloric acid (Rudolph, D. R.-P. 103983; Eng. Pat. 19088 of 1898). Its *chloride* forms rhombic prisms, m.p. 95° (Cleve, Ber. 1887, 20, 73).

Reactions.—(1) When heated with 25 p.c. ammonia solution under pressure at 200°–210°, it is converted into α-*naphthylamine*-5-*sulphonic acid* (Oehler, D. R.-P. 72336 of 1893).

(2) By digestion with 8 p.c. caustic soda solution at 240°–250°, it yields α-*naphthol*-5-*sulphonic acid* (Oehler, D. R.-P. 77446 of 1893).

(iii.) α-**Chloronaphthalene-6-sulphonic acid**, mixed with the 7-*sulphonic acid*, is formed when α-chloronaphthalene is heated with 1–1·5 times its weight of sulphuric acid at 160°–170° for many hours (Oehler, D. R.-P. 76396 of 1893); or when a solution of sodium naphthalene-β-sulphonate is chlorinated by means of chlorine or of sodium chlorate and hydrochloric acid (Rudolph, D. R.-P. 101349; Eng. Pat. 19088 of 1898). By fractional crystallisation its calcium, barium, or sodium salt can be separated from the more soluble salt of the 7-acid. Its *chloride* forms scales, m.p. 114°–115° (Cleve, Ber. 1887, 20, 74); that of the 7-acid, prisms, m.p. 94° (Cleve, Ber. 1892, 25, 2481).

(iv) α-**Chloronaphthalene-4 : 6-disulphonic acid** (*cf.* Armstrong and Wynne, Chem. Soc. Proc. 1900, 6, 126) is formed when sodium α-chloronaphthalene-6-sulphonate is heated with 10 p.c. anhydro-acid at 110° (Rudolph, D. R.-P. 104902 of 1898).

Reaction.—When heated with caustic soda solution under pressure at 210°–230°, it yields 1 : 6-*dihydroxynaphthalene*-4-*sulphonic acid* (Rudolph, *l.c.*).

(v.) α-**Chloronaphthalene-4 : 7-disulphonic acid** is obtained when α-chloronaphthalene is sulphonated with 45 p.c. anhydro-acid at 20°, or with sulphuric acid at 180° [1] (Oehler, D. R.-P. 74744 of 1893); *or* when sodium α-chloronaphthalene-4-sulphonate is sulphonated with 20 p.c. anhydro-acid at 20° (Oehler, *l.c.*), or at 100° (Armstrong and Wynne, Chem. Soc. Proc. 1890, 6, 18). The *barium* salt dissolves sparingly, but the *sodium* salt easily in water; the *chloride* forms prisms, m.p. 107° (Armstrong and Wynne, *l.c.*).

Reaction.—When heated with 30 p.c. caustic soda solution at 200°–210°, it yields α-*naphthol*-4 : 7-*disulphonic acid* (Oehler, *l.c.*).

(vi.) α-**Chloronaphthalene-2 : 4 : 7-trisulphonic acid** is the chief product of the sulphonation of α-chloronaphthalene with 45 p.c. anhydro-acid at 80°, *or* of sodium α-chloronaphthalene-4-sulphonate with 20 p.c. anhydro-acid at 170° (Oehler, D. R.-P. 76230 of 1893). Its *sodium* salt Na_3A+4H_2O forms small needles (Oehler, *l.c.*), and its *chloride* scales, m.p. 215° (Armstrong and Wynne, Chem. Soc. Proc. 1900, 6, 126).

Reaction.—When heated with 12 p.c. caustic soda solution under pressure at 150°, it yields α-*naphthol*-2 : 4 : 7-*trisulphonic acid* (Oehler, D. R.-P. 77996 of 1893).

II. NAPHTHALENESULPHONIC ACIDS.

Introductory.—Naphthalenesulphonic acids can be obtained by the following methods:—

(1) Action of sulphuric acid [2] on naphthalene or on naphthalenesulphonic acids.

(2) Elimination of the NH_2 radicle from naphthylaminesulphonic acids (*cf.* the 1 : 3-acid).

(3) From naphthylaminesulphonic acids by exchange of the NH_2 for the SH or SO_2H radicle, and oxidation of the resulting mercaptan or sulphinic acid (*v.* the 1 : 2-acid).

Of these methods the first is of technical importance, and by it ten naphthalenesulphonic acids (two mono-, four di-, three tri-, and one tetra-) have been obtained. As sulphonating agents,[2] sulphuric acid, anhydro-acid, chlorosulphonic acid, and anhydro-acid to which common salt has been added, are used, but the constitution of the product depends on the temperature and duration of the reaction as well as on the quantity and concentration of the acid. Attention has been called to the fact that sulphuric acid, unlike other substituting agents, gives rise to β- derivatives in large amount (p. 565). If the conditions leading to the production of naphthalene-β-sulphonic acid or of naphthalene-2 : 6-disulphonic acid, for example, are considered, they show that of the four factors named the concentration and temperature of the acid exercise a predominating influence on the relative positions in which the SO_3H radicles are found at the end of a sulphonation.

From the constitution of the acids obtained from naphthalene or from naphthalenesulphonic acids by sulphonation, it is evident that in no

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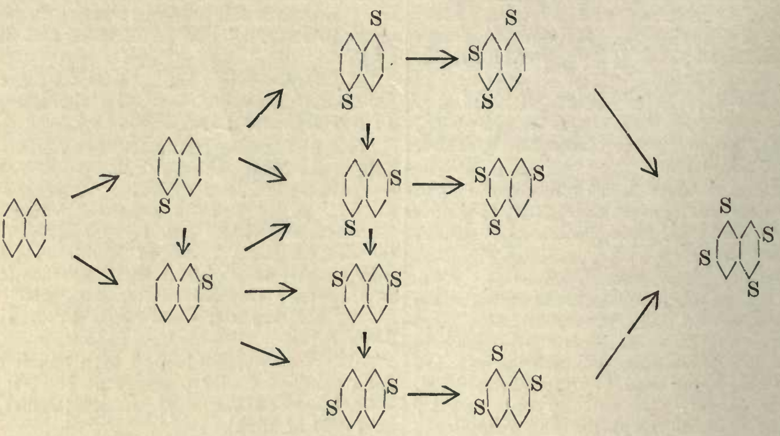
[1] A second acid, possibly the 2 : 7-isomeride, is also formed under these conditions (Oehler, *l.c.*).

[2] In this article, '**sulphuric acid**,' when not otherwise distinguished, is ordinary concentrated sulphuric acid of sp.gr. 1·845; '**monohydrate**' is 100 p.c. sulphuric acid; and '**anhydro acid**' is fuming sulphuric acid containing dissolved sulphur trioxide, the proportion of which is given when known.

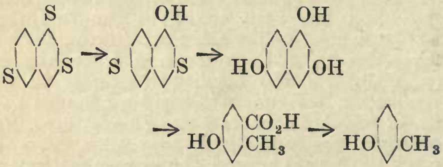
case has a product been isolated containing two sulphonic groups in positions relatively 1:2- (*ortho-*), 1:4- (*para-*), or 1:8- (*peri-*) to one another:



The sulphonic acids and their alkali salts are easily soluble in water, but the lead, barium, and calcium salts differ much in solubility, and in some cases afford a means of separating the constituents of a sulphonation melt. From the alkali salts, crystalline chlorides, amides, and anilides with definite melting-points, which serve to characterise the acids, can be prepared, and, from the chlorides, chloronaphthalenes which serve to fix their constitution.

By hydrolysis, or by sodium amalgam (Friedlaender and Lucht, Ber. 1893, 26, 3028) sulphonic groups in α- positions are more easily eliminated than those in β- positions.

When fused with caustic alkali, or digested under pressure with caustic alkali solution, naphthalenesulphonic acids give rise to hydroxy- compounds, in which one or more sulphonic groups have been exchanged for hydroxyl. The reaction takes place most readily with α-sulphonic groups. Should the naphtholsulphonic acid produced contain a sulphonic group in the 3- position relatively to the hydroxyl further change may occur and hydroxytoluic acids or *m*-cresols (from *m*-hydroxytoluic acids) be formed:



For technical purposes, naphthalenesulphonic acids are valuable as sources of the naphthols, of several naphtholsulphonic acids and of several nitronaphthalenesulphonic acids, furnishing in the last case by reduction naphthylaminesulphonic acids which are not formed from the naphthylamines by sulphonation.

The action of sulphuric acid on naphthalene leads also to the formation of small quantities of two dinaphthylsulphones—the αβ′- melting at 123°, and the ββ′- melting at 177° (Stenhouse and Groves, Ber. 1876, 9, 682; Hofmann, *ibid.* 1884, 17, 1921; Krafft, *ibid.* 1890, 23, 2364).

NAPHTHALENEMONOSULPHONIC ACIDS.

(i.) **Naphthalene-α-sulphonic acid** (sulphonaphthalic acid) $C_{10}H_7{\cdot}SO_3H$.

Formation.—Naphthalene on sulphonation with about its own weight of sulphuric acid yields a product containing varying proportions of α- and β- monosulphonic acids and a small quantity of at least one disulphonic acid, according to the conditions employed. Merz and Weith (Ber. 1870, 3, 195) state that a mixture of naphthalene and sulphuric acid in the proportion of 10:9 gave a product containing 80 p.c. of α-acid and 20 p.c. of β-acid when heated for 3 hours at 100°, but only 25 p.c. of α-acid with 75 p.c. of β-acid when heated for a further 4 hours at 170°, 15 p.c. of the naphthalene employed being recovered in the first case and 25 p.c. in the second. Also, that a mixture in the proportion 5:4 heated for 8 hours at 160° gave 80 p.c. of β-acid, 30 p.c. of the naphthalene employed being recovered. At temperatures below the melting-point of naphthalene—*e.g.* when finely powdered naphthalene is sieved into 1½–2 times its weight of sulphuric acid at 40°, and the mixture stirred continuously for many hours until everything has dissolved—α-acid is said to be the sole product, and the same result is obtained, but more rapidly, when sulphonation is effected by anhydro-acid in the cold (Landshoff, D. R.-P. 50411 of 1889). Sodium hydrogen disulphate, $NaH_3(SO_4)_2$, has been suggested as a sulphonating agent by Lambert (D. R.-P. 113784 of 1899).

Naphthalene-α-sulphonic acid, mixed with a small quantity of naphthalene-1:5-disulphonic acid, but free from β-sulphonic acid, is obtained, when slightly less than the calculated quantity of chlorosulphonic acid is added with continual shaking to a 10 p.c. solution of naphthalene in carbon disulphide (Armstrong and Wynne, Chem. Soc. Proc. 1887, 3, 146; *cf.* Armstrong, Chem. Soc. Trans. 1871, 24, 176).

Preparation.—Naphthalene is heated with an equal weight of sulphuric acid at 90°–95° for 2–3 hours, and the product poured into 6–8 times its bulk of water. The solution, separated from the 30 p.c. or so of unattacked naphthalene which solidifies on cooling, is neutralised with lime and the filtrate concentrated to remove the less soluble calcium salt of the β-acid. By further evaporation of the filtrate, the calcium salt of the α-acid can be separated, the final mother liquors containing the calcium salts of naphthalenedisulphonic acids in small quantity (Merz, Zeit. Chem. 1868, [ii.] 4, 394; Merz and Weith, *l.c.;* Merz and Mühlhäuser, Ber. 1870, 3, 710).

Identification.—The *acid* is a deliquescent substance sparingly soluble in slightly dilute sulphuric acid; the salts crystallise in scales.

Composition of salt (Merz)	1 part of the salt dissolves in	
	parts of water at 10°	parts of 85 p.c. alcohol at 10°
Potassium salt $+\frac{1}{2}H_2O$	13 (at 11°)	108 (at 11°)
Calcium „ $+2H_2O$	16·5	19·5
Barium „ $+H_2O$	87	350
Lead [1] „ $+3H_2O$	27	11

The *chloride*, which forms scales, m.p. 67° (Erdmann, Annalen, 1893, 275, 235), is reduced by zinc dust and dilute sulphuric to *thio-α-naphthol*, an oil b.p. 286° (Krafft and Schönherr, Ber. 1889, 22, 822).

Reactions.—(1) It is converted into a mixture of the 1 : 5- and 1 : 6-*disulphonic acids* by anhydro-acid in the cold, and into the 1 : 6-*disulphonic acid* by sulphuric acid at 110°.

(2) On fusion with caustic potash or soda it yields *α-naphthol* (Schaeffer, Annalen, 1869, 152, 281).

(ii.) **Naphthalene-β-sulphonic acid.**

Formation.—*v.* Naphthalene-α-sulphonic acid.

Preparation.—Naphthalene is heated with an equal weight of sulphuric acid at 160° during 3 hours, then at 170° during an hour, and finally at 180°, the operation being complete in about 8 hours. The product is either mixed with brine, whereby the less soluble β-salt is separated from the small amount of α-salt and disulphonate also present, or, after dilution with water, is neutralised by lime, and the calcium salt of the β-acid converted into sodium salt.

Identification.—The *acid* forms non-deliquescent scales; the salts crystallise in small scales, and, except those of the alkali metals, are sparingly soluble in cold water (*cf.* Burt, Boulton and Hayward, Eng. Pat. 4459 of 1894).

Composition of Salt (Merz)	1 part of the salt dissolves in	
	parts of water at 10°	parts of 85 p.c. alcohol at 10°
Potassium salt $+\frac{1}{2}H_2O$	15	115
Calcium „ (anhydrous) . . .	76	437
Barium „ $+H_2O$.	290	1950
Lead salt „ $+1\frac{1}{3}H_2O$	115 [2]	305

The *sodium* salt dissolves in 16·5 parts of water, and in 15·4 parts of N-, or 41 parts of 5N-hydrochloric acid at 23·9° (E. Fischer, Ber. 1906, 39, 4144). The *chloride* forms scales, m.p. 78° (E. Fischer and Bergell, Ber. 1902, 35, 3780), and, when reduced with zinc dust and dilute sulphuric acid, gives *thio-β-naphthol,* scales, m.p. 81°, b.p. 286° (Krafft and Schönherr, *ibid.* 1889, 22, 824).

Reactions.—(1) It is less readily hydrolysed than the α-acid. On sulphonation at 100° it yields the 1 : 6-, and at 160°–170° the 2 : 6- and 2 : 7-*disulphonic acids.*

(2) On fusion with caustic potash or soda it yields *β-naphthol* (Schaeffer, *l.c.*), for the preparation of which it is extensively employed.

Naphthalenedisulphonic Acids.

Introductory.—The four naphthalenedisulphonic acids obtained by sulphonation are the 1 : 5-, 1 : 6-, 2 : 6-, and 2 : 7- isomerides and are all heteronucleal. Their relationship is shown in the scheme on p. 574.

(i.) **Naphthalene-1 : 2-disulphonic acid** is formed from α-naphthylamine-2-sulphonic acid by conversion into the thionaphthol by Leuckart's method (Bayer, D. R.-P. 70296; Eng. Pat. 11465 of 1892; Armstrong and Wynne, Chem. Soc. Proc. 1893, 9, 168) or into the sulphinic acid (Gattermann, Ber. 1899, 32, 1156), and oxidation of these compounds by potassium permanganate in alkaline solution.

Identification.—The *potassium* salt ($+\frac{2}{3}H_2O$) forms very soluble flat prisms, and yields not a chloride but an *anhydride* (prisms, m.p. 198°, from benzene) by interaction with phosphorus pentachloride (Armstrong and Wynne, *l.c.*).

(ii.) **Naphthalene-1 : 3-disulphonic acid** is obtained from β-naphthylamine-6 : 8-disulphonic acid (amino-G-acid) or β-naphthylamine-5 : 7-disulphonic acid by boiling the corresponding hydrazines with copper sulphate solution (Armstrong and Wynne, Chem. Soc. Proc. 1890, 6, 13, 129), *or* from amino-G-acid by boiling its diazo-compound with alcohol (*cf.* Badische, D. R.-P. 57910; Eng. Pat. 9537 of 1890).

Identification.—The *barium* salt, $BaA+4H_2O$, *potassium* salt, K_2A+2H_2O, and the *sodium* salt are crystalline and very soluble in water. The *chloride* forms easily soluble prisms, m.p. 137°, from benzene, convertible into 1 : 3-*dichloronaphthalene* (Armstrong and Wynne, *l.c.*).

Reactions.—Fusion with caustic soda at 200°–220° converts the sodium salt into *α-naphthol-3-sulphonic acid* (Badische, *l.c.*), but digestion with 60 p.c. caustic soda solution at 250°–300° under pressure gives *o-toluic acid* (Kalle, D. R.-P. 79028 of 1893; *cf.* Friedlaender and Rüdt, Ber. 1896, 29, 1611).

(iii.) **Naphthalene-1 : 4-disulphonic acid** is obtained from naphthionic acid, as described under the 1 : 2-acid (*cf.* also Bayer, D. R.-P. 95830; Eng. Pat. 26139 of 1896).

Identification.—The *potassium* $K_2A+1\frac{1}{3}H_2O$ and *sodium* salts are crystalline and easily soluble. The *chloride* forms four-sided plates, m.p. 160°, from benzene (Armstrong and Wynne, Chem. Soc. Proc. 1893, 9, 168).

(iv.) **Naphthalene-1 : 5-disulphonic acid** (so-called Armstrong's acid; naphthalene-[γ-]disulphonic acid of Armstrong and Wynne (Chem. Soc. Proc. 1886, 2, 231); naphthalene-[δ-]disulphonic acid of Beilstein, Schultz, &c.) is formed together with the 1 : 6-acid when naphthalene is mixed gradually with five times its

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[1] According to Euwes (Rec. trav. chim. 1909, 28, 303) the *lead* salt is $PbA+2H_2O$, and 4·195 grams of it dissolve in 100 grams of water at 24·9°.

[2] According to Euwes (Rec. trav. chim. 1909, 28, 304), 0·407 gram of the lead salt of the β-acid dissolves in 100 grams of water at 24·9°.

weight of 23 p.c. anhydro-acid in the cold (Aktienges., D. R.-P. 45776; Eng. Pat. 4625 of 1888). If four times the weight of 30 p.c. anhydro-acid be used, and the product poured into 3–4 parts of water, a quantitative separation of the 1 : 5-acid is obtained (Ewer and Pick, D. P. Anm. E. 2619 of 1889). Or, as acid sodium salt, the 1 : 5-acid can be separated from the 1 : 6-isomeride by adding common salt to the sulphonation product. It is obtained free from its isomerides by the action of sulphuric anhydride (Armstrong and Wynne, Chem. Soc. Proc. 1887, 3, 42) or of chlorosulphonic acid in calculated quantity on naphthalene, or on naphthalene-*α*-monosulphonic acid (Armstrong and Wynne, *ibid.* 1886, 2, 231).

Preparation.—Dry sodium naphthalene-*α*-monosulphonate is stirred into twice its weight of anhydro-acid at 20°, and the mixture afterwards heated for an hour at 60°–70°. To the product, diluted with 5 times its weight of water, an equal volume of hot brine is added, and the acid sodium salt, which separates as the solution cools, is purified by recrystallisation (Schultz, Chemie d. Steinkohlenth., 3rd ed., 1, 189).

Identification.—The *acid* crystallises in very soluble lustrous, white, non-hygroscopic scales. The *lead* salt, $PbA+3H_2O$, *barium* salt, $BaA+4H_2O$, and *calcium* salt, $CaA+3H_2O$, are easily soluble in water, but when dehydrated dissolve only very slowly in it. The *potassium* salt, K_2A+2H_2O, in scales, dissolves in 8·04 parts of water at 12°; the *sodium* salt ($+2H_2O$), in scales dissolves in 8·78 parts of water at 16·5° (Armstrong and Wynne) or in 7·99 parts at 19° (Ewer and Pick, D. R.-P. 41934 of 1887). The *chloride* forms needles or small prisms, m.p. 183°, convertible into 1 : 5-*dichloronaphthalene* (Armstrong, Ber. 1882, 15, 205).

Reactions.—(1) On fusion with caustic soda, the sodium salt is converted into *α-naphthol*-5-*sulphonic acid* and 1 : 5-*dihydroxynaphthalene* (Ewer and Pick, *l.c.*; Armstrong and Wynne, Chem. Soc. Proc. 1887, 3, 43; Bernthsen and Semper, Ber. 1887, 20, 938).

(2) On nitration, the sodium salt yields as chief product *α-nitronaphthalene*-4 : 8-*disulphonic acid* (Bernthsen, Ber. 1889, 22, 3327; Schultz, *ibid.* 1890, 23, 77), together with *β-nitronaphthalene*-4 : 8-*disulphonic acid* (Cassella, D. R.-P. 65997 of 1890); and by further nitration 1 : 6-*dinitronaphthalene*-4 : 8-*disulphonic acid* (Kalle, D. R.-P. 72665 of 1893; Friedlaender and Kielbasinski, Ber. 1896, 29, 1982, 2574).

(v.) 1 : 6-**Naphthalenedisulphonic acid** (naphthalene-? : *β*-disulphonic acid of Armstrong and Wynne; naphthalene-[*γ*-]disulphonic acid of Beilstein and Schultz) is formed together with naphthalene-1:5-disulphonic acid when naphthalene is sulphonated with 23 p.c. anhydro-acid in the cold. It also occurs in the product formed when naphthalene is heated with 5 times its weight of sulphuric acid at 160° for 4 hours (Armstrong, Ber. 1882, 15, 204). A uniform acid is obtained when naphthalene is heated with 5 times its weight of monohydrate at 90°–110°, or with sulphuric acid at 90°, and subsequently with strong anhydro-acid at 110°–120° (Badische, D. P. Anm. B. 9514 of 1889; Bernthsen, Ber. 1889, 22, 3328; *cf.* Schultz, *ibid.* 1890, 23, 77).

Preparation.—Dry sodium naphthalene-*β*-sulphonate, mixed with twice its weight of 25 p.c. anhydro-acid, is heated on a water-bath, and the product is converted into sodium salt; on concentration of the solution to a relatively small bulk, this very soluble salt separates in characteristic needles (Ewer and Pick, D. R.-P. 45229 of 1887). A pure product is also obtained when an excess of chlorosulphonic acid is employed instead of anhydro-acid (Armstrong and Wynne, Chem. Soc. Proc. 1886, 2, 231; Armstrong, *ibid.* 1889, 5, 10).

Identification.—The *lead* salt, $PbA+3\frac{1}{2}H_2O$, *barium* salt, $BaA+4H_2O$, and *calcium* salt, $CaA+4H_2O$, are readily soluble in water; the *potassium* salt K_2A+H_2O dissolves in 3·4 parts and the *sodium* salt Na_2A+7H_2O in 3·34 parts of water at 16·5°. The *chloride* forms small prismatic aggregates from light petroleum, m.p. 129°, convertible into 1 : 6-*dichloronaphthalene* (Armstrong and Wynne, Chem. Soc. Proc. 1886, 2, 232; 1888, 4, 106).

Reactions.—(1) Fusion with caustic soda converts the sodium salt into 1 : 6-*dihydroxynaphthalene* (Ewer and Pick, *l.c.*).

(2) On nitration, the sodium salt yields, as chief product, *α-nitronaphthalene*-3 : 8-*disulphonic acid* (Aktienges., D. R.-P. 45776; Eng. Pat. 4625 of 1888; Ewer and Pick, D. R.-P. 52724 of 1888; Bernthsen, *l.c.*; Schultz, *l.c.*), the minor product being *β-nitronaphthalene*-4 : 7-*disulphonic acid* (Schultz, *l.c.*; Armstrong and Wynne, Chem. Soc. Proc. 1891, 7, 27), and by further nitration 1 : 6 - *dinitronaphthalene*-3 : 8 - *disulphonic acid* (Friedlaender and Kielbasinski, Ber. 1896, 29, 1980, 2574).

(vi.) **Naphthalene-1 : 7-disulphonic acid** can be obtained from *α*-naphthylamine-4 : 6-disulphonic acid (Dahl's No. II. acid) by boiling the corresponding hydrazine with copper sulphate solution (Armstrong and Wynne, Chem. Soc. Proc. 1890, 6, 126).

Identification.—The *potassium* salt ($+H_2O$), is microcrystalline. The *chloride* forms scales from acetic acid, m.p. 122·5°, convertible into 1 : 7-*dichloronaphthalene.*

(vii.) **Naphthalene-1 : 8-disulphonic acid** is formed from *α*-naphthylamine-8-sulphonic acid by oxidation of the corresponding thionaphthol as described under the 1 : 2-acid (Bayer, *l.c.*; Armstrong and Wynne, *l.c.*).

Identification.—The *potassium* salt K_2A+H_2O forms sparingly soluble four-sided scales, and yields not a chloride, but an *anhydride* (sparingly soluble prisms, m.p. 227°, from benzene) by interaction with phosphorus pentachloride (Armstrong and Wynne, *l.c.*).

(viii.) **Naphthalene-2 : 6-disulphonic acid** ([*β*-] naphthalenedisulphonic acid of Ebert and Merz). For formation and preparation, *v.* naphthalene-2 : 7-disulphonic acid.

Identification.—The *acid* forms small, deliquescent scales, extremely soluble in water. The normal salts (*v.* 2 : 7-acid) contain less water of crystallisation, crystallise less readily, and are less soluble than the corresponding salts of the 2 : 7-acid; the lead, barium, and calcium salts of the 2 : 6-acid are characterised, moreover, by the slowness with which they again dissolve when once separated from solution. The *chloride* forms small needles, m.p. 226°, from benzene, convertible into 2 : 6-*dichloronaphthalene* (Ebert and Merz, Ber. 1876, 9, 598; Cleve, Bull. Soc. chim. 1876, [ii.] 26, 244;

Armstrong and Wynne, Chem. Soc. Proc. 1890, 6, 127).

Reactions.—(1) On fusion with caustic potash, the potassium salt is converted first into *β-naphthol-6-sulphonic acid* (Ebert and Merz, *l.c.*), and finally into 2 : 6-*dihydroxynaphthalene* (Armstrong and Graham, Chem. Soc. Trans. 1881, 39, 141; Emmert, Annalen, 1887, 241, 369).

(2) On nitration, this acid yields *α-nitro-3 : 7-disulphonic* and 1 : 5-*dinitro*-3 : 7-*disulphonic acids* (Cassella, D. R.-P. 61174; Eng. Pat. 15346 of 1890).

(ix.) **Naphthalene-2 : 7-disulphonic acid** ([α-] naphthalenedisulphonic acid of Ebert and Merz) is obtained, together with the 2 : 6-acid (Ebert and Merz, Ber. 1876, 9, 592), when naphthalene is heated above 150° with excess of sulphuric acid. These acids—distinguished as [α-] and [β-]—are formed in about equal amounts, when a mixture of 1 part of naphthalene and 5 parts of sulphuric acid is heated at 160° for 4 hours, the product being free from naphthalenemonosulphonic acids; when heated at 180° for 24 hours, however, the same mixture gives a product consisting almost entirely of the [β-]acid. Pure [α-]acid, also, is converted into [β-]acid by prolonged heating with sulphuric acid at this temperature. On repeating these experiments Armstrong found that the product formed by heating the mixture at 180° for 24 hours contains a smaller proportion of the [β-]acid than stated by Ebert and Merz; that a third acid, subsequently recognised as the 1 : 6-disulphonic acid is present in the 160° product; and that sulphonation at 140° leads to the formation of a product differing greatly from that obtained at 160°, owing, no doubt, to the presence of an increased proportion of the 1 : 6-acid and almost entire absence of the [β-]acid.

Preparation.—(1) Naphthalene is heated with 5 times its weight of sulphuric acid at 160° for 5 hours, and the product converted into calcium salt in the usual way. The separation of the isomeric disulphonic acids can be based on the very slight solubility in water of the calcium [β-]disulphonate, after it has been dehydrated at 200°–230° (Ebert and Merz, *l.c.*; *cf.* Freund, D. R.-P. 27346; Eng. Pat. 1069 of 1883). As an alternative, advantage may be taken of the difference in solubility of the calcium salts of the [α-], [β-], and 1 : 6-acids in concentrated brine, as the [β-]salt is practically insoluble in hot and cold, the [α-]salt tolerably soluble in hot but very sparingly soluble in cold, and the 1 : 6-salt fairly soluble in cold brine (Landshoff, D. R.-P. 48053 of 1888).

(2) Two methods, in neither of which is reference made to the occurrence of 1 : 6-acid in the sulphonation product, have been described by Baum (D. R.-P. 61730 of 1890) for the production and separation of the [α-] and [β-]acids:—

(*a*) Sodium naphthalene-β-sulphonate (230 kilos.) is stirred into monohydrate (500 kilos.) or sulphuric acid (600 kilos.) kept at 160°–170°, and afterwards heated at 180° for 6–8 hours. The product, converted into calcium salt, is concentrated until the solution contains about 30 p.c. of the salt and then allowed to cool. By this means the greater part of the [β-]salt (52 kilos.) is separated. The filtrate, converted into sodium salt, is evaporated to dryness, and the [α-]salt (200 kilos.) extracted by 2 parts of warm water, the solution being allowed to cool to 20° before filtration. The residue is a mixture of sodium [α-] and [β-] salts (80 kilos.).

(*b*) Potassium pyrosulphate (300 kilos.) is dissolved in fused naphthalene-β-sulphonic acid (250 kilos.) at 160°–165°, and the solution mixed with monohydrate (120 kilos.) also heated at 160°–170°. By fractional crystallisation of the potassium salts, the less soluble [β-]salt (54–60 kilos.) is separated from the [α-]salt (386–390 kilos.), the yield of the latter being much greater than in the first process.

Identification.—The *acid* crystallises in long, deliquescent needles, very soluble in water. The salts are more soluble and crystallise better than those of the [β-]acid; their composition, and the solubility of the anhydrous salts of both [α-] and [β-]acids in water at 18° are compared in the table (Ebert and Merz, *l.c.*):—

2 : 7 or [α-]		2 : 6 or [β-]	
$PbA+2H_2O$	easily	$PbA+H_2O$	sparingly
$BaA+2H_2O$	82·2 (19°)	$BaA+H_2O$	„
$CaA+6H_2O$	6·2	CaA	16·2
K_2A+2H_2O	1·4	K_2A	19·2
Na_2A+6H_2O	2·2	Na_2A+H_2O	8·4 (19°)

The *chloride* forms four- or six-sided prisms, m.p. 158°, from benzene, convertible into 2 : 7-*dichloronaphthalene* (Ebert and Merz, *l.c.*; Cleve, Bull. Soc. chim. 1876, [ii.] 26, 244; Armstrong and Wynne, Chem. Soc. Proc. 1890, 6, 12).

Reactions.—(1) Fusion of the sodium salt with caustic soda results in the production of *β-naphthol-7-sulphonic acid* ([δ-] or F- acid); Weinberg, Ber. 1887, 20, 2906; Cassella, D. R.-P. 42112; Eng. Pat. 12908 of 1886), or 2 : 7-*dihydroxynaphthalene* (Ebert and Merz, *l.c.*), according to the conditions employed.

(2) On nitration, it yields 1 : 8-*dinitro*-3 : 6-*disulphonic acid* (Cassella, D. R.-P. 67062 of 1890; Eng. Pat. 1742 of 1891; Bayer, D. R.-P. 69190 of 1891; Eng. Pat. 11522 of 1892).

NAPHTHALENETRISULPHONIC ACIDS.

Introductory.—According to Gürke and Rudolph, a naphthalenetrisulphonic acid is obtained by the sulphonation of naphthalene either with 8 times its weight of 24 p.c. anhydrosulphuric acid at 180°, or with 6 times its weight of 40 p.c. anhydro-acid at 80°–100°; also by the sulphonation of naphthalenemono- and disulphonic acids or their salts with a proportionately smaller quantity of anhydro-acid (D. R.-P. 38281; Eng. Pat. 15716 of 1885). Two acids, at least, are obtained by this process, the 1 : 3 : 5-acid being the chief product at the lower temperature, as Erdmann states (Ber. 1899, 32, 3188), and the 1 : 3 : 6-acid the chief product at the higher temperature. As a third acid, the 1 : 3 : 7-derivative, can be obtained by the sulphonation of naphthalene-3 : 7-disulphonic acid, its presence in the mixture, although not recorded, is at least probable.

The naphthalenetrisulphonic acids in which two of the three sulphonic groups are relatively in the *meta-* position yield hydroxytoluic acids by digestion with caustic soda solution at 250° (Kalle, D. R.-P. 91201 of 1893) and brown dyes, possibly derived from them, by digestion with sodium sulphide, sulphur and water at 240° (*ibid.* D. R.-P. 98439 of 1897).

(i.) **Naphthalene-1 : 3 : 5-trisulphonic acid** is formed when sodium naphthalene-1 : 5-disulphonate (2 pts.) is heated with monohydrate (2 pts.) and chlorosulphonic acid (8 pts.) at 160° (Fischesser & Co., D. P. Anm. F. 7059 of 1893); or, mixed with monohydrate (3 pts)., is heated with 70 p.c. anhydro-acid (2·5 pts.) at 80°–90° until a thin liquid is obtained (Kalle, D. P. Anm. K. 11104 of 1893; Eng. Pat. 1641 of 1894; D. R.-P. 82563 of 1893; *cf.* Bayer, D. P. Anm. F., 7004; Eng. Pat. 17141c of 1893; Erdmann, Ber. 1899, 32, 3188). It is also formed by oxidising β-thionaphthol-4 : 8-disulphonic acid with permanganate (Bayer, D. R.-P. 70296; Eng. Pat. 11465 of 1892).

Identification.—The *acid* is very soluble in water; the *sodium* salt Na_3A+4H_2O forms very soluble needles. The *chloride*, m.p. 146° (Gattermann, Ber. 1899, 32, 1159), is convertible into 1 : 3 : 5-*trichloronaphthalene* (Kalle, *l.c.*).

Reactions.—(1) When fused with caustic alkali it gives 1 : 5-*dihydroxynaphthalene*-3-*sulphonic acid* (Bayer, D. R.-P. 166768; Eng. Pat. 18569 of 1902), but when digested with strong caustic soda solution at 250° under pressure, it yields o-*hydroxy*-o-*toluic acid* (Kalle, D. R.-P. 91201 of 1893; Eng. Pat. 16559 of 1894).

(2) On nitration, it is converted into α-*nitronaphthalene*-4 : 6 : 8-*trisulphonic acid* (Kalle, D. R.-P. 82563 of 1893; Bayer, D. R.-P. 80741; Eng. Pat. 17141c of 1893).

(ii.) **Naphthalene-1 : 3 : 6-trisulphonic acid** is obtained when naphthalene in coarse powder is heated with 3½–4 times its weight of chlorosulphonic acid at 150°–155° for an hour (Armstrong and Wynne, Chem. Soc. Proc. 1887, 3, 146); or when sodium naphthalene-1 : 6- or 2 : 7-disulphonate is further sulphonated (*cf.* Bayer, D. R.-P. 63015 of 1891). It is formed also from α-naphthylamine-2 : 4 : 7-trisulphonic acid by boiling the hydrazine with copper sulphate solution (Armstrong and Wynne, Chem. Soc. Proc. 1890, 6, 125).

Identification.—The *sodium* salt Na_3A+5H_2O forms very soluble needles. The *chloride* forms small prisms, m.p. 194°, from benzene (Armstrong and Wynne, *l.c.*).

Reaction.—When heated with caustic soda solution at 170°–180° under pressure, it yields α-*naphthol*-3 : 6-*disulphonic acid* (Friedlaender and Taussig, Ber. 1897, 30, 1462).

(iii.) **Naphthalene-1 : 3 : 7-trisulphonic acid** is obtained when sodium naphthalene-2 : 6-disulphonate (1 pt.), dissolved in monohydrate (3 pts.), is heated with 60 p.c. anhydro-acid (1 pt.) on a water-bath until a test, on addition of common salt, gives no separation of disulphonate (Cassella, D. R.-P. 75432 of 1891). It is also formed when the thionaphthols from α-naphthylamine-3 : 7-disulphonic acid and amino-G-acid are oxidised by alkaline permanganate (Bayer, D. R.-P. 70296; Eng. Pat. 11465 of 1892).

Reactions.—(1) When heated with 50 p.c. caustic soda solution at 260° under pressure, it yields p-*hydroxy*-o-*toluic acid* (Kalle, D. R.-P. 91201 of 1893; Eng. Pat. 16559 of 1894).

(2) By nitration it forms α-*nitronaphthalene*-3 : 5 : 7-*trisulphonic acid* (Cassella, *l.c.*).

(iv.) **Naphthalene-2 : 3 : 6-trisulphonic acid** is obtained when β-naphthylamine-3 : 6-disulphonic acid (amino-R-acid) is converted into the thionaphthol by Leuckart's method, and the latter oxidised by potassium permanganate in alkaline solution (Bayer, D. R.-P. 70296; Eng. Pat. 11465 of 1892; Armstrong and Wynne, Chem. Soc. Proc. 1893, 9, 168).

Identification.—The *potassium* salt ($+5H_2O$) is microcrystalline; the *chloride* forms flat prisms, m.p. 200° (Armstrong and Wynne, *l.c.*).

(v.–ix.) The sodium salts of the **naphthalene-1 : 2 : 5-, 1 : 2 : 6-, 1 : 3 : 8-, 1 : 4 : 7-, and 1 : 4 : 8-trisulphonic acids**, obtained, like the 2 : 3 : 6-acid, from the corresponding thionaphthol-α- or β-disulphonic acids are very soluble in water (Bayer, *l.c.*). The 1 : 4 : 8-*trisulphonyl chloride* forms clusters of needles, m.p. 156°–157° (Gattermann, Ber. 1899, 32, 1158).

NAPHTHALENETETRASULPHONIC ACIDS.

Introductory.—By heating naphthalene with 5 times its weight of 40 p.c. anhydro-acid at 160° for 9 hours, a product is obtained in which two naphthalenetetrasulphonic acids at least are stated to be present (Bayer, D. R.-P. 40893 of 1886). One of these acids, formed by sulphonation of naphthalene-2 : 6-disulphonic acid, is the 1 : 3 : 5 : 7 derivative (*ibid.* D. R.-P. 79054; Eng. Pat. 25074 of 1893), but the other, obtained by sulphonation of naphthalene-3 : 6-di- or 1 : 3 : 6-tri- sulphonic acid (*ibid.* D. R.-P. 80464; Eng. Pat. *l.c.*), has not been identified.

Two naphthalenetetrasulphonic acids are said to be formed when naphthalene is heated with sulphuric acid and phosphoric anhydride at 260° for 3–4 hours (Senhofer, Monatsh. 1882, 3, 111). Of these, one, forming the less soluble barium or copper salt, has been described by Senhofer as crystallising in very soluble prisms which retain $4H_2O$ at 100°. Its *copper* salt, Cu_2A+12H_2O; *barium* salt Ba_2A with 7, 10, 13, or $15H_2O$; *potassium* salt, K_4A+2H_2O; and *sodium* salt, Na_4A+10H_2O, are crystalline. The identity of this acid has not been established and little is known about the isomeride.

(i.) **Naphthalene-1 : 3 : 5 : 7-tetrasulphonic acid** is obtained when calcium naphthalene-2 : 6-disulphonate, dried at 200°, is heated with 3 times its weight of 25 p.c. anhydro-acid at 90° during 4 hours, whereby trisulphonic acid is formed, and then at 260° during 6 hours. The product is converted into sodium salt, which can be separated from a hot concentrated solution by common salt as a heavy, sand-like precipitate (Bayer, D. R.-P. 79054; Eng. Pat. 25074 of 1893). Instead of the 2 : 6-disulphonic acid, naphthalene-1 : 3 : 7-trisulphonic acid can be used (*ibid.* D. P. Anm. F. 7224; Eng. Pat. *l.c.*).

Identification.—The *chloride* forms compact, cubical crystals, m.p. 261°–262°, very sparingly soluble in benzene or acetone (Bayer, D. P. Anm. F. 7224 of 1893).

Reactions.—When heated with caustic soda solution under pressure, it yields α-*naphthol*-3 : 5 : 7-*trisulphonic acid*, and with a stronger (60 p.c.) solution the isomeric 1 : 3-*dihydroxy*-5 : 7-*disulphonic* (Gelbsäure) and 1 : 5-*dihydroxy*-3 : 7-*disulphonic* (Rotsäure) *acids* (Bayer, D. R.-P. 79054; Eng. Pat. *l.c.*), together with 1 : 3 : 5-*trihydroxynaphthalene*-7-*sulphonic acid* (*ibid.* Eng. Pat. 19624 of 1893).

(ii. and iii.) The following acids have been prepared by oxidation of the thionaphthols obtained by Leuckart's method from the corresponding β-naphthylaminetrisulphonic acids (Bayer, D. R.-P. 70296; Eng. Pat. 11465 of 1892):

Naphthalene-1 : 3 : 6 : 7-tetrasulphonic acid.

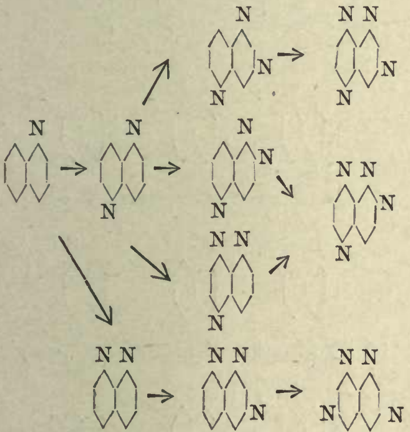
Identification.—The *sodium* salt forms a very soluble granular mass. The *chloride* forms needles, m.p. 309°–310°, sparingly soluble in benzene (Bayer, D. P. Anm. F. 7224 of 1893).

Naphthalene-1 : 3 : 6 : 8-tetrasulphonic acid.

Identification.—The *barium* salt is sparingly soluble, and the crystalline *sodium* salt easily soluble. The *chloride* forms short prisms, m.p., 282°–283°, very sparingly soluble in benzene, but more readily in acetone (*ibid.*).

III. NITRO- DERIVATIVES.

Introductory.—The first nitro- derivatives of naphthalene were prepared by Laurent (Ann. Chim. Phys. 1835, [ii.] 59, 376; 66, 152; *cf.* Lautemann and Aguiar, Bull. Soc. chim. 1865, [ii.] 3, 261) who described α-nitronaphthalene under the name nitronaphthalase. It is now recognised that one mono-,[1] two di-, four tri-, and three tetra-nitronaphthalenes can be obtained from naphthalene by nitration under suitable conditions, the relationship between them being shown in the scheme (N is used for NO_2):—

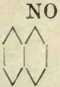


From this scheme it will be seen that, unlike SO_3H radicles in the presence of sulphuric acid, NO_2 radicles in nitration products of nitronaphthalene are found in 1 : 2-(*ortho-*), 1 : 4-(*para-*), and 1 : 8-(*peri-*) positions. Further, as illustrating the difference between nitrobenzene and nitro-α-naphthalene, it may be pointed out that the former yields *meta*dinitrobenzene as chief product, but the latter two *heteronucleal* αα-dinitronaphthalenes by further nitration.

The nitronaphthalenesulphonic acids are described in this section, the nitronaphthylamines and nitronaphthols in connection with the corresponding naphthylamines and naphthols (*q.v.*).

By reduction, usually with iron and dilute sulphuric acid, the nitronaphthalenesulphonic acids are converted into the corresponding naphthylaminesulphonic acids, which in not a few cases are of technical importance, being isomeric with those obtained from the naphthylamines by sulphonation.

NITRONAPHTHALENES.



(i.) α-**Nitronaphthalene.** In the laboratory, α-nitronaphthalene is best prepared by Piria's method, in which powdered naphthalene is nitrated with 5–6 times its weight of nitric acid of sp.gr. 1·33 in the cold, and the product extracted with carbon disulphide, to remove insoluble dinitronaphthalene (Annalen, 1851, 78, 32; *cf.* Beilstein and Kuhlberg, *ibid.* 1873, 169, 81).

On the large scale, finely-powdered naphthalene (2·5 pts.) is added gradually through a sieve to a mixture of nitric acid of sp.gr. 1·38 (2 pts.), sulphuric acid (2 pts.), and spent acid from a previous operation (6 pts.); the temperature being maintained at 45°–50° throughout the operation, and the nitration completed in one day. When cold, the spent acid is run off from the solid cake of nitronaphthalene, and the latter, after being washed with hot water, is either granulated by allowing it to flow in a thin stream into cold water (Witt, Chem. Ind. 1887, 10, 216) or crystallised from solution in one-tenth its weight of cumene or solvent naphtha (Paul, Zeitsch. angew. Chem. 1897, 146). The nitration can be effected by mixing naphthalene with powdered nitre, and stirring the mixture into sulphuric acid (Höchst, D. R.-P. 201623 of 1906, with sketch of nitration vessels). To avoid the use of sulphuric acid, and yet admit of the employment of a weaker nitric acid (below sp.gr. 1·33) than will attack naphthalene in its absence, an electrolytic method has been proposed (Tryller, D. R.-P. 100417 of 1897).

Properties.—α-Nitronaphthalene crystallises in long, slender, lustrous needles, m.p. 61° (Aguiar, Ber. 1872, 5, 371), b.p. 304° (Koninck and Marquart, *ibid.* 12), and is practically non-volatile with steam. It dissolves in 35·6 parts of 87·5 p.c. alcohol at 15°, and is readily soluble in benzene, carbon disulphide, ether or hot alcohol.

Reactions.—(1) With chromic acid in acetic acid solution it is oxidised to 3-*nitrophthalic acid* (Beilstein and Kurbatow, Annalen, 1880, 202, 217); with 5 p.c. potassium permanganate to 3-*nitrophthalonic acid* and 3-*nitrophthalic acid* (Friedlaender and Weisberg, Ber. 1895, 28, 1642); and with caustic soda solution at 170°–250° under pressure to both *phthalic* and *benzoic acids* (Bindschedler, D. R.-P. 136410, *cf.* 140999; Eng. Pat. 15527 of 1901).

(2) When boiled with ammonium sulphite it is converted into a mixture of '*thionaphthamic' acid*, $C_{10}H_7{\cdot}NH{\cdot}SO_3H$, and *naphthionic acid* (Piria, *l.c.*), but with sodium bisulphite into α-*naphthylamine*-2 : 4-*disulphonic acid* (Höchst, D. R.-P. 92082 of 1895).

(3) Reduction in acid solution converts it into α-*naphthylamine* (*q.v.*). In alcoholic solution with sodium amalgam *azoxynaphthalene* is formed (Jaworsky, J. pr. Chem. 1865, 94, 285). Distillation with zinc dust converts it into αβ-*naphthazine* (Laurent's naphthase; Doer, Ber. 1870, 3, 291; Klobukowsky, *ibid.* 1877, 10, 573; Witt, *ibid.* 1886, 19, 2794).

(4) On sulphonation with anhydro-acid it

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[1] Accompanied by a very small amount of the isomeric β-mononitronaphthalene (*q.v.*).

yields a mixture of the *α-nitronaphthalene*-5-, 6-, and 7- *sulphonic acids*, the first named being the chief product (Palmaer, Ber. 1888, 21, 3260).

(5) When finely-divided sulphur is added carefully to about 4 times its weight of α-nitronaphthalene heated at 200°–220°, sulphur dioxide is evolved, and a green dye-stuff, 'naphthylthiazin,' is obtained (Bennert, Eng. Pat. 14646 of 1887; D. R.-P. 48802, 49966 of 1888).

(ii.) **β-Nitronaphthalene** has been separated in small quantity from crude mononitronaphthalene (Armstrong, *priv. comm.*), and its production in the nitration of naphthalene has long been inferred from the fact that technical α-naphthylamine contains β-naphthylamine in small quantity (Reverdin and Noelting, Sur la constitution de la naphtaline et de ses dérivés, ed. 1888, 33; Erdmann, Annalen, 1893, 275, 217; Chem. Fab. Weiler-ter Meer, D. R.-P. 205076 of 1906; Eng. Pat. 16446 of 1907; *cf.*, however, Witt, Chem. Ind. 1887, 10, 220).

Preparation.—It can be obtained from 2-nitro-α-naphthylamine by the diazo-reaction (Lellmann and Remy, Ber. 1886, 19, 236; Lellmann, *ibid.* 1887, 20, 891); in 7 p.c. yield from β-diazonaphthalene nitrite by treatment with cuprous oxide (Sandmeyer, *ibid.* 1887, 20, 1496); and, in 25 p.c. yield, from diazotised β-naphthylamine sulphate by interaction with cuprocupric sulphite and potassium nitrite solution at the ordinary temperature (Hantzsch and Blagden, *ibid.* 1900, 33, 2554).

Properties.—It crystallises from dilute alcohol in small yellow needles, melts at 79°, has an odour of cinnamon, and volatilises only slowly with steam.

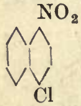
Reactions.—(1) On reduction it yields *β-naphthylamine* (Lellmann and Remy, *l.c.*).

(2) When warmed with methyl alcoholic potash it is converted into *2-nitroso-α-naphthol* (Meisenheimer and Witte, Ber. 1903, 36, 4167).

(3) On sulphonation with anhydro-acid it gives a mixture of the 5- and 8-*sulphonic acids* (Kappeler, Ber. 1912, 45, 633).

CHLORO-α-NITRONAPHTHALENES.

Introductory.—By nitration α-chloronaphthalene yields the three possible α-nitro- derivatives. Of these the 4-chloro-α-nitronaphthalene, unlike the 5- and 8-isomerides, but like 4- or *p*-chloronitrobenzene, exchanges the Cl for the NH_2 or OH radicle by interaction with ammonia or caustic alkali.



(i.) **4-Chloro-α-nitronaphthalene** is obtained as chief product, mixed with some of the 5-chloro- and a small quantity of the 8-chloro-α-nitronaphthalene, when α-chloronaphthalene is nitrated with nitric acid of sp.gr. 1·4 in the cold (Atterberg, Ber. 1876, 9, 927; Griesheim, D. R.-P. 120585 of 1900). It crystallises in yellow needles, m.p. 85°.

Reactions.—(1) When heated with 8 p.c. alcoholic ammonia under pressure at 150°–170°, it is converted into *4-nitro-α-naphthylamine* (Griesheim, D. R.-P. 117006; Eng. Pat. 7692 of 1900; *l.c.*).

(2) With solutions of alkali hydroxides, carbonates or acetates under pressure at 150°–155° it yields *4-nitro-α-naphthol* (*ibid.* D. R.-P. 117731; Eng. Pat. 7692 of 1900).

(ii.) **8-Chloro-α-nitronaphthalene** is formed as chief product, mixed with 5-chloro-α-nitronaphthalene, when α-nitronaphthalene is chlorinated at 40°–60° in the presence of ferric chloride, and separates as a crystalline magma from the product (Aktienges., D. R.-P. 99758 of 1897; Ullmann and Consonno, Ber. 1902, 35, 2808). It forms needles, m.p. 94°; the 5- *compound* has m.p. 111°.

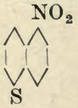
Reaction.—When heated with sulphuric acid at 80°, it is converted into *8-chloro-α-nitro-5-sulphonic acid*, whereas 5-chloro-α-nitronaphthalene does not undergo sulphonation under these conditions (Aktienges., D. R.-P. 103980 of 1897).

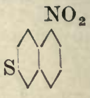
(iii.) **Dichloro-1 : 5-dinitronaphthalene**, also **chloro-** and **dichloro-1 : 8-dinitronaphthalene,** have been prepared by chlorinating the respective dinitronaphthalenes in a fused state in the presence of ferric chloride (Pollak, D. R.-P. 134306 of 1901).

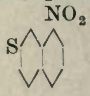
NITRONAPHTHALENEMONOSULPHONIC ACIDS.

Introductory.—The six nitronaphthalenemonosulphonic acids which are known with certainty are α- compounds, and are obtained either by the sulphonation of α-nitronaphthalene, or by the nitration of naphthalene-α- or β-monosulphonic acid. The products from each of these sources are:

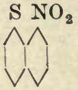
(*a*) By sulphonation of α-nitronaphthalene:

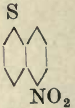


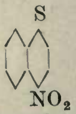




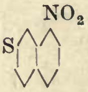
(*b*) By nitration of naphthalene-α-sulphonic acid:[1]

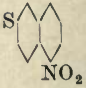


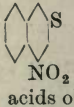




(*c*) By nitration of naphthalene-β-sulphonic acid:







The separation of the isomeric acids obtained by these methods is not easy, and for technical purposes is not attempted, as the naphthylaminesulphonic acids, for the production of which they are made, can be isolated from the reduction product with much less difficulty.

On comparing the products of the nitration of naphthalene-α- and β-sulphonic acids with those of naphthalenedi- and tri-sulphonic acids, it will be found that in the former case, isomerides are always, but in the latter only rarely formed; also that the NO_2 group can assume the 1 : 4- (*para-*) or the 1 : 8- (*peri-*) but not the 1 : 2- (*ortho-*) position relatively to the SO_3H group.

(i.) **α-Nitronaphthalene-3-sulphonic acid**

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[1] According to Friedlaender (Heumann, Anilinfarben 1898, ii. 517), β-nitronaphthalene-4-sulphonic acid occurs in small quantity in the product from this source, but no description of the acid has been given.

(Cleve's [γ-]nitronaphthalenesulphonic acid[1]) is formed in small amount when sodium naphthalene-β-sulphonate is nitrated (*v.* the 6-acid), and is obtained from its chloride by boiling it with water (Cleve, Ber. 1886, 19, 2179; *cf.* Armstrong and Wynne, Chem. Soc. Proc. 1895, 11, 239).

Identification.—The *lead* salt PbA_2+3H_2O, *barium* salt BaA_2+3H_2O, and *potassium* salt KA, crystallise in sparingly soluble needles. The *chloride* forms needles, m.p. 140°, from acetic acid, convertible into 1 : 3-*dichloronaphthalene* (Cleve, *l.c.*). On reduction, it yields the [γ-] *α-naphthylamine-*3-*sulphonic acid* (Cleve, Ber. 1888, 21, 3271).

(ii.) α-**Nitronaphthalene-4-sulphonic acid** is formed in small quantity by the nitration of sodium naphthalene-α-sulphonate (*v.* the 8-acid), and is isolated from the product by means of its chloride (Cleve, Ber. 1890, 23, 959).[2]

Identification.—The *barium* salt BaA_2+H_2O forms needles soluble in 66 parts of cold and 33 parts of boiling water; the *calcium* salt CaA_2+2H_2O, scales soluble in 37 parts of water at 17° and 16 parts at 100°; the *potassium* salt, KA needles; and the *sodium* salt, $NaA+H_2O$ needles. The *chloride* forms prisms, m.p. 99°, from benzene. Reduction with ammonium sulphide converts the acid into *α-naphthylamine-*4-*sulphonic acid* (Cleve, *l.c.*).

(iii.) α-**Nitronaphthalene-5-sulphonic acid** (Cleve's [α-]acid). This acid is obtained as chief product (about 80 p.c.) when α-nitronaphthalene is sulphonated with anhydro-acid, and (*v.* the 8-acid) as minor product (about 20 p.c.) when sodium naphthalene-α-sulphonate is nitrated. It is said to be the only product of the interaction of α-nitronaphthalene and chlorosulphonic acid (Armstrong and Williamson, Chem. Soc. Proc. 1886, 2, 233).

Preparation.—(1) Finely divided dry α-nitronaphthalene (20 pts.) is added gradually to a mixture of sulphuric acid (35 pts.), and 24 p.c. anhydro-acid (25 pts.) at such a rate that the temperature does not rise above 90°, at which it is maintained during 8 hours or until sulphonation is completed. The product, poured on to an equal weight of ice, gives a crystalline separation of the pure 5-acid (Witt, Chem. Ind. 1887, 10, 218). From the mother liquor, the isomeric 6- and 7-acids can be isolated by conversion into and fractional crystallisation of the nitronaphthalenesulphonyl chlorides (Palmaer, Ber. 1888, 21, 3260).

(2) The formation of dark resinous substances, unavoidable when α-nitronaphthalene is sulphonated by anhydro-acid, does not occur if fused salt is added to the acid in quantity sufficient to convert the dissolved anhydride into chlorosulphonic acid. Thus, α-nitronaphthalene (10 pts.) is added to the mixed sulphuric and chlorosulphonic acids obtained from 20 p.c. anhydro-acid (26 pts.), and the mixture heated on a water-bath until sulphonation is complete (Erdmann, Annalen, 1888, 247, 311).

Identification.—The *acid* $HA+4H_2O$ crystallises in easily soluble pale-yellow needles, the *lead* salt PbA_2+3H_2O in scales; and the *barium* salt BaA_2+3H_2O in sparingly soluble needles (Cleve, Bull. Soc. chim. 1875, [2] 24, 510). The *calcium* salt CaA_2+2H_2O forms sparingly soluble needles; the *potassium* salt KA forms scales, or as $KA+H_2O$ hexagonal tables soluble in 25 parts of water at 17° (Erdmann, Annalen, 1893, 275, 247); the *sodium* salt $NaA+\frac{1}{2}H_2O$ forms very soluble tables (Cleve, *l.c.*). The *chloride* forms needles, m.p. 113°, from ether, convertible into 1 : 5-*dichloronaphthalene* (Cleve, *l.c.*).

Reactions.—On reduction with ammonium sulphide, or with iron and sulphuric acid, it is converted into *α-naphthylamine-*5-*sulphonic acid* (Cleve, *l.c.*; Erdmann, Annalen, 1888, 247, 316), with sodium amalgam it yields α-naphthylamine (Claus, Ber. 1877, 10, 1303); and electrolytically it forms 1-*amino-*4-*naphthol-*5-*sulphonic acid* (Bayer, D. R.-P. 81621 of 1893; Gattermann, Ber. 1893, 26, 1852).

(iv.) α-**Nitronaphthalene-6-sulphonic acid** (Cleve's [θ-] acid). A mixture of this acid with about an equal quantity of the 7-acid, forms almost the entire product of the nitration of sodium naphthalene-β-sulphonate, the 4-acid being present only in very small amount. A mixture of the two acids constitutes the minor product of the sulphonation of α-nitronaphthalene (*v.* the 5-acid).

Preparation.—(1) Sodium naphthalene-β-sulphonate (23 pts.) is stirred into sulphuric acid (115 pts.) at a temperature not exceeding 30°, the whole cooled to 0°, a mixture of nitric acid (7 pts.) and sulphuric acid then added at 0°–10°, the nitration being completed at this temperature (Cassella, D. R.-P. 67017; Eng. Pat. 6972 of 1891). The product is a mixture of the 6- and 7-acids (*ibid.* D. R.-P. 85058 of 1894).

(2) Sodium naphthalene-β-sulphonate is stirred into cold nitric acid of sp.gr. 1·3, and the mixture warmed to complete the nitration. By extraction of the barium salt with boiling water, the sparingly soluble 6-salt is obtained, the separation of the 6-, 7-, and 3-isomerides in the filtrate being effected by converting them into chlorides, extraction by carbon disulphide in which the 7-chloride is sparingly soluble, and fractional crystallisation of the residue (Cleve, Bull. Soc. chim. 1876, [2] 26, 444; 1878 [2], 29, 414; Ber. 1886, 19, 2179; *cf.* Erdmann and Süvern, Annalen, 1893, 275, 251).

Identification.—The *acid* crystallises in readily soluble brown needles; the *barium* salt BaA_2+H_2O in needles soluble in 782 parts of water at 22°; the *calcium* salt CaA_2+H_2O in scales; the *potassium* salt KA in tables soluble in 29 parts of water at 20°; the *sodium* salt, $NaA+3H_2O$, in crusts consisting of scales. The *chloride* forms prisms, m.p. 125·5°, from benzene, convertible into 1 : 6-*dichloronaphthalene* (Cleve, *l.c.*).

Reactions.—(1) On reduction with ammonium sulphide it is converted into *α-naphthylamine-*6-*sulphonic acid* (Cleve, *ibid.*); and electrolytically it forms 1-*amino-*4-*naphthol-*6-*sulphonic acid* (Bayer, D. R.-P. 81621 of 1893).

(2) On nitration the chloride is converted into 1 : 8-*dinitronaphthalene-*3-*sulphonyl chloride*, m.p. 145° (Hellström, Förhandl. 1888, 10, 613).

(v.) α-**Nitronaphthalene-7-sulphonic acid** (Cleve's [θ-] or [δ-]nitronaphthalenesulphonic

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[1] In every case where the constitution of an α-nitronaphthalenesulphonic acid is given, the nitro- group is supposed to be in the position '1.'

[2] Erdmann and Süvern did not succeed in finding this acid among the nitration products of naphthalene-α-sulphonyl chloride (Annalen, 1893, 275, 249).

acid[1]) constitutes about one-half the product when sodium naphthalene-β-sulphonate (*v.* the 6-acid; *cf.* Cassella, D. R.-P. 85058 of 1894), or when naphthalene-β-sulphonyl chloride (Erdmann and Süvern, Annalen, 1893, 275, 238) is nitrated, but is formed only in small amount when α-nitronaphthalene is sulphonated (*v.* the 5-acid).

Identification.—The *acid* forms brown needles, very soluble in water, but, unlike the 6-acid, almost insoluble in concentrated hydrochloric acid, and less soluble than the 6-acid in 33 p.c. sulphuric acid. The *barium* salt $BaA_2+3\frac{1}{2}H_2O$ forms granular aggregates of needles, soluble, when anhydrous, in 377 parts of water at 17° but in 9·1 parts of boiling water; the *calcium* salt, very soluble needles; the *potassium* salt $KA+\frac{1}{2}H_2O$, needles readily soluble in water; the *sodium* salt, spherical aggregates of needles (Palmaer, Ber. 1888, 21, 3261). The *chloride* forms prisms, m.p. 169°, from acetic acid, dissolves very sparingly in carbon disulphide, and is convertible into 1 : 7-*dichloronaphthalene* (Cleve, Bull. Soc. chim. 1878, [ii.] 29, 414; Armstrong and Wynne, Chem. Soc. Proc. 1889, 5, 19).

Reaction.—On reduction (Cleve, Ber. 1888, 21, 3264) with iron and acetic acid (Erdmann, Annalen, 1893, 275, 272) it yields [δ-] or [θ-]α-*naphthylamine*-7-*sulphonic acid*, and electrolytically it forms 1-*amino*-4-*naphthol*-7-*sulphonic acid* (Bayer, D. R.-P. 81621 of 1893).

(vi.) α-**Nitronaphthalene-8-sulphonic acid** is obtained as chief product (60–70 p.c.) when sodium naphthalene-α-sulphonate is nitrated.

Preparation.—(1) Sodium naphthalene-α-sulphonate (4 pts.) is stirred into nitric acid of sp.gr. 1·45 (5 pts.), and the product converted into calcium salt. From the solution of the calcium salt, the greater part of the 5-salt is separated by concentration, the more soluble 8-salt being contained in the mother liquors (Cleve, Ber. 1890, 23, 958). For technical purposes the separation is unnecessary, as the corresponding naphthylaminesulphonic acids differ to a much greater degree in solubility, and are more easily isolated (*cf.* Schöllkopf, D. R.-P. 40571; Eng. Pat. 15775 of 1885).

(2) The acid can be obtained by stirring naphthalene-α-sulphonyl chloride into 3 times its weight of nitric acid of sp.gr. 1·475 at −5°; extracting the isomeric chlorides from the product by carbon disulphide; and hydrolysing the residue (Erdmann and Süvern, Annalen, 1893, 275, 237).

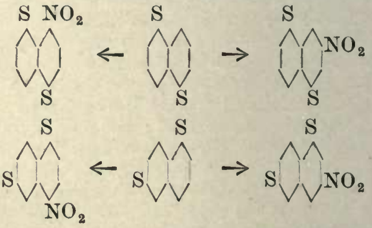
Identification.—The *acid* forms needles; the *barium* salt $BaA_2+2\frac{1}{2}H_2O$, crusts; the *calcium* salt $CaA_2+4\frac{1}{2}H_2O$, scales; the *potassium* salt $KA+H_2O$, needles, or $KA+2\frac{1}{2}H_2O$, scales, all easily soluble in water. The *chloride* forms prisms, m.p. 161°, from chloroform, but is almost insoluble in carbon disulphide (Erdmann and Süvern, *l.c.*).

Reaction.—On reduction, it yields α-*naphthylamine*-8-*sulphonic acid*, the S-acid of the Schöllkopf Co.'s D. R.-P. 40571 (Erdmann, Annalen, 1888, 247, 318).

(vii. and viii.) β-**Nitronaphthalene-5-sulphonic acid**, mixed with the 8-**acid**, is obtained by sulphonating β-nitronaphthalene with ice-cooled anhydro-acid, and is separated from it by fractional crystallisation of the mixed chlorides from benzene. The 5-*sulphonyl chloride*, prisms, m.p. 127°, is more soluble in benzene than the 8-*chloride*, needles, m.p. 169°–170° (Kappeler, Ber. 1912, 45. 634).

NITRONAPHTHALENEDISULPHONIC ACIDS.

Introductory.—The nitronaphthalenedisulphonic acids are obtained for the most part from naphthalenedisulphonic acids by nitration. In two cases, both α- and β-nitro-acids are formed, the α-nitro- derivative being the chief product:



but with the 1 : 4- (*cf.* Bayer, D. R.-P. 70857 of 1892), 2 : 6-, and 2 : 7-disulphonic acids only one, and that the α-nitro-acid is obtained.

(i.) α-**Nitronaphthalene-3 : 6-disulphonic acid** (Alén's [α-]acid) is obtained by nitration of naphthalene-2 : 7-disulphonic acid (Freund, D. R.-P. 27346; Eng. Pat. 1069 of 1883; *cf.* Armstrong and Wynne, Chem. Soc. Proc. 1895, 11, 82), and its chloride is formed, together with 1 : 8-dinitronaphthalene-3 : 6-disulphonyl chloride by nitrating naphthalene-2 : 7-disulphonyl chloride with nitrosulphuric acid at the ordinary temperature (Alén, Bull. Soc. chim. 1883, [2] 39, 63).

Identification.—The *acid* and salts crystallise in small needles; the *barium* salt, $BaA+5H_2O$, is sparingly; the *potassium* salt K_2A+3H_2O and *sodium* salt Na_2A+6H_2O are readily soluble in water. The *chloride* forms needles, m.p. 140°–141°, from benzene, convertible into [θ-] or 1 : 3 : 6-*trichloronaphthalene* (Alén, Förhandl. 1884, 2, 95; Cleve, Ber. 1892, 25, 2487; Armstrong and Wynne, *l.c.*).

Reactions.—Reduction with ammonium sulphide converts it into α-*naphthylamine*-3 : 6-*disulphonic acid*, and with sodium amalgam into α-*naphthylamine* (Alén, Förhandl. 1883, 8, 3).

(ii.) α-**Nitronaphthalene-3 : 7-disulphonic acid** (Alén's [β-]acid). To prepare this acid, sodium naphthalene-2 : 6-disulphonate (33 pts.), dissolved in sulphuric acid (50 pts.), is nitrated in the cold with 50 p.c. nitric acid (25 pts.). If the melt, containing chiefly 2 : 6-disulphonic acid, which is formed by sulphonating naphthalene at 160°–200° be used for the nitration, the nitro-acid can be salted out from the product (Freund, D. R.-P. 27346; Eng. Pat. 1069 of 1883; *cf.* Cassella, D. R.-P. 61174; Eng. Pat. 15346 of 1890). Its chloride is formed, as sole product, when naphthalene-2 : 6 disulphonyl chloride is nitrated with nitro-

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[1] This acid was originally termed [δ-] by Cleve, and is so described in his communication to the Paris Chemical Society (Bull. Soc. chim. 1878, [ii.] 29, 414). In the Swedish paper (Förhandl. 1878, 2, 32), which is practically identical with the French, the term [θ-] is employed, since 'the acid yields a new dichloronaphthalene which being the eighth known is distinguished as θ.'

sulphuric acid (Alén, Bull. Soc. chim. 1883, [ii.] 39, 64).

Identification.—The *barium* salt $BaA+2H_2O$, tablets; *calcium* salt $CaA+2H_2O$, needles; *potassium* salt K_2A, needles; and *sodium* salt Na_2A+2H_2O, needles, are less soluble than the salts of the 3 : 6-acid. The *chloride* (with 1 mol. C_6H_6), forms prisms, m.p. 190°–192°, from benzene, convertible into [η-] or 1 : 3 : 7-*trichloronaphthalene* (Alén, Förhandl. 1884, 2, 95; Armstrong and Wynne, Chem. Soc. Proc. 1890, 6, 13).

Reactions.—Reduction with ammonium sulphide converts it into *α-naphthylamine*-3 : 7-*disulphonic acid*, and with sodium amalgam into *α-naphthylamine* (Alén, Förhandl. 1883, 8, 21).

(iii.) α-**Nitronaphthalene-3 : 8-disulphonic acid** is formed as chief product, together with some β-nitronaphthalene-4 : 7-disulphonic acid (Schultz, Ber. 1890, 23, 77; *cf.* Armstrong and Wynne, Chem. Soc. Proc. 1891, 7, 27), by nitrating naphthalene-1 : 6-disulphonic acid or its salts.

Preparation.—Sodium naphthalene-β-sulphonate (50 pts.), sulphonated with 2½–3 times its weight of 20 p.c. anhydro-acid at 100°, is cooled to 10°–15°, and nitrated below 25° with nitric acid of sp.gr. 1·4 (22·5 pts.). After dilution, the nitro-acid can easily be separated owing to its sparing solubility in alkalis or brine (Ewer and Pick, D. R.-P. 52724 of 1888).

It is also obtained, together with α-nitronaphthalene-4 : 8-disulphonic acid, when the product formed by sulphonating naphthalene (10 pts.) with 23 p.c. anhydro-acid (50 pts.) at 15° is nitrated with nitric acid of sp. gr. 1·45 (7 pts.) (Aktienges., D. R.-P. 45776 of 1887; Eng. Pat. 4625 of 1888). Or, the product obtained by sulphonating naphthalene with 5 times its weight of sulphuric acid at 90°–110° is nitrated, and poured into brine to separate the nitro-acid (Badische, D. P. Anm. B. 9514, B. 9548 of 1889; Bernthsen, Ber. 1889, 22, 3328).[1]

Salts.—The salts crystallise in easily soluble needles; the *potassium* salt K_2A is almost insoluble in dilute caustic potash solution (Friedlaender, Ber. 1895, 28, 1535).

Reactions.—(1) On reduction in acid solution it is converted into [ε-]*α-naphthylamine*-3 : 8-*disulphonic acid* (Bernthsen, *l.c.*); but in neutral solution with sodium bisulphite it yields *α-naphthylamine*-3 : 6 : 8-*trisulphonic acid* (Fischesser & Co., D. R.-P. 76438 of 1893; Eng. Pat. 7046 of 1894).

(2) When heated with concentrated caustic soda solution it yields the basic sodium salt of 4-*nitroso-α-naphthol*-2 : 5-*disulphonic acid* (Friedlaender, Ber. 1895, 28, 1535).

(iv.) α-**Nitronaphthalene-4 : 8-disulphonic acid** is obtained, together with the 3 : 8-acid, as already described (Aktienges., D. R.-P. 45776 of 1887; Eng. Pat. 4625 of 1888). It is also formed, together with β-nitronaphthalene-4 : 8-disulphonic acid, by nitration of naphthalene-1 : 5-disulphonic acid, and separated from it by the greater solubility of the sodium α-salt in brine (Cassella, D. R.-P. 65997 of 1890).

(v.) α-**Nitronaphthalene-5 : 8-disulphonic acid** is formed when barium naphthalene-1 : 4-disulphonate (5 pts.), mixed with sulphuric acid (30 pts.), is nitrated at 10°–15° with 25 p.c. nitric acid (3 pts.). The product is free from isomerides (Bayer, D. R.-P. 70857 of 1892).

(vi.) β-**Nitronaphthalene-4 : 7-disulphonic acid** is formed, together with α-nitronaphthalene-3 : 8-disulphonic acid, by nitration of naphthalene-1 : 6-disulphonic acid (Schultz, Ber. 1890, 23, 77; Armstrong and Wynne, Chem. Soc. Proc. 1891, 7, 27).

(vii.) β-**Nitronaphthalene-4 : 8-disulphonic acid** is obtained when naphthalene-1 : 5-disulphonic acid (28 pts.), suspended in well-cooled sulphuric acid (90 pts.), is nitrated with a mixture of nitric acid of 90°(? 40°) Bé. (10 pts.) and sulphuric acid (10 pts.). The product is poured on to ice, and soda (40 pts.) added to separate the β-salt from the more soluble α-salt (Cassella D. R.-P. 65997 of 1890).

Nitronaphthalenetrisulphonic Acids.

(i.) α-**Nitronaphthalene-3 : 5 : 7-trisulphonic acid** is formed when sodium naphthalene-1 : 3 : 7-trisulphonate, dissolved in sulphuric acid, is nitrated at 15°–20° with nitrosulphuric acid containing 43 p.c. nitric acid, and the crystalline nitro-acid separated by the addition of salt to the product after dilution with water (Cassella, D. R.-P. 75432 of 1891).

(ii.) α-**Nitronaphthalene-3 : 6 : 8-trisulphonic acid** is obtained by the nitration of naphthalene-1 : 3 : 6-trisulphonic acid, dissolved in sulphuric acid (Koch, D. R.-P. 56058; Eng. Pat. 9258 of 1890).

Reactions.—On reduction in acid solution it yields *α-naphthylamine*-3 : 6 : 8-*trisulphonic acid* (Koch, *l.c.*), but when heated with ammonia at 150°–170° it is converted into *β-naphthylamine*-3 : 6 : 8-*trisulphonic acid* with elimination of nitrogen (Kalle, D. R.-P. 176621 of 1905).

(iii.) α-**Nitronaphthalene-4 : 6 : 8-trisulphonic acid** is produced by the nitration of sodium naphthalene-1 : 3 : 5-trisulphonate (10 pts.), dissolved in monohydrate (30 pts.), with 25 p.c. nitric acid (6·1 pts.), at 40°–50° (Kalle, D. P. Anm. K. 11104 of 1893; Eng. Pat. 1641 of 1894; D. R.-P. 82563 of 1893; Bayer, D. R.-P. 80741; D. P. Anm. F. 7004; Eng. Pat. 17141c of 1893).

Dinitronaphthalenes.

Introductory.—Two dinitronaphthalenes, the 1 : 5- and 1 : 8- compounds, are obtained when naphthalene or α-nitronaphthalene is nitrated with strong nitric acid or with a mixture of nitric and sulphuric acids. The proportion in which they are formed varies to some extent, but may be taken as 1 to 2 (Friedlaender and Scherzer, Chem. Zentr. 1900, i. 410), although according to Gassmann, who used more concentrated acid mixtures, the best yield of 1 : 8-dinitronaphthalene (about 70 p.c.) is obtained only when the temperature beyond the stage of mononitronaphthalene is the lowest possible (Ber. 1896, 29, 1244, 1521).

(i.) **1 : 3-Dinitronaphthalene** ([γ-]dinitronaphthalene) is prepared by boiling diazotised 2 : 4-dinitro-α-naphthylamine with alcohol. The statement that it is a product of the nitration of naphthalene (Höchst, D. R.-P. 96227 of

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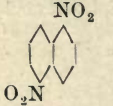
[1] According to Friedlaender (Heumann, Anilinfarben, 1898, ii. 518), the product obtained by any of these methods contains at least four nitro-acids, of which the α-nitronaphthalene-3 : 8-disulphonic acid constitutes only about 40 p.c.

1897) has been shown to be erroneous by Friedlaender (Ber. 1899, 32, 3531). It crystallises from dilute alcohol in bright yellow needles, m.p. 144° (Liebermann and Hammerschlag, Annalen, 1876, 183, 274; *cf.* Friedlaender, Ber. 1895, 28, 1951).



(ii.) 1 : 5-**Dinitronaphthalene** ([α-] or *ana*-dinitronaphthalene) is obtained as minor product, together with the 1 : 8-compound, when α-nitronaphthalene, dissolved in sulphuric acid (4–5 pts.) is nitrated at 0° by the calculated quantity of a mixture of nitric acid, sp.gr. 1·4 (1 pt.) with sulphuric acid (2 pts.). The solution, at first red, becomes white owing to the separation of the dinitronaphthalenes as a thick magma. When dry, the product is dissolved in 6 parts of boiling pyridine, and from the solution, when cold, almost the whole of the 1 : 5-isomeride separates in the pure state (Friedlaender, Ber. 1899, 32, 3531). Or, by increasing the proportion of sulphuric acid, and, at the close of the nitration, heating the mixture at 80°–90° until dissolved, and afterwards cooling to 20° an almost complete separation of the 1 : 5-isomeride is achieved (Friedlaender, *l.c.*; Kalle, D. R.-P. 117368 of 1899).

The separation from the 1 : 8-derivative can also be effected by extraction of the washed and dried nitration product with acetone (Beilstein and Kurbatow, Annalen, 1880, 202, 219), chloroform (Darmstaedter and Wichelhaus, *ibid.* 1869, 152, 301), benzene (Aguiar, Ber. 1870, 3, 29; Beilstein and Kuhlberg, Annalen, 1873, 169, 85), or acetic acid (Aguiar, Ber. 1872, 5, 372), in which the 1 : 5-compound is only sparingly soluble.

Properties.—1 ·5-Dinitronaphthalene crystallises from acetic acid in six-sided yellow needles and melts at 216° (Aguiar, Ber. 1872, 5, 372). It is only sparingly soluble in the ordinary solvents, and practically insoluble in carbon disulphide or cold nitric acid. With phosphorus pentachloride it yields 1 : 5-*dichloronaphthalene* (Atterberg, Ber. 1876, 9, 1188, 1730).

Reactions.—(1) Reduction with alcoholic ammonium sulphide converts it into 5-*nitro-α-naphthylamine* and 1 : 5-*diaminonaphthalene* (Beilstein and Kuhlberg, Annalen, 1873, 169, 87), but with tin and hydrochloric acid only into the latter (Erdmann, *ibid.* 1888, 247, 360).

(2) When boiled with ammonium sulphite or sodium bisulphite solution it yields 1 : 5-*diaminonaphthalenedisulphonic acid* (Fischesser & Co., D. R.-P. 79577 of 1894), but if reducing agents, such as glucose, milk sugar, sodium stannite, &c., be present, brown *dyestuffs* are formed (Badische, D. R.-P. 92538; Eng. Pat. 20250 of 1896).

(3) When heated with 12–23 p.c. anhydrosulphuric acid at 40°–50°, it is converted into 8-*nitro*-4-*nitroso-α-naphthol* (Badische, D. R.-P. 91391; Eng. Pat. 14955 of 1896; Graebe, Ber. 1899, 32, 2879; Friedlaender, *ibid.* 3528; Friedlaender and Scherzer, *cf.* J. Soc. Chem. Ind. 1900, 19, 339).

If, however, a reducing agent, such as sulphur or zinc be present, a *naphthazarin intermediate product* is formed (*cf.* Bayer, D. R.-P. 71386, 77330; Eng. Pat. 17673 of 1892).

By the use of boric acid, instead of reducing agents, with monohydrate at 200°–300°, two dyestuffs are obtained which dye chromed wool black (Bayer, D. R.-P. 82574 of 1894).

(iii.) 1:6-**Dinitronaphthalene** ([δ-]dinitronaphthalene) is obtained by boiling diazotised 1 : 6-dinitro-β-naphthylamine with alcohol. It crystallises from alcohol in bright-yellow needles, m.p. 161·5° (Graebe and Drews, Ber. 1884, 17, 1170; *cf.* Kehrmann and Matis, *ibid.* 1898, 31, 2419).

(iv.) 1 : 8-**Dinitronaphthalene** ([β-] or *peri*-dinitronaphthalene) is the major product of the dinitration of naphthalene. For its purification, *v.* 1 : 5-dinitronaphthalene.

Properties.—1 : 8-Dinitronaphthalene crystallises in large, yellow rhombic tables, and melts at 170° (Aguiar, Ber. 1872, 5, 372). In ordinary solvents, and in concentrated sulphuric acid it is more soluble than the 1 : 5- compound. According to Beilstein and Kuhlberg (Annalen, 1873, 169, 86), one part dissolves in 91·4 parts of chloroform, in 530 parts of 88 p.c. alcohol, or in 139 parts of benzene at 19°; and according to Friedlaender (Ber. 1899, 32, 3531), 1 part dissolves in 10 parts of cold and in 1·5 parts of hot pyridine. With phosphorus pentachloride it yields 1 : 8-*dichloronaphthalene* in small quantity, the chief product being 1 : 4 : 8-*trichloronaphthalene* (Atterberg, Ber. 1876, 9, 1188, 1732).

Reactions.—(1) Reduction with phosphorus iodide and water (Aguiar, Ber. 1874, 7, 309; Meyer and Muller, *ibid.* 1897, 30, 775), or with tin and hydrochloric acid (Ladenburg, *ibid.* 1878, 11, 1651; Erdmann, Annalen, 1888, 247, 363), converts it into 1 : 8-*diaminonaphthalene*.

(2) When digested with sodium or ammonium sulphite at 70°–90°, the alkali set free being removed as formed, it is converted into *α-naphthylsulphamino*-4 : 7-*di-* and 2 : 4 : 7-*trisulphonic acids* (Höchst, D. R.-P. 215338 of 1908), but when boiled with sodium bisulphite solution, it yields 1 : 8-*diaminonaphthalenetrisulphonic acid* (Fischesser & Co., D. R.-P. 79577; Eng. Pat. 13156 of 1894).

(3) Blue, violet, or black dyestuffs are obtained when it is heated with alkali, sodium bisulphite, and reducing agents, such as glucose (Badische, D. R.-P. 79208; Eng. Pat. 10996 of 1893; D. R.-P. 88236 of 1895; Eng. Pat. 7766 of 1896), milk sugar, sodium stannite, or sodium sulphide (*ibid.* D. R.-P. 92471; Eng. Pat. 20250 of 1896); or, omitting alkali, with sodium sulphide (*ibid.* D. R.-P. 84989; Eng. Pat. 10996 of 1893; D. R.-P. 88847; Eng. Pat. 22603 of 1894), or sodium disulphide (Höchst, D. R.-P. 117188, 117189 of 1898).

(4) When heated with 12–23 p.c. anhydroacid, it yields 5-*nitro*-4-*nitroso-α-naphthol* (Badische, D. R.-P. 90414 of 1895; Eng. Pat. 14955 of 1896; Graebe, Ber. 1899, 32, 2877; Friedlaender, *l.c.*; Friedlaender and Scherzer, *l.c.*).

By heating it with sulphuric acid and reducing agents, such as aniline or tin or iron (Badische, D. R.-P. 76922 of 1893; Eng. Pat. 3828 of 1894), or electrolysing its solution in sulphuric acid (*ibid.* D. R.-P. 79406; Eng. Pat. *l.c.*) it forms a *naphthazarin intermediate product* isomeric with that obtained from 1 : 5-dinitronaphthalene.

If sulphuretted hydrogen or antimony sulphide be used with the sulphuric acid, black dyestuffs are formed (Badische, D. R.-P. 114264 of

1899; Eng. Pat. 890 of 1900), which by interaction with sodium thiosulphate give violet shades (*ibid.* D. R.-P. 147945; Eng. Pat. 1864 of 1903).

(5) When it is heated in caustic soda solution with phenols (Höchst, D. R.-P. 122476 of 1900) or aminophenols or phenolcarboxylic acids (*ibid.* D. R.-P. 125133 of 1900), alkali soluble products are obtained.

DINITRONAPHTHALENEMONOSULPHONIC ACIDS.

(i.) 1:5-**Dinitronaphthalene**-3-[or 7-]**sulphonic acid** is obtained when α-nitronaphthalene-6-sulphonic acid, dissolved in sulphuric acid, is nitrated at 0°–15°, and salt is added to the product after dilution with water (Cassella, D. R.-P. 85058 of 1894). It is also stated to be formed when 1 : 5-dinitronaphthalene, dissolved in 6 times its weight of monohydrate, is heated at 100°–110° with rather more than twice its weight of 20 p.c. anhydro-acid (Höchst, D. R.-P. 117268 of 1900), but according to Eckstein (Ber. 1902, 35, 3403), 1 : 5-dinitronaphthalene is not sulphonated by 15–25 p.c. anhydro-acid at 140°, and at higher temperatures or with stronger acid is destroyed.

Identification.—The *sodium* salt forms needles, soluble in 12 parts of boiling water; the *chloride* prisms, m.p. 118°, from chloroform (Höchst, *l.c.*).

Reactions.—(1) With sodium sulphite or bisulphite solution it yields a *nitro-α-naphthylaminesulphonic acid* (Höchst, *l.c.*).

(2) Anhydro-acid in presence of a reducing agent converts it into a soluble blue "intermediate product," which yields a *naphthazarinsulphonic acid* when boiled with water (*ibid.*).

(ii.) 1 : 8-**Dinitronaphthalene** - 3 - [or 6 -] **sulphonic acid** is formed, together with the 1 : 5-dinitro-acid, when sodium naphthalene - β - sulphonate, dissolved in sulphuric acid, is dinitrated below 10°, and is precipitated by stirring the product into twice its volume of brine, the 1 : 5-isomeride remaining in solution (Cassella, D. R.-P. 67017; Eng. Pat. 6972 of 1891; D. R.-P. 85058 of 1894). It is also produced when 1 : 8-dinitronaphthalene, dissolved in monohydrate, is sulphonated at 100°–110° with twice its weight of 20 p.c. anhydro-acid (Höchst, D. R.-P. 117268 of 1900; Eckstein, Ber. 1902, 35, 3403).

Identification.—The *barium* salt BaA_2+5H_2O forms needles soluble in 8·5 parts of boiling or 20 parts of cold water (Eckstein); the *sodium* salt, needles soluble in 6·5 parts of boiling water. The *chloride* has m.p. 143°–144° (Höchst, *l.c.*; *cf.* Hellström, Förhandl., 1888, 10, 613).

(iii.) 1 : 8-**Dinitronaphthalene**-4-[or 5-] **sulphonic acid** is formed when the monosulphonation product of α-nitronaphthalene, consisting chiefly of the 5-acid, is nitrated at 15°–20°, and the 1 : 8-dinitro-acid separated by stirring the mixture into brine (Cassella, D. R.-P. 70019 of 1892; Eng. Pat. 4613 of 1893).

(iv.) 2 : 4-**Dinitronaphthalene** - 8 - **sulphonic acid** is obtained when naphthasultam or 2 : 4-dinitronaphthasultam is heated with fuming nitric acid (Dannerth, J. Amer. Chem. Soc. 1907, 29, 1327).

DINITRONAPHTHALENEDISULPHONIC ACIDS.

(i.) 1 : 5-**Dinitronaphthalene**-3 : 7-**disulphonic acid** is obtained when sodium naphthalene-2 : 6-disulphonate (or α-nitronaphthalene-3 : 7-disulphonate), dissolved in sulphuric acid, is dinitrated (or nitrated) at 20°–30°, and the product salted out (Cassella, D. R.-P. 61174; Eng. Pat. 15346 of 1890; *cf.* Oehler, D. P. Anm. O. 1430 of 1890; Bayer, D. R.-P. 126198 of 1900).

Reaction.—When dissolved in monohydrate, and heated at 50° with a solution of sulphur in 20 p.c. anhydro-acid, a blue mordant dye of the naphthazarin 'intermediate product' type is produced (Bayer, *l.c.*).

(ii.) 1 : 6-**Dinitronaphthalene**-3 : 8-**disulphonic acid**, obtained by nitration of α-nitronaphthalene-3 : 8-disulphonic acid or naphthalene-1 : 6-disulphonic acid (Friedlaender and Kielbasinski, Ber. 1896, 29, 1982) has not been characterised.

(iii.) 1 : 6-**Dinitronaphthalene**-4 : 8-**disulphonic acid** is obtained when sodium naphthalene-1 : 5-disulphonate (or its mononitration product), dissolved in monohydrate, is dinitrated (or nitrated) below 30°. The product is free from isomerides (Kalle, D. R.-P. 72665 of 1893; Friedlaender and Kielbasinski, *l.c.*).

(iv.) 1 : 8-**Dinitronaphthalene**-3 : 6-**disulphonic acid** is obtained free from isomerides when sodium naphthalene-2 : 7-disulphonate, dissolved in sulphuric acid, is dinitrated at 20°–30°. (Cassella, D. R.-P. 67062 of 1890; Eng. Pat. 1742 of 1891; Bayer, D. R.-P., 69190 of 1891; Eng. Pat. 11522 of 1892). Its chloride is formed, together with the mononitro- derivative, by nitrating naphthalene-2 : 7-disulphonyl chloride (Alén, Förhandl., 1883, 8, 13).

Identification.—The *barium* salt $BaA+5H_2O$ prisms, and the *potassium* salt needles, K_2A from hot, or K_2A+4H_2O from cold solution, are easily soluble. The *chloride* (with 1 mol. C_6H_6), has m.p. 218·5°–219·5° (Alén, *l.c.*).

Reactions.—(1) Reduction converts it into 1 : 8-*diaminonaphthalene*-3 : 6-*disulphonic acid* (Cassella, *l.c.*), but with sodium sulphite or bisulphite solution it yields 1-*amino*-8-*naphthol*-3 : 6-*disulphonic acid* (Bayer, D. R.-P. 113944; Eng. Pat. 21138 of 1899).

(2) Dilute caustic soda solution converts it into *sodium* 5-*nitro*-4-*nitroso*-α-*naphthol*-2 : 7-*disulphonate*, or 4 : 5-*dinitrosodihydroxynaphthalene*-2 : 7-*disulphonate*, or both (Kalle, D. R.-P. 113063 of 1899).

TRINITRONAPHTHALENES.

Three trinitronaphthalenes, the 1 : 2 : 5-, 1 : 3 : 5-, and 1 : 4 : 5- derivatives, are obtained by the nitration of 1 : 5-dinitronaphthalene, and a fourth, the 1 : 3 : 8- derivative, by the nitration of 1 : 8-dinitronaphthalene. The constitution of these compounds has been determined by oxidation to the respective nitrophthalic acids.

1:2:5- or [δ-]Trinitronaphthalene (Will, Ber. 1895, 28, 377) crystallises from alcohol in needles, m.p. 112°–113°.

1:3:5- or [α-]Trinitronaphthalene (Aguiar, Ber. 1872, 5, 373, 897) crystallises from alcohol in scales, m.p. 122°.

1:4:5- or [γ-]Trinitronaphthalene (Beilstein and Kuhlberg, Annalen, 1873, 169, 97; *cf.* Will, *l.c.*) crystallises from chloroform in bright yellow scales, m.p. 154° (Aguiar, *l.c.* 903).

1:3:8- or [β-]Trinitronaphthalene (Beilstein and Kuhlberg, *l.c.*; Friedlaender, Ber.

1899, 32, 3531; Kalle, D. R.-P. 117368 of 1889) crystallises in needles, m.p. 218°. It dissolves in cold sodium bisulphite solution without undergoing change, but is converted into *nitroaminonaphtholsulphonic acids* when the solution is warmed (Friedlaender and Scherzer, *cf.* J. Soc. Chem. Ind. 1900, 19, 339).

TETRANITRONAPHTHALENES.

Four tetranitronaphthalenes have been described, and to three of them constitutional formulæ have been assigned.

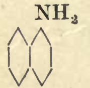
From 1 : 5-dinitronaphthalene, [α-]tetranitronaphthalene, which melts at 259° (Beilstein and Kuhlberg; Aguiar, *l.c.*); 1 : 2 : 5 : 8 or [δ-]tetranitronaphthalene, which decomposes at about 300° without fusion (Will, Ber. 1895, 28, 369); and 1 : 3 : 5 : 8- or [γ-]tetranitronaphthalene, which melts at 194°–195° (Will, *l.c.* 368) have been obtained; while, from 1 : 8-dinitronaphthalene, 1 : 3 : 6 : 8- or [β-] tetranitronaphthalene, which melts at 203°, has been prepared (Aguiar, *l.c.*; Will, *l.c.* 379).

IV. AMINO- DERIVATIVES.

Introductory.—α-Naphthylamine and several α-naphthylaminesulphonic acids are obtained by reduction of the corresponding α-nitro- derivatives with iron and dilute sulphuric acid. As β-nitro- derivatives are not readily accessible, β-naphthylamine and, with two exceptions, the β-naphthylaminesulphonic acids are prepared not by this reduction method, but by heating β-naphthol or the corresponding β-naphtholsulphonic acids with ammonia under pressure. α-Naphthylamine also can be prepared by heating α-naphthol with ammonia, although the yield is less satisfactory than in the case of the β-compound.

Secondary aminonaphthalenes are formed when the corresponding hydroxynaphthalenes are heated with primary amines under pressure.

AMINONAPHTHALENES.



(i.) α-**Naphthylamine** (α-aminonaphthalene; naphthalidam; naphthalidine) is formed by the reduction of α-nitronaphthalene with alcoholic ammonium sulphide (Zinin, J. pr. Chem. 1842, 27, 141; *cf.* Piria, Annalen, 1851, 78, 31); iron filings and acetic acid (Béchamp, Ann. Chim. Phys. 1854, [iii.] 42, 195; Balló, Ber. 1870, 3, 288, 673); tin and hydrochloric acid (Roussin, Compt. rend. 1861, 52, 797); zinc and hydrochloric acid (Böttger, Dingl. poly. J. 1870, 197, 458); alcoholic potash (Klobukowsky, Ber. 1877, 10, 571); zinc dust and aqueous calcium chloride (Dechend, D. R.-P. 43230 of 1887); or hydrogen and reduced copper at 330°–350° (Sabatier and Senderens, Compt. rend. 1902, 135, 225; *cf.* Senderens, D'Andoque, and Chefdebien, D. R.-P. 139457 of 1901).

It is also obtained when α-naphthol is heated with ammonia under pressure at 150°–160° for 60–70 hours (Badische, D. R.-P. 14612 of 1880). The yield may reach 70 p.c. of that calculated if the naphthol be heated with ammonia-calcium chloride at 270° for 8 hours, but dinaphthylamine is also formed in quantities varying with the conditions employed (Benz, Ber. 1883, 16, 14). Substitution of acetamide at 270° for ammonia gives a 50 p.c. yield of acet-α-naphthalide, together with about 15 p.c. of dinaphthylamine (Calm, Ber. 1882, 15, 615), but replacement of ammonia by sodamide at 220° leads to the production of 1-*amino*-5-*naphthol* (Sachs, D. R.-P. 181333 of 1905).

Preparation.—On the large scale α-naphthylamine is prepared by reducing granulated α-nitronaphthalene (15 pts.) with soft iron borings or 'swarf' (20 pts.) and hydrochloric acid (1 pt.)[1] at 50°–70° in an apparatus similar to that used in the manufacture of aniline, but provided with a wide exit-pipe for the escaping gases instead of a condenser. To remove the acid, milk of lime is added to the product, and the naphthylamine separated by distillation, superheated steam being used to drive the vapour into the condenser as rapidly as possible. The yield amounts to about 70 p.c. of that calculated.[2] The crude base is purified by a second distillation, but always contains appreciable quantities of naphthalene, owing to decomposition during the first distillation (Witt, Chem. Ind. 1887, 10, 218; Paul, Zeitsch. angew. Chem. 1897, 145). It also contains a small quantity of β-naphthylamine (*q.v.*).

To obtain α-naphthylamine free from the β- compound, the hydrochloride of the technical base can be fractionally crystallised to remove the more soluble β-salt (Reverdin and Noelting, Sur la constitution de la naphthaline, ed. 1888, 35), or the technical base can be (*a*) repeatedly crystallised from warm light petroleum (Erdmann, Annalen, 1893, 275, 217, footnote), or (*b*) fractionally crystallised from a relatively small quantity of xylene (Chem. Fab. Weiler-ter Meer, D. R.-P. 205076 of 1906; Eng. Pat. 16446 of 1907).

Identification.—α-Naphthylamine crystallises from most solvents in colourless scales or flat needles, melts at 50°, boils at 300° (Zinin, *l.c.*), and is but little volatile with steam. It is easily soluble in alcohol, ether, or aniline, but almost insoluble in water, of which 100 c.c. dissolve about 0·167 gram at the ordinary temperature (Balló, *l.c.*). On exposure to the air, the technical product changes colour gradually to greyish-violet, owing possibly to the presence of a small quantity of 1 : 8-diaminonaphthalene (Witt, *l.c.*). Its odour is characteristic and unpleasant.

The salts are for the most part sparingly soluble in water. The *hydrochloride* $B{\cdot}HCl$ and the *sulphate* $B_2{\cdot}H_2SO_4+2H_2O$ form scales; the *platinichloride* $(B{\cdot}HCl)_2PtCl_4$ is a crystalline powder. The *picrate*, $B{\cdot}HA$, forms sparingly soluble prisms, m.p. 161° (Smolka, Monatsh. 1885, 6, 923; *cf.* Suida, Ber. 1908, 41, 1913).

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[1] Under these conditions, ferrous chloride in the presence of water is probably the reducing agent, thus:—

$$(1)\ 24FeCl_2 + 4C_{10}H_7{\cdot}NO_2 + 4H_2O = 12Fe_2Cl_4O + 4C_{10}H_7{\cdot}NH_2;$$

$$(2)\ 12Fe_2Cl_4O + 9Fe = 3Fe_3O_4 + 24FeCl_2.$$

[2] Other processes for the recovery of the base have been devised in which either the iron and iron oxide are removed electromagnetically from the reduction product fused at 50°–60° (Landshoff, D. R.-P. 83560 of 1895), or the reduction product is extracted by a relatively small quantity of a solvent, such as benzene (*ibid.* D. R.-P. 184497 of 1905).

Reactions.—(1) With nitrous acid, in the absence of sufficient mineral acid, it forms *aminoazonaphthalene*, m.p. 180°, as a brown precipitate (Liebermann, Annalen, 1876, 183, 265; Nietzki and Goll, Ber. 1885, 18, 298); but in acid solution the *diazo-* compound is produced, from which *α-naphthol* (Griess, Journ. Chem. Soc. 1867, 20, 89) and many *azo-* dyes have been obtained.

(2) Digestion with water under pressure at 200° converts it into *α-naphthol* (Höchst, D. R.-P. 74879; Eng. Pat. 14301 of 1892).

(3) When heated with potassium dichromate and dilute sulphuric acid it is oxidised to 1 : 4-[*α*]*naphthaquinone* and to *phthalic acid* (Monnet, Reverdin, and Noelting, Ber. 1879, 12, 2306).

(4) Oxidising agents such as ferric chloride, silver nitrate, mercuric chloride, or chromic acid when added to an α-naphthylamine salt in aqueous solution produce an azure-blue precipitate of *naphthameïn*, which rapidly becomes purple, dissolves in chloroform, and is not bleached by sulphurous acid (Piria, Annalen, 1851, 78, 64; Schiff, *ibid.* 1857, 101, 92; 1864, 129, 255).

(5) Reduction in boiling amyl alcohol solution with sodium converts it into ar.-*tetrahydronaphthylamine* (Bamberger and Althausse, Ber. 1888, 21, 1789).

(6) When heated with zinc chloride or calcium chloride at 280° it undergoes partial decomposition into *αα′-dinaphthylamine* and ammonia (Benz, *l.c.*).

Commercial tests.—Commercial α-naphthylamine should have the right melting-point and dissolve almost completely in dilute acids. The proportion of naphthalene present can be determined by distilling the sample with excess of hydrochloric acid in a current of steam and extracting the distillate with ether.

Acetyl derivatives.—Acetyl-α-naphthylamine (*acet-α-naphthalide*) $C_{10}H_7{\cdot}NH{\cdot}CO{\cdot}CH_3$ is formed by heating α-naphthol with ammonium acetate at 270°–280° (Calm, Ber. 1882, 15, 615), and prepared by boiling α-naphthylamine with 1·25 times its weight of glacial acetic acid for 4–5 days (Liebermann and Dittler, Annalen, 1876, 183, 229).

Properties.—It crystallises in needles, m.p. 159°, and is easily soluble in alcohol or acetic acid, but almost insoluble in cold water (Liebermann and Dittler, *l.c.;* Tommasi, Bull. Soc. chim. 1873, [ii.] 20, 20). On nitration in acetic acid solution it yields a mixture of 2-*nitroacet-α-naphthalide* and 4-*nitroacet-α-naphthalide* (Andreoni and Biedermann, Ber. 1873, 6, 342; Lellmann and Remy, *ibid.* 1886, 19, 797); and by further nitration 2 : 4-*dinitroacet-α-naphthalide* (Liebermann and Dittler, *l.c.* 274; Meldola and Forster, Chem. Soc. Proc. 1893, 9, 8).

Acetyl-α-naphthylaminesulphonic acids. Acet-α-naphthalide, when warmed with 20–25 p.c. anhydro-acid is converted chiefly into *acetyl-α-naphthylamine-5-sulphonic acid*, some 4-acid also being formed (Ewer and Pick, D. R.-P. 42874 of 1887; Schultz, Ber. 1887, 20, 3161). With 35 p.c. anhydro-acid below 30°, it yields the 5 : 7-*disulphonic acid* (Badische, D. R.-P. 69555 of 1892; Eng. Pat. 2370 of 1893).

The 2-, 4-, 5-, 6-, 7-, and 8-*sulphonic acids*, and the 3 : 6-, 4 : 6-, and 4 : 7-*disulphonic acids* can be prepared by heating solutions of the sodium salts of the respective α-naphthylamine-sulphonic acids at 50°–60° with acetic anhydride for a few minutes (Höchst, D. R.-P. 129000 of 1899; Eng. Pat. 17366 of 1898; *cf.* Nietzki and Zübelen, Ber. 1899, 22, 451; Cassella, D. R.-P. 74177; Eng. Pat. 15444 of 1893). Both acids and salts are very soluble in water, and each acid can be deacetylated by boiling it with water.

Alkyl derivates. *Methyl-α-naphthylamine* (Fischer, Annalen, 1895, 286, 159) is an oil, b.p. 293° (Landshoff, Ber. 1878, 11, 638); *dimethyl-α-naphthylamine* (Landshoff, *l.c.;* Hantzsch, Ber. 1880, 13, 1348) an oil, b.p. 272° (Friedlaender and Welmans, Ber. 1888, 21, 3124; *cf.* Bamberger and Helwig, *ibid.* 1889, 22, 1315; Pinnow, *ibid.* 1899, 32, 1406); *ethyl-α-naphthylamine* (Limpricht, Annalen, 1856, 99, 117; Friedlaender and Welmans, *l.c.*), an oil, b.p. 303° under 722·5 mm. (Bamberger and Helwig, *l.c.*); *diethyl-α-naphthylamine*, an oil, b.p. 283°–285° (Friedlaender and Welmans, *l.c.*).

Alkyl-α-naphthylaminesulphonic acids. Of these derivatives, *methyl-α-naphthylamine*-4-*sulphonic acid* has been made from α-naphthol-4-sulphonic acid by interaction with methylamine, and methylamine bisulphite at 150° (Badische, D. R.-P. 121683; Eng. Pat. 18726 of 1900), but *methyl-α-naphthylamine*-6-*sulphonic acid*, and *dimethyl-α-naphthylamine*-4-, 5-, 7-, and 8- *sulphonic acids* have been prepared by methylating the corresponding α-naphthylaminesulphonic acids (Füssganger, Ber. 1902, 35, 977). Dimethyl-α-naphthylamine-5-sulphonic acid, with an easily soluble isomeride, is obtained when dimethyl-α-naphthylamine is sulphonated with 95 p.c. sulphuric acid at 130° (Fussgänger, *l.c.*).

Aryl derivatives. *Phenyl-α-naphthylamine* forms prisms, m.p. 62°, b.p. 226° under 15 mm. (Girard and Vogt, Bull. Soc. chim. 1872, [ii.] 18, 68; Streiff, Annalen, 1881, 209, 152; Friedlaender, Ber. 1883, 16, 2077); o-*tolyl-α-naphthylamine*, needles, m.p. 94°–95° (Friedlaender, *l.c.*); p-*tolyl-α-naphthylamine*, prisms, m.p. 78°–79°, b.p. 236° under 15 mm. (Girard and Vogt, *l.c.*; Friedlaender, *l.c.*; Gnehm and Rübel, J. pr. Chem. 1901, [ii.] 64, 497).

Aryl-α-naphthylaminesulphonic acids. Of these derivatives, the phenyl- (*o*- or *p*-tolyl-) 3-, 4-, 5-, 6-, 7-, and 8-sulphonic acids have been prepared by heating the corresponding α-naphthylaminesulphonic acids with aniline (*o*- or *p*-toluidine) and its hydrochloride at 160°–170° (Bayer, D. R.-P. 70349, 71158, 71168; Eng. Pat. 7337A of 1892). Less satisfactory results are obtained when α-naphtholsulphonic acids (*cf.* Aktienges., D. R.-P. 38424 of 1886) are used instead of the α-naphthylamine compounds. The acids are very sparingly soluble in water; the sodium salts crystallise in scales, and, with the exception of the 3-, 7-, and 8-salts, are sparingly soluble (Bayer, *l.c.*).

Little is known of the aryl-α-naphthylamine-di- or tri-sulphonic acids. From two series of these acids, each containing SO_3H in the same nucleus as the NH_2 group, the corresponding aryl-derivative has not been isolated, but:

(*a*) Owing to the elimination of the 4-sulphonic group, *phenyl-* (p-*tolyl-*)*α-naphthylamine*-6-, 7- or 8-*sulphonic acid* is the product when α-naphthylamine-4 : 6-, 4 : 7-, or 4 : 8-disulphonic acid is phenylated (Aktienges., D. R.-P. 158923 of 1903; 159353; Eng. Pats. 15624, 24669 of 1904);

(*b*) Owing to the replacement of the 3-sulphonic group by the phenyl- (*p*-tolyl-) amino-group, *diphenyl*-(*di*-p-*tolyl*-)-1 : 3-*diaminonaphthalene sulphonic acids* result from phenylation of the acids derived from α-naphthylamine-3-sulphonic acid (Bayer, D. R.-P. 75296, 76414; Eng. Pat. 8898 of 1893).

α-NAPHTHYLAMINESULPHONIC ACIDS.

Introductory. — α - Naphthylaminesulphonic acids can be prepared by the following methods, of which the last two are technically unimportant:

(1) By the sulphonation of α-naphthylamine.

(2) By nitration of the corresponding naphthalenesulphonic acids and subsequent reduction.

(3) By sulphonation of α-naphthylamine-sulphonic acids obtained from nitronaphthalene-sulphonic acids.

(4) By heating α-naphtholsulphonic acids, other than those which contain sulphonic groups in the 2- or 3- position, with ammonium sulphite and ammonia at 100°–150°, and afterwards acidifying the products.

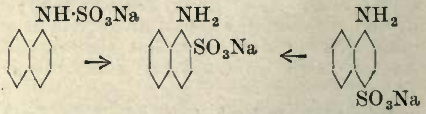
(5) By heating α-chloronaphthalenesulphonic acids with ammonia under pressure.

(6) By partial hydrolysis of α-naphthylamine-di- or tri-sulphonic acids.

Two of the monosulphonic acids, moreover, are obtained by methods applicable only to them:

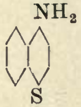
(*a*) Naphthionic acid, one of the three monosulphonic acids formed from α-naphthylamine by sulphonation, is obtained free from its isomerides by baking the acid sulphate of α-naphthylamine at 180°–200°;

(*b*) α-Naphthylamine-2-sulphonic acid is the only monosulphonic acid formed when sodium α-naphthylsulphamate or sodium naphthionate is heated at about 200°:

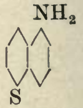


Three mono-, two di-, and two tri-sulphonic acids are known to be formed by the action of sulphuric acid on α-naphthylamine, and a third di- and third tri-sulphonic acid can be obtained by the sulphonation of α-naphthylamine-2-sulphonic acid, itself producible from α-naphthylamine and sulphuric acid, but only under special conditions (*v. supra*).

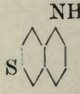
The nature of the sulphonation product depends on the four factors, concentration and relative quantity of the sulphuric acid, and temperature and duration of the reaction; but Erdmann (Annalen, 1893, 275, 192) has shown that it is possible to obtain, as chief product, successively the 4-, 5-, and 6-monosulphonic acid by prolonging the reaction without altering the temperature or the concentration of the sulphuric acid—



I.

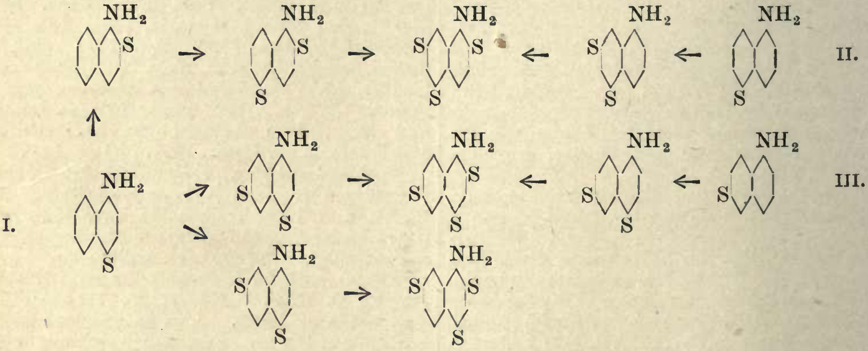


II.



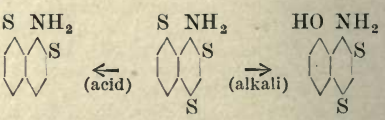
III.

From the scheme, which indicates the course of the sulphonation of α-naphthylamine, it will be seen that the 2- position is not occupied until trisulphonation occurs, and that neither the 3- nor the 8- position is attacked under any conditions—



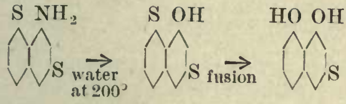
For the preparation of α-naphthylamine-8-sulphonic and 3 : 8-disulphonic acids, as well as of other acids not obtainable from α-naphthylamine by sulphonation, recourse is had to the second general method, in which the corresponding nitronaphthalenesulphonic acids are reduced.

As is usually the case, the sulphonic groups in α- are more easily eliminated than those in β-positions, whether the agent be caustic alkali, water, or dilute acid at high temperatures, or sodium amalgam in the cold. But the α-sulphonic groups differ in the degree of readiness with which they can be displaced; for example, the 4-sulphonic group is eliminated more easily than either the 5- or the 8- group by hydrolysis with dilute acids; but is replaced by hydroxyl least easily, and the 8-group most easily, of the three by fusion or digestion with caustic alkali—



If, instead of being fuesd or digested with caustic alkali at a high temperature, α-naphthylaminesulphonic acids be boiled with dilute caustic alkali solution and zinc dust, partial hydrolysis occurs, the α-sulphonic group eliminated being usually the one which, in the potash fusion, is exchanged for hydroxyl.

From α-naphthylaminesulphonic acids, the corresponding naphtholsulphonic acids can be obtained, not only by the diazo- reaction, but by heating the acids with water at 180°–200° under pressure. The latter reaction takes place most readily when sulphonic groups are present in the same nucleus as, or in the 8-position relatively to, the amino- group, and, as the example shows, the amino- group is replaced more readily than the α-sulphonic group by hydroxyl—



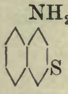
α-Naphthylaminesulphonic acids containing a 3-sulphonic group, by prolonged heating with caustic alkali solution at 260°–280°, yield hydroxytoluic acids, and, with ammonia (or aniline) at 180°, give 1 : 3-diaminonaphthalene derivatives.

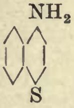
α-Naphthylamine-di- and tri-sulphonic acids containing an 8-sulphonic group are characterised by forming internal anhydrides (sultams), which yield yellow normal salts, and are less readily hydrolysed than the sultones derived from α-naphthol-8-sulphonic acids.

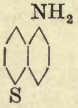
From solutions of the alkali monosulphonates the acids are precipitated, but from those of the di- and tri-sulphonates, acid salts separate on the addition of a mineral acid. A comparison of the relative strengths of the monosulphonic acids shows that the 2-acid is about 10 times as strong as the 4-, 5-, 6-, or 7-acid, and about 2000 times as strong as the 8-acid (Erdmann, Annalen, 1893, 275, 276).

A volumetric method for estimating α- (or β-) naphthylaminesulphonic acids, based on their different capacity for absorbing bromine has been devised by Vaubel (Chem. Zeit. 1893, 17, 1265). Most of these acids can be estimated accurately by titration with diazotised *p*-nitraniline (Bucherer, *cf.* J. Soc. Chem. Ind. 1907, 26, 818).

Azo- dyes of two types, *para-* and *ortho-*, can be obtained from α-naphthylaminesulphonic acids. Those usually formed are *para*-azo-dyes, but the sulphonic acids which contain one sulphonic group in the 3-, or 4-, or 5- position







do not form *para-* but *ortho*-azo- dyes (Gattermann and Schulze, Ber. 1897, 30, 50). In the production of azo-dyes, α-naphthylaminesulphonic acids are either themselves diazotised or are coupled as middle or end components with diazotised bases. Particularly valuable in the latter respect are the 6- and 7-monosulphonic acids, of which extensive use has been made in the series of disazo- and trisazo- dyes. In this article, however, it is not possible to refer, under each acid, to more than two or three typical illustrations of its application in the azo- dye industry.

α-Naphthylaminemonosulphonic Acids.[1]

(i.) **α - Naphthylamine - 2 - sulphonic acid** is obtained by heating sodium naphthionate at 200°–250° (Landshoff, D. R.-P. 56563; Eng. Pat. 6195 of 1890). The yield does not exceed 50 p.c., ammonia, α-naphthylamine, α-naphthylaminedisulphonic acids, sulphur dioxide and other substances being also formed (Erdmann, Annalen, 1893, 275, 225), but if the naphthionate is suspended in boiling naphthalene it becomes nearly quantitative, and the product contains as impurity only a small quantity of α-naphthylamine (Bayer, D. R.-P. 72833 of 1892). This acid is also formed when α-naphthylamine is heated with sulphanilic acid or its homologues at 180°–250° (*ibid.* D. R.-P. 75319 of 1892); or with naphthionic or β-naphthylamine-8-sulphonic acid at 160°–230° (*ibid.* D. R.-P. 77118 of 1892); or when α-naphthylsulphamic acid is heated at 170°–240° (Tobias, D. R.-P. 79132 of 1893; Eng. Pat. 15067 of 1894).

Identification.—The *acid* crystallises in needles, soluble in 244 parts of water at 20°, or in 31·3 parts at 100° (Doliński, Ber. 1905, 38, 1836). The *barium* BaA_2+H_2O and *calcium* CaA_2 salts form sparingly soluble scales; the *potassium* salt KA, needles sparingly soluble in cold water; the *sodium* salt NaA, scales soluble in 60 parts of cold water. It is convertible into *α-chloronaphthalene-2-sulphonyl chloride*, m.p. 80°, and into 1 : 2-*dichloronaphthalene*, m.p. 34° (Cleve, *ibid.* 1891, 24, 3472).

Reactions.—(1) From its sparingly soluble diazo- compound, Schaeffer's *α-naphthol-2-sulphonic acid* (Landshoff, *l.c.*), and *azo-* dyes (*cf.* Bayer, D. R.-P 66021; Eng. Pat. 5984 of 1891; D. R.-P. 75293 of 1892; Eng. Pat. 558 of 1893) have been obtained.

(2) On sulphonation with anhydro-acid, it yields *α-naphthylamine-*2 : 5-*disulphonic acid* (Landshoff, *l.c.*), and 2 : 5 : 7-*trisulphonic acid* (Bayer, D. P. Anm. F. 7001; Eng. Pat. 17141B of 1893).

(3) On fusion with caustic soda at 240°–270°, it is converted into 1-*amino*-5-*naphthol*-2-*sulphonic acid* (Landshoff, D. P. Anm. C. 4479 of 1892).

(ii.) **α-Naphthylamine-3-sulphonic acid** (Cleve's [γ-] acid) can be obtained by the reduction of α-nitronaphthalene-3-sulphonic acid with ferrous sulphate (Cleve, Ber. 1886, 19, 2181). It is also formed when sodium α-naphthylamine-3 : 8-disulphonate is boiled with 75 p.c. sulphuric acid (Kalle, D. R.-P. 64979 of 1892), or with zinc dust and 30 p.c. caustic soda solution (*ibid.* D. R.-P. 233934 of 1909), or is acted on by sodium amalgam (Friedlaender and Lucht, Ber. 1893, 26, 3032; *cf.* Bayer, Fr. Pats. 438737, 439010 of 1912; *v.* p. 592, footnote 1).

Identification.—The *acid* forms sparingly soluble needles; the *barium* BaA_2+H_2O in scales, *calcium*, *potassium*, and *sodium* NaA, salts are very soluble in water (Cleve, Ber. 1888, 21, 3271). It is convertible into *α-chloronaphthalene-3-sulphonyl chloride*, m.p. 106°, and into 1 : 3-*dichloronaphthalene*, (Cleve, *l.c.*; Armstrong and Wynne, Chem. Soc. Proc. 1889, 5, 18).

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[1] In every case where the constitution of an α-naphthylaminesulphonic acid is given, the NH_2 group is supposed to be in the position '1.'

For phenyl- (or *p*-tolyl-)-α-naphthylaminesulphonic acids, see p. 587.

Reactions.—(1) From its diazo- compound *α-naphthol-3-sulphonic acid* has been obtained (Kalle, *l.c.*; Friedlaender, Ber. 1895, 28, 1952; Gattermann and Schulze, *ibid.* 1897, 30, 54).

It couples with diazotised bases[1] as the middle component of *disazo*-dyes (*cf.* Bayer, D. R.-P. 65262; Eng. Pat. 22641 of 1891; D. R.-P. 67261 of 1892), but has been little used for this purpose.

(2) Fused with caustic alkalis at 250°–260° it gives 1-*amino-3-naphthol* (Friedlaender, *l.c.*), and, in closed vessels at 250°–280°, o-*toluic acid* (Kalle, D. R.-P. 79028 of 1893).

(3) When heated with ammonia at 160°–180° it yields 1:3-*diaminonaphthalene* (Kalle, D. R.-P. 89061 of 1894; Eng. Pat. 9103 of 1895); or with aniline (or *p*-toluidine) at 150°–170° it forms *diphenyl-(di-*p*-tolyl-)*-1:3-*diaminonaphthalene* (Bayer, D. R.-P. 75296; Eng. Pat. 8898 of 1893).

(iii.) α-**Naphthylamine**-4-**sulphonic acid** (naphthionic acid). Naphthionic acid, mixed with α-naphthylsulphamic acid, was first obtained by boiling α-nitronaphthalene with ammonium sulphite in alcoholic solution (Piria, Annalen, 1851, 78, 31). It is formed, with some of the more soluble 5-acid, when α-naphthylamine is sulphonated with 'fuming' sulphuric acid (*cf.* Erdmann, Annalen, 1888, 247, 315), and constitutes the sole product when it is heated with 4–5 times its weight of sulphuric acid at 100°–120°, or with 3 times its weight of acid at 130° until the product is soluble in alkali (Witt, Ber. 1886, 19, 57, 578; *cf.* Verein, Eng. Pat. 2237 of 1883). Pure naphthionic acid is obtained by 'baking' acid α-naphthylamine sulphate, or a mixture of α-naphthylamine and sulphuric acid in the proportion to form this salt, at 180°–200° (Nevile and Winther, Chem. Soc. Trans. 1880, 37, 632; Verein, *l.c.*), *or* by heating α-naphthylamine with 3 times its weight of potassium bisulphate at 200° (Bischoff and Brodsky, Ber. 1890, 23, 1914). It is also formed by boiling α-naphthylamine-4:8-disulphonic acid with zinc dust and dilute caustic soda solution (Kalle, D. R.-P. 233934 of 1909).

It is also formed when sodium α-naphthol-4-sulphonate is heated with 40 p.c. ammonium sulphite solution and 20 p.c. ammonia at 100°–150°, and the product acidified (Badische, D. R.-P. 117471 of 1899; Eng. Pat. 1387 of 1900); *or* when sodium α-chloronaphthalene-4-sulphonate is heated with 25 p.c. ammonia at 200°–210° (Oehler, D. R.-P. 72336 of 1893).

Preparation.—According to Schultz (Chem. d. Steinkohlenth. 3rd ed., 1, 202), naphthionic acid is prepared by heating α-naphthylamine (50 kilos.) and sulphuric acid (36·5 kilos.) at 170°–180° until a homogeneous mass is obtained. Crystallised oxalic acid (2·5 kilos.) is then stirred in, and the frothy mass, spread on lead plates, is heated in an oven at 170°–180° during 8 hours. The porous product is converted into sodium naphthionate (64 kilos.) in the usual way.

Identification.—The *acid* $HA+\frac{1}{2}H_2O$ forms small lustrous needles, which dissolve in 3225 parts of water at 20°, or in 438·5 parts at 100° (Doliński, Ber. 1905, 38, 1836). The *barium* salt BaA_2+8H_2O in scales, *calcium* salt CaA_2+8H_2O in monoclinic tables, *potassium* salt KA in scales, and *sodium* salt $NaA+4H_2O$ in large monoclinic prisms, dissolve readily in water, and, like the acid, show marked blue fluorescence in dilute solution. It is convertible into *α-chloronaphthalene-4-sulphonyl chloride*, m.p. 95°, and into 1:4-*dichloronaphthalene* (Cleve, Ber. 1887, 20, 73).

Reactions.—(1) From its sparingly soluble, micro-crystalline, yellow *diazo-* compound, *α-naphthol-4-sulphonic acid* (Nevile and Winther, *l.c.*; Dahl, D. P. Anm. D. 1486 of 1883), *dinitro-α-naphthol* (Nevile and Winther, *l.c.*), and many *azo*-dyes (*cf.* Bayer, D. R.-P. 75293 of 1892; Eng. Pat, 558 of 1893), have been obtained.

It couples with diazotised bases (*cf.* Aktienges., D. R.-P. 58505 of 1890), forming ortho-*azo*-dyes, but is valueless as a middle component, owing to the amino- group, when in the *ortho-* position to the diazo-complex, being difficult to diazotise.

(2) When heated with 50 p.c. caustic soda solution at 240°–260° it is converted into *α-naphthol-4-sulphonic acid* (Aktienges., D. R.-P. 46307 of 1888).

(3) The sodium salt, when heated with sodium bisulphite solution at 85°–90° for 24 hours yields *α-naphthol-4-sulphonic acid* after the product has been acidified and boiled (Bayer, D. R.-P. 109102; Eng. Pat. 16807 of 1899).

(4) Prolonged heating with sulphuric acid at 130° converts it successively into the 5-acid and the 6-acid, and it is the most easily hydrolysed acid of the three (Erdmann, Annalen, 1893, 275, 193). Its sodium salt, when heated at 200°–250°, is converted into sodium α-naphthylamine-2-sulphonate (*q.v.*).

(5) The *acetyl* derivative, obtained by heating the sodium salt with acetic anhydride, yields, on nitration, the *acetyl* derivative of 5-*nitro-α-naphthylamine-4-sulphonic acid* (Nietzki and Zübelen, Ber. 1889, 22, 451; Bucherer and Uhlmann, J. pr. Chem. 1909, [ii.] 80, 221).

(iv.) α-**Naphthylamine-5-sulphonic acid** (Laurent's acid; Cleve's [α-]naphthalidinesulphonic acid).[2] This acid is obtained by reduction of α-nitronaphthalene-5-sulphonic acid (Laurent, Compt. rend. 1850, 31, 538; *cf.* Cleve, Förhandl., 1875, 9, 13; Bull. Soc. chim. 1875, [ii.] 24, 511; Erdmann, Annalen, 1893, 275, 264; Schöllkopf, D. R.-P. 40571; Eng. Pat. 15775 of 1885). It constitutes the chief product (*cf.* Erdmann, Annalen, 1888, 247, 315), naphthionic acid being the subsidiary product, when α-naphthylamine is warmed with twice its weight of 'fuming' sulphuric acid (Cleve, Förhandl., 1876, 7, 39; *cf.* Schmidt and Schaal, Ber. 1874, 7, 1367); *or* when α-naphthylamine hydrochloride is sulphonated in the cold with 20–25 p.c. anhydro-acid (Witt, Ber. 1886, 19, 578; Schultz, *ibid.* 1887, 20, 3161; Mauzelius, *ibid.* 3403); *or* when acet-α-naphthalide is sulphonated with 3–4 times its weight of 20–25 p.c. anhydro-acid and the product de-acetylated by boiling the melt with water (Lange, Ber. 1887, 20, 2940; Ewer and Pick, D. R.-P. 42874 of 1887;

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[1] Diazobenzene chloride is an exception (*cf.* Gattermann and Schulze, Ber. 1897, 30, 54).

[2] The 'α-naphthylamine-[δ-]sulphonic acid' obtained by Hirsch by heating α-naphthylamine with 5 times its weight of sulphuric acid at 125°–130° for 8–9 hours (Hirsch, D. P. Anm. H. 7291 of 1887; Ber. 1888, 21, 2370), is a mixture of 5-acid with some 6-acid (Erdmann, Annalen, 1893, 275, 223).

Schultz, *l.c.*). It is also formed when sodium α-chloronaphthalene-5-sulphonate is heated with 25 p.c. ammonia solution at 200°–210° (Oehler, D. R.-P. 72336 of 1893).

Preparation.—The product obtained by sulphonating α-nitronaphthalene with 20 p.c. anhydro-acid, to which salt has been added (*v.* α-nitronaphthalene-5-sulphonic acid), is poured on to ice, reduced by iron, and converted into sodium salt in the usual way. Or the product of the sulphonation of acet-α-naphthalide or of α-naphthylamine hydrochloride with 20–25 p.c. anhydro-acid in the cold, is converted into the calcium salt and, by fractional crystallisation, separated from the more soluble naphthionate.

Salts.—The *acid* crystallises in anhydrous needles, soluble in about 940 parts of cold water. The *barium* salt BaA_2+6H_2O, in aggregates of small scales; *calcium* salt CaA_2+9H_2O, in tables; *potassium* salt $KA+H_2O$, in needles; and *sodium* salt $NaA+H_2O$, in aggregates of needles, dissolve readily in water; both acid and salts show greenish fluorescence in dilute aqueous solution (Cleve, Bull. Soc. chim. 1875, [ii.] 24, 511; Witt, *l.c.*; Mauzelius, Ber. 1887, 20, 3401). It is convertible into *α-chloronaphthalene-5-sulphonyl chloride*, m.p. 95°, and into 1 : 5-*dichloronaphthalene* (Erdmann, Annalen, 1888, 247, 353).

Reactions.—(1) From its sparingly soluble, yellow, crystalline *diazo-* compound *α-naphthol-5-sulphonic acid* (Cleve, *l.c.*; Erdmann, *l.c.* 343), and many *azo*-dyes (*cf.* Bayer, D. R.-P. 66693, 67259; Eng. Pat. 5984 of 1891), have been obtained.

It couples with diazotised bases (*cf.* Aktienges., D. R.-P. 58505 of 1890), forming ortho-*azo*-dyes (*cf.* the 4-acid).

(2) It yields 2 : 4-*dinitro-α-naphthol* when boiled with nitric acid (Witt, *l.c.*).

(3) Concentrated aqueous caustic soda at 240°–250° converts it into 1-*amino*-5-*naphthol* (Aktienges., D. R.-P. 49448 of 1889; *cf.* Friedlaender and Lagodzinski, J. Soc. Chem. Ind. 1897, 16, 793).

(4) On sulphonation with 35 p.c. anhydro-acid at 90°–120°, it yields *α-naphthylamine-*2 : 5 : 7-*trisulphonic acid* (Cassella, D. R.-P. 188505 of 1905). With 30 p.c. anhydro-acid in the cold and subsequent de-acetylation by boiling the melt with water, its acetyl- compound is converted into *α-naphthylamine*-5 : 7-*disulphonic acid* (Badische, D. R.-P. 69555 of 1892; Eng. Pat. 2370 of 1893).

(v.) α-**Naphthylamine-6-sulphonic acid** (Cleve's [β-]acid; Erdmann's μ-acid) is formed when the 4-acid or 5-acid is heated with sulphuric acid at 125°–130° for many hours (Erdmann, Annalen, 1893, 275, 200), and is prepared by reduction of α-nitronaphthalene-6-sulphonic acid by ammonium sulphide or by iron and dilute sulphuric acid (Cleve, Ber. 1887, 20, 74).

Identification.—The *acid*, $HA+2H_2O$, forms needles soluble in 1000 parts of water at 16°. The *barium* salt BaA_2+H_2O, in needles, is sparingly; and the *calcium* salt CaA_2+7H_2O in tablets; *potassium* salt $KA+H_2O$ in scales; and *sodium* salt $NaA+4\frac{1}{2}H_2O$ in thin tablets are easily soluble in water (Cleve, Förhandl. 1876, 7, 54; Bull. Soc. chim. 1876, [ii.] 26, 447; Erdmann, *l.c.*, 265). It is convertible into *α-chloronaphthalene-*6-*sulphonyl chloride*, m.p. 114–115° (Cleve, Ber. *l.c.*), and into 1 : 6-*dichloronaphthalene* (Erdmann *l.c.*).

Reactions.—(1) From its *diazo*-compound, *α-naphthol*-6-*sulphonic acid* (Erdmann and Süvern, Annalen, 1893, 275, 304), and many *azo*-dyes (*cf.* Bayer, D. R.-P. 67261 of 1892) have been obtained.

It couples with diazotised bases, and is of importance as the middle component (*cf.* Bayer, D. R.-P. 65262; Eng. Pat. 22641 of 1891; *ibid.* D. R.-P. 92799; Eng. Pat. 5112 of 1892, Cassella, D. R.-P. 83572 of 1891) or end component (*cf.* Cassella, D. R.-P. 121667, 127362; Eng. Pat. 23615 of 1898) of *disazo*-dyes.

(2) On fusion with caustic alkali, it yields 1-*amino*-6-*naphthol* (Bayer, D. R.-P. 74060; Eng. Pat. 11533 of 1892).

(3) The sodium salt, when heated with sodium bisulphite solution at 120°–150° for 15 hours, yields *α-naphthol*-6-*sulphonic acid*, after the product has been acidified and boiled (Bayer, D. R.-P. 109102; Eng. Pat. 16807 of 1899).

(4) When heated with anhydro-acid, it is converted into the 4 : 6-*disulphonic acid* (Cassella, D. P. Anm. C. 4021 of 1891), and the 2 : 4 : 6-*trisulphonic acid* (Bayer, D. P. Anm. F. 7016; Eng. Pat. 15223 of 1893).

(vi) α-**Naphthylamine-7-sulphonic acid** (Cleve's [θ-] or [δ-]acid; Cleve's acid) is obtained by the reduction of α-nitronaphthalene-7-sulphonic acid (Cleve, Ber. 1888, 21, 3264; Erdmann, Annalen, 1893, 275, 272); *or* by the partial hydrolysis of α-naphthylamine-2 : 7-disulphonic acid (Kalle, D. R.-P. 62634 of 1891); *or* from α-naphthol-7-sulphonic acid by the ammonium sulphite method (Badische, D. R.-P. 117471 of 1899; Eng. Pat. 1387 of 1900).

Identification.—The *acid* $HA+H_2O$ forms scales soluble in 220 parts of water at 25°. The *barium* salt BaA_2 in needles, is sparingly, but the *calcium* salt CaA_2+2H_2O, *potassium* salt in scales, and *sodium* salt $NaA+\frac{1}{2}H_2O$ in needles, are easily soluble in water (Cleve, *l.c.*). It is convertible into *α-chloronaphthalene*-7-*sulphonyl chloride*, m.p. 94° (Cleve, Ber. 1892, 25, 2481), and into 1 : 7-*dichloronaphthalene* (Armstrong and Wynne, Chem. Soc. Proc. 1889, 5, 49).

Reactions.—(1) From its very soluble *diazo*-compound, *α-naphthol*-7-*sulphonic acid*, and (*cf.* Bayer, D. R.-P. 75293 of 1892; Eng. Pat. 558 of 1893) *azo*-dyes have been obtained.

It couples with diazotised bases, and is of much importance as a middle component (*cf.* Kalle, D. R.-P. 73901, 84460 of 1891; Eng. Pat. 2718 of 1892; Bayer, D. R.-P. 121421; Eng. Pat. 3673 of 1900; Cassella, D. P. Anm. C. 10219; Eng. Pat. 22306 of 1901) or the end component (*cf.* the 6-acid) of *disazo* or *trisazo*-dyes.

(2) When fused with caustic soda it yields 1-*amino*-7-*naphthol* (Cassella, D. R.-P. 69458 of 1891; Friedlaender and Zinberg, Ber. 1896, 29, 41).

(3) On sulphonation with anhydro-acid it is converted into the 4 : 7-*disulphonic acid* (Cassella, D. P. Anm. C. 3939 of 1891), and the 2 : 4 : 7-*trisulphonic acid* (Bayer, D. P. Anm. F. 6550; Eng. Pat. 15223 of 1893).

(vii.) α-**Naphthylamine-8-sulphonic acid** (Schöllkopf or S-acid) is obtained by reducing α-nitronaphthalene-8-sulphonic acid. Usually, however, the nitro-acid is not isolated but the nitration product of naphthalene-α-sulphonic acid, after dilution with water, is reduced by iron, neutralised by lime, and converted into sodium salt. The mixed sodium salts of the 8-acid and 5-acid thus obtained are easily separated owing to the sparing solubility of the 8-salt in water (Schöllkopf, D. R.-P. 40571; Eng. Pat. 15775 of 1885). It is also formed when sodium 1 : 8-naphthasultam-2 : 4-disulphonate is heated with 20 p.c. hydrochloric acid (Dressel and Kothe, Ber. 1894, 27, 2140).

Identification.—The *acid* $HA+H_2O$ forms needles soluble in 4800 parts of water at 21° or in 238 parts of boiling water; the *potassium* salt KA scales, soluble in 280 parts of water at 19°, or in 67 parts at 100°; the *sodium* salt NaA scales or tables, soluble in 885 parts of water at 24°, or in 375 parts at 100° (Erdmann, Annalen, 1888, 247, 320). It is convertible into *α-chloronaphthalene-*8*-sulphonyl chloride*, m.p. 101°, and into 1 : 8-*dichloronaphthalene* (Armstrong and Wynne, Chem. Soc. Proc. 1895, 11, 84).

Reactions.—(1) From its sparingly soluble *diazo-* compound *naphthasultone* (the anhydride of α-naphthol-8-sulphonic acid) has been obtained (Erdmann, *l.c.* 344).

It couples with diazotised bases, and has been used as end component in *disazo*-dyes (Bayer, D. R.-P. 96083 of 1892; Eng. Pat. 1851 of 1893), or, like its phenyl derivative (*ibid.* D. R.-P. 75571 of 1893), in the production of *monazo* dyes (Leonhardt, D. R.-P. 108546; Eng. Pat. 24830 of 1898).

(2) When heated at 130° with phosphorus oxychloride it gives *naphthasultam* (Dannerth, J. Amer. Chem. Soc. 1907, 29, 1320), and with 40 p.c. anhydro-acid at 80°–90° it forms 1 : 8-*naphthasultam*-2 : 4-*disulphonic acid* (Bayer, D. R.-P. 79566; Eng. Pat. 4979 of 1893).

(3) When heated with water at 200° under pressure it is converted into *α-naphthol*-8-*sulphonic acid* (Höchst, D. R.-P. 74644; Eng. Pat. 14301 of 1892); with 9 p.c. caustic soda solution at 220°–260° under pressure it yields 1 : 8-*dihydroxynaphthalene* (*ibid.* D. P. Anm. F. 6311 of 1892); and with fused alkali at 200° it gives 1-*amino*-8-*naphthol* (Badische, D. R.-P. 55404 of 1889; Eng. Pat. 9676 of 1890).

(4) On sulphonation with 10 p.c. anhydro-acid in the cold, it yields *α-naphthylamine*-4 : 8-*disulphonic acid* (Schöllkopf, *l.c.*). Its acetyl derivative with 25 p.c. anhydro-acid forms both the 4 : 8- and 6 : 8-*disulphonic acids* (Bayer, D. R.-P. 75084 of 1893).

α-NAPHTHYLAMINEDISULPHONIC ACIDS.[1]

(i.) **α-Naphthylamine-2 : 4-disulphonic acid** is formed[1] when α-nitronaphthalene is heated with sodium bisulphite solution at 100°. Its *sodium* salt is easily soluble in water.

Reactions.—From its *diazo-* compound, 2 : 4-*dinitro-α-naphthol* and *naphthalene*-1 : 3-*disulphonic acid* have been obtained (Höchst, D. R.-P. 92082 of 1895).

(ii.) **α-Naphthylamine-2 : 5-disulphonic acid** is obtained from α-naphthylamine-2-sulphonic acid by sulphonation with 10 p.c. anhydro-acid in the cold (Landshoff, D. R.-P. 56563; Eng. Pat. 6195 of 1890). It is easily soluble, but its acid salts are only very sparingly soluble in water.

Reactions.—(1) By the diazo- reaction, it yields *naphthalene*-1 : 6-*disulphonic acid* (Tobias, Ber. 1890, 23, 1631).

(2) By partial hydrolysis with dilute sulphuric acid at 160° it gives *α-naphthylamine*-5-*sulphonic acid* (Landshoff, *l.c.*).

(3) When heated with 50 p.c. caustic soda solution at 240°–270°, it is converted into 1-*amino*-5-*naphthol*-2-*sulphonic acid* (*ibid.*, D. P. Anm. C. 4479 of 1892; Eng. Pat. 6195 of 1890).

(4) On sulphonation with 40 p.c. anhydro-acid at 120°, it gives *α-naphthylamine*-2 : 5 : 7-*trisulphonic acid* (Bayer, D. P. Anm. F. 7001; Eng. Pat. 17141B of 1893).

(iii.) **α-Naphthylamine-2 : 7-disulphonic acid** is obtained by partial hydrolysis either of α-naphthylamine-2 : 4 : 7-trisulphonic acid with water at 230° under pressure (Kalle, D. R.-P. 62634 of 1891), *or* of α-naphthylamine-2 : 5 : 7-trisulphonic acid by boiling it with zinc dust and dilute caustic soda solution[1] (*ibid.* D. R.-P. 233934 of 1909). It crystallises in needles; its *barium* salt is very sparingly soluble in water, and solutions of its alkali salts show bluish-green fluorescence (Kalle, D. R.-P. 62634 of 1891).

Reactions.—By the diazo- reaction, it yields *naphthalene*-2 : 7-*disulphonic acid*, and, by partial hydrolysis with dilute sulphuric acid under pressure, it gives *α-naphthylamine*-7-*sulphonic acid* (Kalle, *l.c.*).

(iv.) **α-Naphthylamine-2 : 8-disulphonic acid** is obtained from naphthasultam-2 : 4-disulphonic acid by partial hydrolysis with 40 p.c. sulphuric acid at 110° (Cassella, D. R.-P. 75710 of 1893; *cf.* Dressel and Kothe, Ber. 1894, 27, 2140). It crystallises in moderately soluble needles; the solutions of its alkali salts show green fluorescence.

Reaction.—When fused with caustic soda, it yields 1-*amino*-8-*naphthol*-2-*sulphonic acid* (Cassella, *l.c.*).

(v.) **α-Naphthylamine-3 : 6-disulphonic acid** (Alén's [α-]acid) is obtained by reduction of α-nitronaphthalene-3 : 6-disulphonic acid (Alén, Förhandl., 1883, 8, 3; Freund, D. R.-P. 27346; Eng. Pat. 1069 of 1883;[2] Armstrong and Wynne, Chem. Soc. Proc. 1895, 11, 82); *or* by boiling α-naphthylamine-3 : 6 : 8-trisulphonic acid with zinc dust and 7 p.c. caustic soda solution (Kalle, D. R.-P. 233934 of 1909).

Identification.—The *acid* forms needles, and, like the *barium* $BaA+4H_2O$ and *calcium* $CaA+5H_2O$ in tablets, also the *acid potassium* $KHA+3H_2O$ and *acid sodium* $NaHA+3H_2O$ salts in needles, is easily soluble in water (Alén, *l.c.*). It is convertible into *α-chloronaphthalene*-3 : 6-*disulphonyl chloride*, m.p. 114° or 127°, and into 1 : 3 : 6-*trichloronaphthalene* (Armstrong and Wynne, *l.c.*).

Reactions.—(1) From its *diazo*-compound (Freund, *l.c.*), or when it is heated with water at 180° under pressure (Cassella, D. P. Anm.

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[1] By electrolytic reduction in a divided cell, with its compartments connected by a layer of mercury and containing 25 p.c. caustic soda solution in the anode compartment, SO_3H in the position italicised is eliminated from the following naphthylaminesulphonic acids—1 : 3 : *8*, 1 : 4 : *8*, 1 : 2 : 4 : *6*, 1 : 2 : *5* : 7, 1 : 3 : *5* : 7, 2 : *4* : 8, 2 : *5* : 7, and from the naphtholsulphonic acid 1 : 3 : *8* (Bayer, Fr. Pat. 439010 of 1912, with sketch; *cf.* J. Soc. Chem. Ind., 1912, 31, 579).

[2] This acid, like the 3 : 7-acid, was regarded by Freund as a β-naphthylaminedisulphonic acid.

C. 4375 of 1892; Friedlaender and Taussig, Ber. 1897, 30, 1462), *α-naphthol*-3 : 6-*disulphonic acid* is obtained.

(2) When boiled with 75 p.c. caustic potash solution, it is converted into a mixture of 1-*amino*-3-*naphthol*-6-*sulphonic* and 1-*amino*-6-*naphthol*-3-*sulphonic acids* (Cassella, D. R.-P. 82676 of 1894).

(3) Ammonia at 180° under pressure converts it into 1 : 3-*diaminonaphthalene*-6-*sulphonic acid* (Kalle, D. R.-P. 89061 of 1894; Eng. Pat. 9103 of 1895); aniline (or *p*-toluidine) at 150°–160° converts it into *diphenyl*-(*di*-p-*tolyl*-)-1 : 3-*diaminonaphthalene*-6-*sulphonic acid* (Bayer, D. R.-P. 76414; Eng. Pat. 8898 of 1893).

(vi.) **α-Naphthylamine-3 : 7-disulphonic acid** (Alén's [β-]acid) is prepared by reduction of α-nitronaphthalene-3 : 7-disulphonic acid (Freund, D. R.-P. 27346; Eng. Pat. 1069 of 1883; Cassella, D. R.-P. 57007, 58352 of 1890; Levinstein, Eng. Pat. 2682 of 1891), *or* by boiling α-naphthylamine-3 : 5 : 7-trisulphonic acid with zinc-dust and dilute caustic soda solution (Kalle, D. R.-P. 233934 of 1909; *cf.* p. 592, footnote 1). It is easily soluble in water, and, like its salts, shows blue fluorescence in solution. The *barium* salt $BaA + H_2O$, *calcium* salt $CaA + 2H_2O$, and *acid potassium* salt KHA form sparingly soluble needles (Alén, Förhandl. 1883, 8, 26).

Reactions.—(1) When heated with water at 180° under pressure it is converted into *α-naphthol*-3 : 7-*disulphonic acid* (Cassella, D. P. Anm. C. 5069 of 1892).

(2) Digestion with caustic soda solution at 200° converts it into a mixture of 1-*amino*-3-*naphthol*-7-*sulphonic acid* and 1-*amino*-7-*naphthol*-3-*sulphonic acid* (Cassella, D. R.-P. 57007 of 1890).

(3) Ammonia at 180° under pressure converts it into 1 : 3-*diaminonaphthalene*-7-*sulphonic acid* (Kalle, D. R.-P. 89061 of 1894; Eng. Pat. 9103 of 1895); aniline (or *p*-toluidine) at 150°–160° converts it into *diphenyl*-(*di*-p-*tolyl*-)-1 : 3-*diaminonaphthalene*-7-*sulphonic acid* (Bayer, D. R.-P. 76414; Eng. Pat. 8898 of 1893).

(vii.) **α-Naphthylamine-3 : 8-disulphonic acid** ([ε-] acid) is obtained by reduction of α-nitronaphthalene-3 : 8-disulphonic acid. In practice, the mixture of this acid with α-nitronaphthalene-4 : 8-disulphonic acid, and some β-nitronaphthalenedisulphonic acids, obtained by nitrating a disulphonation melt containing the naphthalene-1 : 5- and 1 : 6-disulphonic acids, is freed from the excess of sulphuric acid by lime, reduced with iron, and converted into sodium salt. On concentration of the solution the first separations consist of the normal sodium salt of the 4 : 8-acid, the more soluble 3 : 8-salt which is retained in the mother liquor being precipitated from it as acid sodium salt by the addition of hydrochloric acid (Aktienges., D. R.-P. 45776; Eng. Pat. 4625 of 1888; Ewer and Pick, D. R.-P. 52724 of 1888; Bernthsen, Ber. 1889, 22, 3328; Schultz, *ibid.* 1890, 23, 77).

Identification.—The *acid* $H_2A + 3H_2O$ forms very soluble scales. The *barium* salt $BaA + 4H_2O$ forms needles sparingly soluble, and the *acid barium* salt $BaH_2A_2 + 5H_2O$, microscopic needles almost insoluble in cold water; the *normal sodium* salt $Na_2A + 6H_2O$ very soluble, and the *acid sodium* salt $NaHA + 2H_2O$, soluble in about 30 parts of cold water, crystallise in long needles or thin prisms (Bernthsen, *l.c.*). It is convertible into *α-chloronaphthalene*-3 : 8-*disulphonyl chloride*, m.p. 110°, and into 1 : 3 : 8-*trichloronaphthalene* (Armstrong and Wynne, Chem. Soc. Proc. 1890, 6, 16).

Reactions.—(1) The *diazo-* compound, when boiled with dilute sulphuric acid, yields *naphthasultone*-3-*sulphonic acid* (Ewer and Pick, *l.c.*; Bernthsen, *l.c.*).

(2) When heated with water at 180° under pressure it gives *α-naphthol*-3 : 8-*disulphonic acid* (Höchst, D. R.-P. 71494; Eng. Pat. 14301 of 1892), but yields *α-naphthylamine*-3-*sulphonic acid* when boiled with 75 p.c. sulphuric acid (Kalle, D. R.-P. 64979 of 1892), or by interaction with sodium amalgam (Friedlaender and Lucht, Ber. 1893, 26, 3032; *cf.* p. 592, footnote 1).

(3) Fusion with alkalis below 210° converts it into 1-*amino*-8-*naphthol*-3-*sulphonic acid* (Bayer, D. P. Anm. F. 4723; Eng. Pat. 13443 of 1890), but digestion with 9 p.c. caustic soda solution at 250° under pressure converts it into 1 : 8-*dihydroxynaphthalene*-3-*sulphonic acid* (Höchst, D. P. Anm. F. 7112 of 1892).

(4) Ammonia at 180° under pressure converts it into 1 : 3-*diaminonaphthalene*-8-*sulphonic acid* (Kalle, D. R.-P. 89061 of 1894; Eng. Pat. 9103 of 1895); aniline (or *p*-toluidine) at 150°–160° converts it into *diphenyl*-(*di*-p-*tolyl*-)1 : 3-*diaminonaphthalene*-8-*sulphonic acid* (Bayer, D. R.-P. 75296; Eng. Pat. 8898 of 1893).

(viii.) **α-Naphthylamine-4 : 6-disulphonic acid** (Dahl's No. II acid)[1] constitutes about 30 p.c. of the product obtained by sulphonating naphthionic acid with 25 p.c. anhydro-acid in the cold (*v.* 4 : 7-acid), and is separated by extraction of the mixed calcium salts with 85 p.c. alcohol in which it is soluble (Dahl, D. R.-P. 41957 of 1886).

It is formed when α-naphthylamine-6-sulphonic acid is sulphonated with 10 p.c. (Cassella, D. P. Anm. C. 4021 of 1891) or 25 p.c. anhydro-acid (Bayer, D. P. Anm. F. 7016; Eng. Pat. 15223 of 1893), *or* when α-naphthylamine-4 : 6 : 8-trisulphonic acid is boiled with zinc dust and 7 p.c. caustic soda solution (Kalle, D. R.-P. 233934 of 1909); and can be obtained from α-naphthol-4 : 6-disulphonic acid by the ammonium sulphite method (Badische, D. R.-P. 117471 of 1899; Eng. Pat. 1387 of 1900).

Identification.—The *calcium* salt $CaA + 5H_2O$ forms needles soluble in 85 p.c. but insoluble in 96 p.c. alcohol (Erdmann, Annalen, 1893, 275, 219), and, like the *potassium* and *sodium* salts, is very soluble in water; the *acid sodium* salt, in needles, is soluble in about 6 parts of water at 20° (Dahl, *l.c.*). It is convertible into *α-chloronaphthalene*-4 : 6-*disulphonyl chloride*, m.p. 126°–127°, and into 1 : 4 : 6-*trichloronaphthalene* (Armstrong and Wynne, Chem. Soc. Proc. 1890, 6, 126).

Reactions.—(1) From its moderately soluble *diazo-* compound *α-naphthol*-4 : 6-*disulphonic acid* (Dahl, *l.c.*), and *azo*-dyes (*cf.* Höchst, D. R.-P. 176640 of 1905; Eng. Pat. 7287 of 1906) have been obtained.

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[1] In Dahl & Co.'s patent (D. R.-P. 41597 of 1886) an acid 'No. I' is described, the calcium salt of which is soluble in 96 p.c. alcohol. This acid, said to constitute 50 p.c. of the product when α-naphthylamine is heated with 4–5 parts of 25 p.c. anhydro-acid at 120°, could not be identified by Erdmann (Annalen, 1895, 275, 218), and is believed by him not to exist.

(2) By fusion with alkalis at 180°–200° it yields 1-*amino*-6-*naphthol*-4-*sulphonic acid* (Dahl, D. R.-P. 68232 of 1891; Friedlaender and Kielbasinski, Ber. 1896, 29, 1979), and at 200°–220° 1:6-*dihydroxynaphthalene*-4-*sulphonic acid* (Dahl, D. R.-P. 57114; Eng. Pat. 735 of 1890; *cf.* Friedlaender and Lucht, Ber. 1893, 26, 3034).

(3) When heated with aniline (or *p*-toluidine) at 180°, it forms *phenyl*- (or p-*tolyl*-)α-*naphthylamine*-6-*sulphonic acid* (Aktienges., D. R.-P. 159353; Eng. Pat. 24669 of 1904).

(4) Sulphonation with 35 p.c. anhydro-acid at 80°–90° converts it into α-*naphthylamine*-2 : 4 : 6-*trisulphonic acid* (Bayer, *l.c.*).

(ix.) α-**Naphthylamine**-4 : 7-**disulphonic acid** (Dahl's No. III acid) is obtained, mixed with about 30 p.c. of the No. II acid (*v.* 4 : 6-acid), by adding sieved naphthionic acid to 3·5 times its weight of 25 p.c. anhydro-acid below 30°. The product converted into dry calcium salt is extracted with 10 times its weight of 85 p.c. alcohol to remove No. II salt, the residue being No. III salt (Dahl, D. R.-P. 41957 of 1886).

It is also formed when α-naphthylamine-7-sulphonic acid is sulphonated with monohydrate at 100°–150° (Cassella, D. P. Anm. C. 3939 of 1891), or 25 p.c. anhydro-acid at 50°–60° (Bayer, D. P. Anm. F. 6550; Eng. Pat. 15223 of 1893); when 1 : 8-dinitronaphthalene is digested with sodium or ammonium sulphite solution at 70°–90°, and the crystalline α-naphthylsulphamino-4 : 7-disulphonate, which separates on cooling, is hydrolysed by a mineral acid (Höchst, D. R.-P. 215338 of 1908); or when sodium α-naphthol-4 : 7-disulphonate is heated with 40 p.c. ammonium sulphite solution and 20 p.c. ammonia at 100°–150°, and the product acidified (Badische, D. R.-P. 117471 of 1899; Eng. Pat. 1387 of 1900).

Identification.—The *barium* salt BaA, in needles, and *calcium* salt $CaA+H_2O$, are sparingly soluble in water; the *potassium* salt K_2A+3H_2O, in efflorescent prisms, and *sodium* salt Na_2A+3H_2O, in efflorescent needles, are readily soluble in water; the *acid sodium* salt in needles, is soluble in 140 parts of water at 20° or 20 parts at the boiling point, but, like the calcium salt, is insoluble in 85 p.c. alcohol (Dahl, *l.c.*; Erdmann, Annalen, 1893, 275, 220). The solutions of the acid and salts show blue fluorescence. It is convertible into α-*chloronaphthalene*-4 : 7-*disulphonyl chloride*, m.p. 107°, and into 1 : 4 : 7-*trichloronaphthalene* (Armstrong and Wynne, Chem. Soc. Proc. 1890, 6, 17).

Reactions.—(1) By the diazo- reaction (Dahl, *l.c.*), or by the bisulphite method (Bucherer, J. pr. Chem. 1904, [2] 70, 347), it yields α-*naphthol*-4 : 7-*disulphonic acid* convertible into 2 : 4-*dinitro*-α-*naphthol*-7-*sulphonic acid* (naphthol yellow S; *cf.* Armstrong and Wynne, *l.c.*).

(2) When heated with aniline (or *p*-toluidine) at 180°, it forms *phenyl*- (or p-*tolyl*-)α-*naphthylamine*-7-*sulphonic acid* (Aktienges., D. R.-P. 159353; Eng. Pat. 24669 of 1904).

(3) Sulphonation with 35 p.c. anhydro-acid at 80°–90° converts it into α-*naphthylamine*-2 : 4 : 7-*trisulphonic acid* (Bayer, *l.c.*).

(x.) α-**Naphthylamine**-4 : 8-**disulphonic acid** ([δ-] acid; disulpho-acid-S) is formed from α-naphthylamine-8-sulphonic acid by sulphonation with 3 times its weight of 10 p.c. anhydro-acid at first in the cold and afterwards at 100° (Schöllkopf. D. R.-P. 40571; Eng. Pat. 15775 of 1885); also, mixed with the 6 : 8-acid, when acetyl-α-naphthylamine-8-sulphonic acid is sulphonated with 25 p.c. anhydro-acid in the cold, the product deacetylated by boiling it with water, and the sodium salt separated from the more soluble 6 : 8-isomeride by fractional crystallisation (Bayer, D. R.-P. 75084 of 1893).

It can be obtained by reduction of α-nitronaphthalene-4 : 8-disulphonic acid, occurring, therefore, with the 3 : 8-acid (*q.v.*), in the product formed when the sulphonation melt containing naphthalene-1 : 5- and 1 : 6-disulphonic acids is nitrated, and the nitro-acids are reduced (Aktienges., D. R.-P. 45776; Eng. Pat. 4625 of 1888; Bernthsen, Ber. 1889, 22, 3327). Further, it can be made from α-naphthol-4 : 8-disulphonic acid by the ammonium sulphite method (Badische, D. R.-P. 117471 of 1899; Eng. Pat. 1387 of 1900).

Identification.—The *normal sodium* salt, Na_2A+2H_2O, forms needles readily soluble in water (Bernthsen, Ber. 1890, 23, 3090, footnote); the *acid sodium* salt scales sparingly soluble in cold water. It is convertible into α-*chloronaphthalene*-4 : 8-*disulphonyl chloride*, m.p. 176°, and into 1 : 4 : 8-*trichloronaphthalene* (Armstrong and Wynne, Chem. Soc. Proc. 1890, 6, 126).

Reactions.—(1) By the diazo- reaction (Schöllkopf, *l.c.*), or by the bisulphite method (Badische, D. R.-P. 115335 of 1899; Eng. Pat. 1387 of 1900), it can be converted into α-*naphthol*-4 : 8-*disulphonic acid.*

(2) Fusion with caustic alkalis at 200°–210° converts it into 1-*amino*-8-*naphthol*-4-*sulphonic acid* (Bayer, D. R.-P. 75317; *cf.* 63074; Eng. Pat. 20275 of 1891), but with 60 p.c. caustic soda at 250° into 1 : 8-*dihydroxynaphthalene*-4-*sulphonic acid* (Bayer, D. R.-P. 71836 of 1890).

(3) When heated with aniline (or *p*-toluidine) at 180°, it yields *phenyl*- (or p-*tolyl*-)α-*naphthylamine*-8-*sulphonic acid* (Aktienges., D. R.-P. 158923 of 1903; Eng. Pat. 15624 of 1904).

(4) On sulphonation with 40 p.c. anhydro-acid, it forms *naphthasultam*-2 : 4-*disulphonic acid* (Bayer, D. R.-P. 79566; Eng. Pat. 4979 of 1893; Dressel and Kothe, Ber. 1894, 27, 2139).

(xi.) α-**Naphthylamine**-5 : 7-**disulphonic acid** is formed when acetyl-α-naphthylamine-5-sulphonic acid is sulphonated with 30 p.c., or acet-α-naphthalide with 35 p.c. anhydro-acid at 20°–30°, and the product deacetylated by boiling it with water (Badische, D. R.-P 69555 of 1892; Eng. Pat. 2370 of 1893; *cf.* Cassella, D. R.-P. 188505 of 1905). It can be obtained from α-naphthol-5 : 7-disulphonic acid by the ammonium sulphite method (Badische, D. R.-P. 117471 of 1899; Eng. Pat. 1387 of 1900). The *acid sodium* salt $NaH_3A_2+5H_2O$ forms very soluble needles and, in alkaline solution, couples with diazotised bases (*ibid.* D. R.-P. 69555 of 1892).

Reactions.—(1) By the diazo- reaction, or by the bisulphite method (Badische, D. R.-P. 115335 of 1899; Eng. Pat. 1387 of 1900), it yields α-*naphthol*-5 : 7-*disulphonic acid.*

(2) When heated with 75 p.c. caustic soda at 170°–180°, it yields 1-*amino*-5-*naphthol*-7-*sulphonic acid* (Badische, D. R.-P. 73276; Eng. Pat. 2370 of 1893).

(3) On sulphonation with 40 p.c. anhydro-acid at 120°–130°, it gives α-*naphthylamine*-

2 : 5 : 7-*trisulphonic acid* (Bayer, D. P. Anm. F. 7001; Eng. Pat. 17141 B of 1893).

(xii.) α-**Naphthylamine**-5 : 8-**disulphonic acid** is obtained from α-nitronaphthalene-5 : 8-disulphonic acid by reduction (Gattermann, Ber. 1899, 32, 1156); also from α-naphthol-5 : 8-disulphonic acid by the ammonium sulphite method (Badische, D. R.-P. 117471 of 1899; Eng. Pat. 1387 of 1900). Both the *acid* and the *acid sodium* salt $NaHA+1\frac{1}{2}H_2O$ form needles very sparingly soluble in water, but easily soluble in alkalis, giving greenish-yellow solutions (Bayer, D. R.-P. 70857 of 1892).

Reactions.—(1) When the *diazo-* compound is boiled with dilute sulphuric acid, *naphthasultone-5-sulphonic acid* is formed (Bayer, *l.c.*).

(2) When heated with 75 p.c. caustic potash at 150°–160°, it yields 1-*amino*-8-*naphthol*-5-*sulphonic acid* (Bayer, D. R.-P. 75055; Eng. Pat. 15269 of 1893), but with 60 p.c. caustic potash under pressure it gives 1 : 8-*dihydroxynaphthalene*-4-*sulphonic acid* (Bayer, D. R.-P. 77285 of 1892; Eng. Pat. 1227 of 1894).

(3) On sulphonation with 40 p.c. anhydro-acid at 80°–90°, it forms *naphthasultamdisulphonic acid*-D. (Bayer, D. R.-P. 79566; Eng. Pat. 4979 of 1893).

(xiii.) α-**Naphthylamine**-6 : 8-**disulphonic acid** can be obtained from α-naphthylamine-4 : 6 : 8-trisulphonic acid by boiling it with 75 p.c. sulphuric acid (Kalle, D. R.-P. 83146 of 1894); or from α-naphthol-6 : 8-disulphonic acid by the ammonium sulphite method (Badische, D. R.-P. 117471 of 1899; Eng. Pat. 1387 of 1900); and it is formed together with the 4 : 8-acid, when acetyl-α-naphthylamine-8-sulphonic acid is sulphonated with 25 p.c. anhydro-acid at the ordinary temperature, and the product boiled with water. Its *sodium* salt is much more soluble than that of the 4 : 8-acid, and in solution shows green fluorescence; its *acid sodium* salt, in needles, is easily soluble (Bayer, D. R.-P. 75084 of 1893).

Reactions.—(1) From its diazo- compound, *naphthasultone*-6-*sulphonic acid* and *naphthalene*-1 : 3-*disulphonic acid* have been prepared (Bayer, *l.c.*).

(2) When heated with 50 p.c. caustic potash solution at 180°–200°, it is converted into 1-*amino*-8-*naphthol*-6-*sulphonic acid* (Bayer, D. R.-P. 80853 of 1893).

α-Naphthylaminetrisulphonic Acids.

(i.) α-**Naphthylamine**-2 : 4 : 6-**trisulphonic acid** is formed when α-naphthylamine-6-sulphonic acid, or 4 : 6-disulphonic acid, is heated with 25 p.c. anhydro-acid (3·5 pts.) at 50°–60°, and afterwards with 70 p.c. anhydro-acid (1 pt.) at 80°–90° (Bayer, D. P. Anm. F. 7016; Eng. Pat. 15223 of 1893). The *acid sodium* salt forms needles, shows blue fluorescence in solution, and does not couple with diazotised bases.[1]

(ii.) α-**Naphthylamine**-2 : 4 : 7-**trisulphonic acid**. To obtain this acid, naphthionic acid is heated with 40 p.c. anhydro-acid at 120° (Höchst, D. R.-P. 22545; Eng. Pat. 2178 of 1882; *cf.* Armstrong and Wynne, Chem. Soc. Proc. 1890, 6, 125); *or* α-naphthylamine-7-sulphonic acid (or 4 : 7-disulphonic acid) is heated with 25 p.c. anhydro-acid (3·5 pts.) at 50°–60°, and afterwards with 70 p.c. anhydro-acid (1 pt.) at 80°–90° (Bayer, D. P. Anm. F. 6550; Eng. Pat. 15223 of 1893). It is also formed when 1 : 8-dinitronaphthalene is heated with sodium or ammonium sulphite solution at 70°–90°, and, after removal of the less soluble 4 : 7-compound, the α-naphthylsulphamino-2 : 4 : 7-trisulphonate is decomposed by a mineral acid (Höchst, D. R.-P. 215338 of 1908). The *acid sodium* salt forms small needles, shows blue fluorescence in alkaline solution, and does not couple with diazotised bases.

Reactions.—(1) Its *diazo-* compound, when warmed with dilute nitric acid, gives *naphthol-yellow*-S. (Höchst, *l.c.*).

(2) When heated with water at 230° it yields α-*naphthylamine*-2 : 7-*disulphonic acid*, but when boiled with 75 p.c. sulphuric acid, the 7-*monosulphonic acid* (Kalle, D. R.-P. 62634 of 1891).

(iii.) α-**Naphthylamine**-2 : 5 : 7-**trisulphonic acid** is obtained when α-naphthylamine-5-sulphonic acid is sulphonated with 35 p.c. anhydro-acid at 90°–120° (Cassella, D. R.-P. 188505 of 1905), *or* when α-naphthylamine-2 : 5- or 5 : 7-disulphonic acid is sulphonated with 40 p.c. anhydro-acid at 120°–130° (Bayer, D. P. Anm. F. 7001; Eng. Pat. 17141B of 1893). Its *acid sodium* salt forms needles easily soluble in water, and like the acid, shows green fluorescence in solution.

Reactions.—When heated with 50 p.c. caustic potash at 180°–200° under pressure, it yields 1-*amino*-5-*naphthol*-2 : 7-*disulphonic acid* (Bayer, *l.c.*; Cassella, *l.c.*); but when boiled with zinc dust and dilute caustic soda solution (Kalle, D. R.-P. 233934 of 1909) or reduced electrolytically (Bayer, Fr. Pat. 439010 of 1912)[1] it gives α-*naphthylamine*-2 : 7-*disulphonic acid*.

(iv.) α-**Naphthylamine**-3 : 5 : 7-**trisulphonic acid** is prepared by reduction of α-nitronaphthalene-3 : 5 : 7-trisulphonic acid (Cassella, D. R.-P. 75432 of 1891). Its salts are easily soluble and in solution show green fluorescence.

Reactions.—(1) By the diazo- reaction it can be converted into α-*naphthol*-3 : 5 : 7-*trisulphonic acid* (Kalle, D. P. Anm. K. 12732 of 1895).

(2) On fusion with caustic soda at 160°–170°, it yields 1-*amino*-5-*naphthol*-3 : 7-*disulphonic acid* (Cassella, *l.c.*).

(v.) α-**Naphthylamine**-3 : 6 : 8-**trisulphonic acid**, obtained by reduction of α-nitronaphthalene-3 : 6 : 8-trisulphonic acid (Koch, D. R.-P. 56058; Eng. Pat. 9258 of 1890), is also formed when sodium α-nitronaphthalene-3 : 8-disulphonate is warmed with sodium bisulphite solution (Fischesser & Co., D. R.-P. 76438 of 1893; Eng. Pat. 7046 of 1894). The *acid disodium* salt forms moderately soluble needles, and the *sodium* salt Na_3A+3H_2O easily soluble scales (Dressel and Kothe, Ber. 1894, 27, 2147).

Reactions.—(1) By the diazo- reaction it yields *naphthasultone*-3 : 6-*disulphonic acid* (Koch, *l.c.*), but when heated with water at 180°–250° under pressure, it gives α-*naphthol*-3 : 6 : 8-*trisulphonic acid* (Höchst, D. R.-P. 71495; Eng. Pat. 14301 of 1892).

(2) On fusion with caustic alkalis at 180°–190° it is converted into 1-*amino*-8-*naphthol*-3 : 6-*disulphonic acid* (Bayer, D. R.-P. 69722; Eng. Pat. 13443 of 1890).

(3) When heated with ammonia at 160°–180° under pressure it gives 1 : 3-*diaminonaphthalene*-

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[1] For reduction product, *cf.* p. 592, footnote 1.

6 : 8-*disulphonic acid* (Kalle, D. R.-P. 90905; Eng. Pat. 9103 of 1895); and with aniline (or *p*-toluidine) at 150°–160° it yields *diphenyl*-(*di-p-tolyl*-)-1 : 3-*diaminonaphthalene*-6 : 8-*disulphonic acid* (Bayer, D. R.-P. 75296; Eng. Pat. 8898 of 1893; *cf.* Cassella, D. P. Anm. C. 13453 of 1905).

(4) By sulphonation with 25 p.c. anhydro-acid at 70°–80° it is converted into *naphthasultam*-3 : (4) : 6-*trisulphonic acid* (Bayer, D. R.-P. 84139 of 1894; Dressel and Kothe, *l.c.*).

(vi.) **α-Naphthylamine-4 : 6 : 8-trisulphonic acid** is obtained by reduction of α-nitronaphthalene-4 : 6 : 8-trisulphonic acid (Bayer, D. P. Anm. F. 7006; D. R.-P. 80741; Eng. Pat. 17141c of 1893; Kalle, D. R.-P. 82563 of 1893). Its solution in alkalis shows strong green fluorescence. It does not couple with diazotised bases.

Reactions.—(1) By the diazo- reaction (Bayer, D. P. Anm. 7004, 7006; Eng. Pat. 17141c of 1893), or by the bisulphite method (Bucherer, J. pr. Chem. 1904, [ii.] 70, 347), it gives *naphthasultone*-4 : 6-*disulphonic acid.*

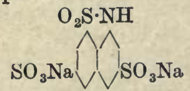
(2) When heated with water at 160°–220° under pressure it is converted into *α-naphthol*-6 : 8-*disulphonic acid* (Kalle, D. R.-P. 82563 of 1893), but when boiled with 75 p.c. sulphuric acid it gives *α-naphthylamine*-6 : 8-*disulphonic acid* (Kalle, D. R.-P. 83146 of 1894).

(3) On fusion with 70 p.c. caustic soda at 170°–175°, it is converted into 1-*amino*-8-*naphthol*-4 : 6-*disulphonic acid* (Bayer, D. R.-P. 80741; Eng. Pat. 17141c of 1893), and at a higher temperature into 1 : 8-*dihydroxynaphthalene*-3 : 5-*disulphonic acid* (Bayer, *l.c.*; *cf.* Cassella, D. R.-P. 108848 of 1895).

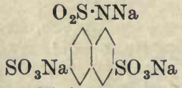
(4) On sulphonation with 25 p.c. anhydro-acid, it gives *naphthasultam*-(2) : 4 : 6-*trisulphonic acid* (Bayer, D. R.-P. 84140 of 1894).

NAPHTHASULTAM DERIVATIVES.

Introductory.—When warmed with anhydro-acid, α-naphthylaminesulphonic acids in which one of the sulphonic groups occupies the *peri*-position relatively to the NH_2 radicle may undergo dehydration, forming naphthasultams, in addition to further sulphonation. Contrasted with the sultones (p. 618), the stability of the sultams is remarkable. Neither by boiling a sultam with caustic alkali solutions, nor by heating it with ammonia is the anhydride ring attacked, although disruption of this ring (accompanied usually by partial de-sulphonation) can be effected if mineral acids be employed. These naphthasultamsulphonic acids, although not diazotisable, can be coupled with diazotised bases, provided the 4- position be free. The salts are of two types:



I. (acid)



II. (normal)

Those of type I are colourless, but those of type II are yellow and give yellow solutions, which show intense green or yellowish-green fluorescence.

(i.) **Naphthasultam** has been obtained from α-naphthylamine-8-sulphonic acid by dehydration with phosphorus oxychloride. It melts at 177°–178°, is converted into iso*naphthasultam* by acetic anhydride, and yields *nitronaphthasultam*, m.p. 253°, or 2 : 4-*dinitronaphthasultam*, m.p. 259°, on nitration (Dannerth, J. Amer. Chem. Soc. 1907, 29, 1320).

2 : 4-*Dinitronaphthasultam*, readily obtained from naphthasultam-2 : 4-disulphonic acid, has been introduced as a dyestuff. It is a pale-yellow powder, soluble in alkalis or alkali carbonates, but almost insoluble in water (Bayer, D. R.-P. 210222 of 1907).

(ii.) **Naphthasultam-2 : 4-disulphonic acid**-S, is obtained when α-naphthylamine-8-sulphonic or 4 : 8-disulphonic acid is sulphonated with 25–40 p.c. anhydro-acid at 80°–90° (Bayer, D. R.-P. 79566; Eng. Pat. 4979 of 1893; Aktienges., D. P. Anm. A. 3346; Eng. Pat. 2984 of 1893; Dressel and Kothe, Ber. 1894, 27, 2139), but the corresponding α-naphthylamine-2 : 4 : 8-trisulphonic acid is unknown.

Identification. — Naphthasultam-2 : 4-disulphonic acid forms a *disodium* salt Na_2HA+2H_2O in colourless needles, soluble in water without fluorescence, and a *trisodium* salt $Na_3A+8\frac{1}{2}H_2O$, in yellow scales, easily soluble in water with green fluorescence. It does not couple with diazotised bases.

Reactions.—(1) On fusion with caustic alkalis at 180°–200°, it yields 1-*amino*-8-*naphthol*-2 : 4-*disulphonic acid* (Bayer, *l.c.*; D. R.-P. 80668; Eng. Pat. 4979 of 1893; Aktienges., *l.c.*); and at 250°, 1 : 8-*dihydroxynaphthalene*-2 : 4-*disulphonic acid* (Bayer, *l.c.*; D. R.-P. 77703 of 1893; Cassella, D. R.-P. 81282 of 1893; Dressel and Kothe, *l.c.*).

(2) When heated at 110° with 40 p.c. sulphuric acid it gives *α-naphthylamine*-2 : 8-*disulphonic acid* (Kalle, D. R.-P. 75710 of 1893), but with 20 p.c. hydrochloric acid at 140°–150° *α-naphthylamine*-8-*sulphonic acid* is the product (Dressel and Kothe, *l.c.*).

(3) When heated in 50 p.c. sulphuric acid solution at 75°–80° with nitric acid of sp.gr. 1·2, it is converted successively into *nitronaphthasultamsulphonic acid* and 2 : 4-*dinitronaphthasultam* (Bayer, D. R.-P. 210222 of 1907).

(iii.) **Naphthasultam-3 : 6-disulphonic acid** is prepared by boiling the acid sodium salt of naphthasultam-3 : (4) : 6-trisulphonic acid with 20 p.c. sulphuric acid. The *trisodium* salt Na_3A+4H_2O forms easily soluble, small, yellow prisms. When boiled with 50 p.c. sulphuric acid it gives *α-naphthylamine*-3 : 6 : 8-*trisulphonic acid* (Bayer, D. R.-P. 84139 of 1894; Dressel and Kothe, Ber. 1894, 27, 2149).

(iv.) **Naphthasultamdisulphonic acid**-ε, obtained by heating sodium α-naphthylamine-3 : 8-disulphonate with 40 p.c. anhydro-acid at 80°–90°; and

(v.) **Naphthasultamdisulphonic acid**-D, obtained similarly from sodium α-naphthylamine-5 : 8-disulphonate, have been described (Bayer, D. R.-P. 79566; Eng. Pat. 4979 of 1893). On fusion with caustic alkali, each gives the corresponding 1-*amino*-8-*naphtholdisulphonic acid* (*ibid.* D. R.-P. 79566, 80668; Eng. Pat. 4979 of 1893).

(vi.) **Naphthasultam-3 : (4) : 6-trisulphonic acid** is formed when the acid sodium salt of α-naphthylamine-3 : 6 : 8-trisulphonic acid is heated with 25 p.c. anhydro-acid at 80° until a test no longer reacts with nitrite. The *acid sodium* salt Na_3HA+4H_2O forms easily soluble, minute needles; the *sodium* salt Na_4A+4H_2O, easily soluble, yellow granules; and the *barium* salt, a very sparingly soluble yellow powder (Bayer, D. R.-P. 84139 of 1894; Dressel and Kothe, Ber. 1894, 27, 2147).

Reactions.—(1) On digestion with 75 p.c. caustic potash solution at 130°, it yields 1-*amino*-8-*naphthol*-3 : 6-*disulphonic acid* (Bayer, *l.c.*; Dressel and Kothe, *l.c.*).

(2) When boiled with 20 p.c. sulphuric acid it is converted into *naphthasultam*-3 : 6-*disulphonic acid*; and with 50 p.c. sulphuric acid into *α-naphthylamine*-3 : 6 : 8-*trisulphonic acid* (Bayer, *l.c.*; Dressel and Kothe, *l.c.*).

(vii.) **Naphthasultam-(2) : 4 : 6-trisulphonic acid** is obtained when the acid sodium salt of α-naphthylamine-4 : 6 : 8-trisulphonic acid is heated with 25 p.c. anhydro-acid at 80°–90° until a test no longer reacts with nitrite (Bayer, D. R.-P. 84140 of 1894). The *acid sodium* salt forms easily soluble needles; the *sodium* salt Na_4A+6H_2O, easily soluble, minute yellow prisms. When heated with caustic alkali at 150°–160°, it is converted into 1-*amino*-8-*naphthol*-(2) : 4 : 6-*trisulphonic acid* (Bayer, D. R.-P. 84597 of 1894).

CHLORO-α-NAPHTHYLAMINES.

8-**Chloro-α-naphthylamine** can be obtained from 1 : 8-diaminonaphthalene by allowing its azimide to interact with copper powder or with cuprous salts and hydrochloric acid at 30°. The base forms needles, m.p. 98° (Badische, D. R.-P. 147852 of 1903; *cf.* Atterberg, Ber. 1876, 9, 1730).

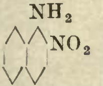
8-**Chloro-α-naphthylamine**-5-**sulphonic acid** is formed similarly from the azimide of 1 : 8-diaminonaphthalene-4-sulphonic acid (Badische, *l.c.*), and when heated with caustic soda solution under pressure at 190°–195° yields 1-*amino*-8-*naphthol*-5-*sulphonic acid* (Badische, D. R.-P. 112778 of 1899).

Several *α-chloro-α-naphthylaminesulphonic acids*, prepared by nitrating α-chloronaphthalenesulphonic acids and reducing the products, have been used in making azo- dyes, but not described in detail (Read, Holliday & Sons, Eng. Pats. 13999 of 1897; 11736 of 1898).

8-**Chloro-α-naphthylamine-3 : 6-disulphonic acid** is prepared similarly from the azimide of 1 : 8-diaminonaphthalene-3 : 6-disulphonic acid. With diazotised bases it forms *azo-* dyes; on fusion with caustic alkali it yields 1-*amino*-8-*naphthol*-3 : 6-*disulphonic acid*, and when heated with dilute sulphuric acid under pressure it is converted into 8-*chloro-α-naphthol*-3 : 6-*disulphonic acid*, from which 1 : 8-*dihydroxynaphthalene*-3 : 6-*disulphonic acid* can be obtained by fusion with alkali (Badische, D. R.-P. 147852 of 1903).

2 : 4-**Dichloro-α-naphthylaminesulphonic acid** is formed when 2 : 4-dichloroacet-α-naphthalide is sulphonated with 23 p.c. anhydro-acid below 45°, and the product deacetylated by boiling it with water. It is sparingly soluble in water; its *sodium* salt forms scales, and its *zinc* and *magnesium* salts long needles. When its sparingly soluble, crystalline *diazo-* compound is heated with sodium carbonate solution at 60°, it is converted into 4-*chloro*-1-*diazo-β-naphtholsulphonic acid* (Badische, D. R.-P. 153298; Eng. Pat. 16995 of 1903).

NITRO-α-NAPHTHYLAMINES.



(i.) 2-**Nitro-α-naphthylamine**, mixed with the 4-derivative, is obtained by nitrating acet-α-naphthalide in acetic acid solution. The product consists of crusts of a molecular compound (m.p. 171°) of the 2- and 4- derivatives mixed with needles of the 1 : 4- derivative, which can be separated mechanically and recrystallised from alcohol. By limited hydrolysis of the molecular compound with aqueous alcoholic caustic potash, 4-nitro-α-naphthylamine can be separated from the 2-nitroacet-α-naphthalide, which is most conveniently hydrolysed by boiling with alcoholic hydrochloric acid (Lellmann and Remy, Ber. 1886, 19, 797; Lellmann, *ibid.* 1887, 20, 892).

Properties.—It crystallises from alcohol in reddish-yellow, monoclinic prisms, m.p. 144° (Lellmann, Ber. 1884, 17, 112), and yields 2-*nitro-α-naphthol* when boiled with excess of caustic potash solution. Its *acetyl* derivative forms yellow needles, m.p. 199°.

(ii.) 4-**Nitro-α-naphthylamine,** prepared from 4-nitroacet-α-naphthalide (*v. supra*) by hydrolysis with alcoholic potash (Liebermann, Annalen, 1876, 183, 232), can also be obtained by mixing α-naphthyloxamic acid with nitric acid (sp.gr. 1·36) at 30°–40°, and hydrolysing the product with alkalis or mineral acids (Lange, D. R.-P. 58227 of 1890); *or* by heating 4-nitro-α-chloronaphthalene with 8 p.c. alcoholic ammonia at 150°–170° (Griesheim, D. R.-P. 117006; Eng. Pat. 7692 of 1900).

Properties.—It crystallises from alcohol in orange needles, m.p. 191°, and yields 4-*nitro-α-naphthol* when boiled with aqueous caustic potash (Andreoni and Biedermann, Ber. 1873, 6, 342). Its *acetyl* derivative forms yellow needles, m.p. 190°. From its *diazo-* compound, *azo-* dyes have been obtained (Höchst, D. R.-P. 68022; Eng. Pat. 18783 of 1891).

(*a*) 4-*Nitro-α-naphthylamine*-5-*sulphonic acid* is formed when α-naphthylamine-5-sulphonic acid, dissolved in 20 times its weight of sulphuric acid, is nitrated below 10°. It forms sparingly soluble, small needles, its *sodium* salt yellow scales (Bayer, D. R.-P. 133951; Eng. Pat. 9498 of 1899; *cf.* Levinstein, Eng. Pat. 13178 of 1899), and its *diazo-* compound furnishes *azo-* dyes (Bayer, D. R.-P. 118124, 119662; Eng. Pat. 9498 of 1899; Badische, D. R.-P. 151042 of 1903).

(*b*) 4-*Nitro-α-naphthylamine*-6-*sulphonic* and 7-*sulphonic acids* are obtained by the nitration of the corresponding α-naphthylaminesulphonic acids (Cassella, D. R.-P. 73502 of 1892), or their acetyl derivatives (*ibid.* D. R.-P. 74177; Eng. Pat. 15444 of 1893) in sulphuric acid solution. The 6-acid and salts are less soluble than the 7-isomerides. From the diazotised acids, *azo-* dyes have been obtained (*cf.* Bayer, D. R.-P. 118124; Eng. Pat. 9498 of 1899; Aktienges., D. R.-P. 222890 of 1908, 222931 of 1909).

(iii.) 5-**Nitro-α-naphthylamine** can be prepared by the partial reduction of 1:5-dinitronaphthalene with alcoholic hydrogen sulphide (Beilstein and Kuhlberg, Annalen, 1873, 169, 87); *or* by hydrolysis of 5-nitro-α-naphthylamine-4-sulphonic acid (Nietzki and Zübelen, Ber. 1889, 22, 452); *or*, mixed with the 4- and 8- compounds, by nitration of α-naphthylamine dissolved in 10 times its weight of sulphuric acid (Meldola and Streatfeild, Chem. Soc. Trans. 1893, 63, 1055).

Properties.—It crystallises in small, red needles, m.p. 119°. Its *acetyl* derivative forms large, brown prisms, m.p. 220° (Höchst, D. R.-P. 145191 of 1902), and its *sulphate* is less soluble than that of the 4- or 8-isomeride.

(*a*) 5-*Nitro-α-naphthylamine*-2-*sulphonic acid* can be prepared by nitrating α-naphthylamine-2-sulphonic acid in sulphuric acid solution below 15°. The acid and its *diazo-* compound are sparingly soluble (Cassella, D. R.-P. 70890 of 1892).

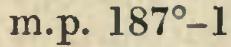
(*b*) 5-*Nitro-α-naphthylamine*-4-*sulphonic acid* is formed when acetyl-α-naphthylamine-4-sulphonic acid, mixed with sulphuric acid, is nitrated in the cold, and the product deacetylated by boiling it with dilute acid. The *acid* HA crystallises in needles; the *diazo-* compound forms *azo-* dyes (Nietzki and Zübelen, Ber. 1889, 22, 452).

(*c*) A *nitro-α-naphthylaminesulphonic acid*, probably isomeric with these acids, is said to be obtained by reduction of 1 : 5-dinitronaphthalene-3-sulphonic acid with sodium sulphite or bisulphite (Höchst, D. R.-P. 117268 of 1900).

(iv.) **8-Nitro-α-naphthylamine** occurs to the extent of 6–8 p.c. in the product obtained by the nitration of α-naphthylamine in sulphuric acid solution. It crystallises in red scales, m.p. 96°–97°, and its *acetyl* derivative in needles, m.p. 187°–188° (Meldola and Streatfeild, *l.c.*).

(v.) **2 : 4-Dinitro-α-naphthylamine** can be obtained from dinitroacet-α-naphthalide by hydrolysis with 50 p.c. sulphuric acid at 100° (Liebermann, Annalen, 1876, 183, 274; Meldola and Forster, Chem. Soc. Proc. 1893, 9, 8); or from 2 : 4-dinitro-α-naphthol by heating it with alcoholic ammonia under pressure at 190°–200° (Witt, Ber. 1886, 19, 2033). It crystallises in yellow needles, m.p. 237°; its *acetyl* derivative in yellow needles, m.p. 250°. When heated with aqueous alkalis, it is converted into 2 : 4-*dinitro-α-naphthol.*

(vi.) **4 : 5-Dinitro-α-naphthylamine** is formed by the nitration of 5-nitroacet-α-naphthalide suspended in sulphuric acid, and hydrolysis of the dinitroacet-α-naphthalide by boiling it with dilute acid. It crystallises in orange scales, m.p. 236°; its *acetyl* derivative in yellow needles, m.p. 244° (Badische, D. R.-P. 145191, 158499 of 1902).



(ii.) **β-Naphthylamine** (β-aminonaphthalene) was first prepared by reduction of 1-bromo-β-nitronaphthalene with tin and hydrochloric acid (Liebermann and Scheiding, Annalen, 1876, 183, 264). It is obtained, mixed with varying proportions of ββ′-dinaphthylamine, when β-naphthol is heated with ammonia at 160° under pressure for 60–70 hours (Badische, D. R.-P. 14612 of 1880), with twice its weight of ammonia-zinc chloride at 200°–210° for 2 hours (Merz and Weith, Ber. 1880, 13, 1300), or with 4 times its weight of anhydrous or hydrated ammonia-calcium chloride at 270°–280° for 8 hours, the yield being 80 p.c., and of ββ′-dinaphthylamine 12–14 p.c., under these conditions (Benz, *ibid.* 1883, 16, 19).

Preparation.—β-Naphthol is heated under pressure with 20–30 p.c. ammonia solution at 200° for a day (Schultz, Chemie des Steinkohlenth., 3rd ed., I, 85), or with caustic soda and ammonium chloride for 60–70 hours at 150°–160° (Badische, *l.c.*); or its dry sodium compound is heated with ammonium chloride at 200° for 24 hours (Oehler, Eng. Pat. prov. spec. 2516 of 1880). The crude product is extracted two or three times with hot caustic soda solution to remove unchanged β-naphthol, dried and finally distilled to remove ββ′-dinaphthylamine.

The conversion can be more easily achieved by the bisulphite method, β-naphthol (1 kilo.) being heated with 40 p.c. ammonium sulphite solution (1·5 litres) and 20 p.c. ammonia (1 litre) in an autoclave at 100°–150° until the change is complete. When cold the β-naphthylamine is separated by filtration, and the filtrate used for a subsequent operation. The product may contain small quantities of β-naphthol and ββ′-dinaphthylamine, which are easily removed, the yield of β-naphthylamine being almost quantitative (Bucherer, J.pr. Chem. 1904, [2] 69, 88; Badische, D. R.-P. 117471 of 1899; Eng. Pat. 1387 of 1900).

Identification.—It crystallises from alcohol in colourless, lustrous scales, melts at 112°, boils at 294° (Liebermann and Jacobson, Annalen, 1882, 211, 41), is only slightly volatile with steam, and dissolves easily in hot but only sparingly in cold water. The solutions of the base show blue fluorescence; those of its salts are non-fluorescent. Unlike α-naphthylamine, it gives no colour reactions with ferric chloride, chromic acid, bleaching powder, or nitrous acid. The *hydrochloride* $B{\cdot}HCl$ forms non-fluorescent scales, easily soluble, and the *nitrate* $B{\cdot}HNO_3$, and *sulphate* $B_2{\cdot}H_2SO_4$, scales sparingly soluble in water. The *platinichloride* crystallises in scales, and the *picrate*, from alcohol, in long yellow needles, m.p. 195°.

Reactions.—(1) From its *diazo-* compound *β-naphthol* (Liebermann, Annalen, 1876, 183, 268), and many *azo-* dyes have been obtained.

(2) On reduction in boiling amyl alcohol solution with sodium, it yields ac.-*tetrahydro-β-naphthylamine* (‘Thermine’) with about 3–4 p.c. of the *ar.*- derivative (Bamberger and Kitschelt, Ber. 1890, 23, 876).

(3) When heated alone, or with calcium or zinc chloride, it is converted partially into *ββ′-dinaphthylamine* and ammonia (Merz and Weith, Ber. 1881, 14, 2343; Benz, *l.c.*), but with sodamide, mixed with naphthalene, at 230° it gives 1 : 6-*diaminonaphthalene* (Sachs, *ibid.* 1906, 39, 3022).

(4) By digestion with bleaching powder and water at 40°–50°, it forms *αβ-naphthazine* (Claus and Jaeck, D. R.-P. 78748 of 1892).

Tests.—β-Naphthylamine should be free from β-naphthol and ββ′-dinaphthylamine, and therefore should be completely soluble in dilute hydrochloric acid. It should also have the right melting-point.

Acyl derivatives. Acetyl-β-naphthylamine (*acet-β-naphthalide*), obtained together with about 14 p.c. of ββ′-dinaphthylamine when β-naphthol is heated with ammonium acetate at 270°–280° for 8 hours (Merz and Weith, Ber. 1881, 14, 2343; Calm, *ibid.* 1882, 15, 610), is best prepared by boiling β-naphthylamine with 1·25–1·5 times its weight of glacial acetic acid for 12 hours, the ββ′-dinaphthylamine (about 10 p.c.) formed being readily separated by crystallisation from alcohol, in which it is only sparingly soluble

(Liebermann and Jacobson, Annalen, 1882, 211, 42).

Properties.—It crystallises in lustrous scales, m.p. 132° (Cosiner, Ber. 1881, 14, 59), dissolves readily in alcohol, sparingly in water, and is more easily hydrolysed by dilute acids than by alkalis (Calm, *l.c.*).

Acetyl-β-naphthylaminesulphonic acids. Two methods can be used for preparing these acids. In the first, acet-β-naphthalide is sulphonated with sulphuric acid, the product being *acetyl-β-naphthylamine*-5-*sulphonic acid* at 20°–30°, or *acetyl-β-naphthylamine*-7-*sulphonic acid* at 150°–160° (Kinzlberger & Co., D. P. Anm. K. 5732 of 1887). In the second, a solution of sodium β-naphthylamine- 5-, 6-, 7-, or 8-sulphonate is warmed with acetic anhydride at 50°–60° for a few minutes (Höchst, D. R.-P. 129000 of 1899; Eng. Pat. 17366 of 1898). The sodium salts obtained by salting out, and the derived acids, are crystalline but much more soluble in water than the corresponding naphthylamine compounds (Höchst, *l.c.*); they can be deacetylated by boiling the acids with water (Kinzlberger & Co., *l.c.*).

β-Naphthylsulphamic acid is formed when β-naphthylamine-1-sulphonic acid is heated at 230° (Tobias, D. R.-P. 74688; Eng. Pat. 15404 of 1893), and its *ammonium* salt when chlorosulphonic acid interacts with β-naphthylamine in chloroform solution, and the product is neutralised by ammonia (Traube, Ber. 1894, 24, 363). Fairly stable in neutral or alkaline solution, this substance decomposes, when warmed in acid solution, into β-naphthylamine and sulphuric acid.

β-Naphthylsulphamino-6:8-disulphonic acid is formed when β-naphthylamine-6:8-disulphonic acid is heated with 40 p.c. anhydro-acid at 90°. Its *barium* salt $Ba_3A_2+10H_2O$ forms sparingly soluble, orange-yellow needles; and the *potassium* salt K_3A+H_2O, orange-red needles. When its acid solution is warmed, it yields *β-naphthylamine*-6:8-*disulphonic* acid, while with 40 p.c. anhydro-acid at 130° it is converted into *β-naphthylamine*-3:6:8-*trisulphonic acid* (Dressel and Kothe, Ber. 1894, 27, 2153).

Alkyl derivatives.—*Methyl-β-naphthylamine*, an oil, b.p. 296° (Pechmann and Heinze, Ber. 1897, 30, 1785); *dimethyl-β-naphthylamine*, scales, m.p. 46°, b.p. 305° (Hantzsch, Ber. 1880, 13, 2054; Bamberger and Müller, *ibid.* 1889, 22, 1306; Pinnow, *ibid.* 1889, 32, 1405); *ethyl-β-naphthylamine* (Henriques, Ber. 1884, 17, 2668), an oil, b.p. 305° under 716 mm. (Bamberger and Müller, Ber. 1889, 22, 1297; O. Fischer, *ibid.* 1893, 26, 193) or 315°–316° under 760 mm. (Vaubel, Chem. Zeit. 1903, 27, 278); *diethyl-β-naphthylamine* (Morgan, Chem. Soc. Trans. 1900, 77, 823), an oil, b.p. 316° under 717 mm. (Bamberger and Williamson, Ber. 1889, 22, 1760).

Alkyl-β-naphthylaminesulphonic acids have been obtained by heating solutions of the respective sodium β-naphthylaminesulphonates with the alkyl chloride or sodium alkylsulphate under pressure (Bayer, D. R.-P. 41506 of 1886). The derived *disazo-* dyes are much bluer in shade than those from the non-alkylated acids (Bayer, D. R.-P. 41510, 41761, 42771; Eng. Pat. 17083 of 1886; D. R.-P. 43169, 43204 of 1887).

Ethyl-β-naphthylaminesulphonic acids. By sulphonating ethyl-β-naphthylamine with weak anhydro-acid at a moderate temperature, the 5-*sulphonic acid*, mixed with a small quantity of the 8-*acid*, is formed; with monohydrate at 140° the 7-*acid* is obtained; and with 20 p.c. anhydro-acid at 110°–120°, the 5:7-*disulphonic acid* is produced. The disulphonic acid, when fused with caustic alkali, yields *ethyl*-2-*amino*-5-*naphthol*-7-*sulphonic* acid (Leonhardt, D. R.-P. 95624; Eng. Pat. 10669 of 1895).

Aryl derivatives.—Phenyl- and tolyl-β-naphthylamines can be prepared by heating β-naphthol with the respective base (or its hydrochloride) under pressure at 200°–210° for 10 hours either alone (Graebe, Ber. 1880, 13, 1850; Badische, D. R.-P. 14612 of 1880; *cf.* Oehler, Eng. Pat. 2516 (prov. spec.) of 1880), or with the addition of ammonia-zinc chloride (Merz and Weith, Ber. 1880, 13, 1300). The yield is almost quantitative when β-naphthol (1 mol.), the base (2 mols.), and anhydrous calcium chloride (1 mol.) are heated together at 280° under pressure for 9 hours (Friedlaender, Ber. 1883, 16, 2077 *et seq.*). These products dissolve in the ordinary organic solvents, and, when heated with hydrochloric acid under pressure at 240°, regenerate β-naphthol and the base (Friedlaender, *l.c.*). *Phenyl-β-naphthylamine* forms needles, m.p. 108°, b.p. 395°–395·5° (Crafts, Annalen, 1880, 202, 5), and in solution shows blue fluorescence; o-*tolyl-β-naphthylamine* scales, m.p. 95°–96°; p-*tolyl-β-naphthylamine* scales, m.p. 104°, and in solution shows violet-blue fluorescence (Witt, Ber. 1887, 20, 578).

Phenyl- and (o- and p- *tolyl*)-*β-naphthylaminesulphonic acids.* Of these derivatives the 5-, 6-, 7-, or 8-sulphonic, and the 3:6- or 6:8-disulphonic acid can be obtained by heating the corresponding β-naphthylaminesulphonic acid with aniline (*o*- or *p*-toluidine) and its hydrochloride at 160°–170° (Bayer, D. R.-P. 70349, 71158, 71168; Eng. Pat. 7337A of 1892). They can also be obtained from the corresponding β-naphtholsulphonic acids by heating them with 40 p.c. sodium bisulphite solution and aniline (toluidine) in a reflux apparatus (Badische, D. R.-P. 122570; Eng. Pat. 18726 of 1900). Less satisfactory results follow when the corresponding β-naphtholsulphonic acid is heated with the base and its hydrochloride at 190°–200° (Aktienges., D. R.-P. 38424 of 1886). By sulphonation of phenyl-β-naphthylamine (Zimmer, D. R.-P. 45940; Eng. Pat. 13798 of 1888; Clayton Aniline Co., D. R.-P. 53649; Eng. Pat. 10934 of 1889) or of *o*-tolyl-β-naphthylamine (Clayton Aniline Co., D. R.-P. 57370 of 1889; Eng. Pat. 5155 of 1890), with 4 times its weight of monohydrate at temperatures below 50°, two isomeric sulphonic acids, A and B, result which have been identified as the 5- and 8- acids respectively (Lesser, Ber. 1894, 27, 2364; Bayer, *l.c.*).

ββ′-Dinaphthylamine[1] $(C_{10}H_7)_2NH$ is formed (3·5 p.c.) when β-naphthylamine is heated at 280°–300° during 8 hours (Benz, Ber. 1883, 16, 14); and in larger amount when it is heated with calcium chloride at 260°–280° (Merz and Weith, *ibid.* 1881, 14, 2343); also when it is

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[1] *αα′-Dinaphthylamine*, obtained by heating α-naphthylamine with its hydrochloride at 150°, forms scales, m.p. 113° (Girard and Vogt, Bull. Soc. chim. 1872, [ii.] 18, 68; *cf.* Calm, Ber. 1882, 15, 615: Benz, *ibid.* 1883, 16, 16). *αβ′-Dinaphthylamine*, obtained by heating α-naphthylamine with β-naphthol and calcium chloride, forms prisms, m.p. 110°–111° (Benz, *l.c.*).

boiled with glacial acetic acid for some hours (Liebermann and Jacobson, Annalen, 1882, 211, 43), or heated at 170°–190° in a current of hydrogen chloride (Klopsch, Ber. 1885, 18, 1586). A secondary product in the manufacture of β-naphthylamine (*q.v.*), it is obtained in large amount when β-naphthol is heated with ammonia-zinc chloride at 280° (Merz and Weith, *l.c.*; Calm, Ber. 1882, 15, 614; Benz, *l.c.*), *or* with β-naphthylamine (Badische, D. R.-P. 14612 of 1880), *or* with β-naphthylamine and calcium chloride at 270°–280° (Benz, *l.c.*). It is also formed by heating β-naphthylamine (2 mols.) with sodium bisulphite solution (1 mol.) and alcohol at 90°–100° for 24 hours (Bayer, D. R.-P. 114974; Eng. Pat. 22804 of 1899).

Properties.—It crystallises in scales, m.p. 171°, b.p. 471° (Ris, Ber. 1887, 20, 2619). Dissolved in alcohol or benzene, it shows intense blue fluorescence. When heated with hydrochloric acid at 240° it yields β-naphthylamine and β-naphthol quantitatively (Ris, *ibid.* 1886, 19, 2017), and, with sulphuric acid, mixtures of the isomeric β-naphthylamine- and β-naphtholsulphonic acids (Sandoz, D. R.-P. 64859 of 1891).

ββ′-Dinaphthylamine-7 : 7′-*disulphonic acid* has been prepared from β-naphthylamine-7-sulphonic acid by the bisulphite method (Bayer, *l.c.*); 5 : 5′-*dihydroxy-ββ′-dinaphthylamine*-7 : 7′-*disulphonic acid* from 2-amino-5-naphthol-7-sulphonic acid by the bisulphite method (Bayer, *l.c.*), or by heating it with water under pressure at 200° (Bayer, D. R.-P. 121094 of 1900; Eng. Pat. 24296 of 1899); and the 8 : 8′-*dihydroxy*-6 : 6′-*disulphonic acid* from 2-amino-8-naphthol-6-sulphonic acid by the latter method (*ibid.*). The dihydroxy- compounds couple with diazotised bases, yielding *azo*- dyes (Bayer, D. R.-P. 114841; Eng. Pat. 24296 of 1899).

β-NAPHTHYLAMINESULPHONIC ACIDS.

Introductory. — β-Naphthylaminesulphonic acids are obtained by the following methods:—

(1) By sulphonation of β-naphthylamine or of the derived β-naphthylaminesulphonic acids. The product in most cases is a mixture of acids, from which the more soluble constituents cannot easily be obtained pure.

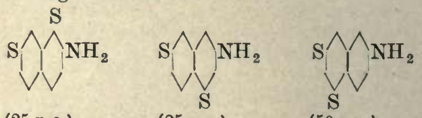
(2) By heating the sodium salts of the corresponding β-naphtholsulphonic acids with ammonia under pressure. Except with β-naphthol-1-sulphonic acid and its derivatives, this reaction gives a satisfactory yield of a pure product, and the ease with which it takes place increases with the number of sulphonic groups in the molecule.

(3) By heating the sodium salts of the corresponding β-naphtholsulphonic acids with ammonium bisulphite solution and ammonia at 100°–150°. The process is applicable to all acids which do not contain a 4-sulphonic group, and is of value for the production of the 6-, or 7-, or 8-monosulphonic acid, as each of the corresponding β-naphtholsulphonic acids is obtained in a pure state much more easily from β-naphthol than is the β-naphthylaminesulphonic acid from the mixed acids of the sulphonation melt (*cf.* Bucherer, J. pr. Chem. 1904, [ii.] 70, 357).

Four monosulphonic acids and one disulphonic acid, all of them heteronucleal, are known to be formed by the sulphonation of β-naphthylamine; six disulphonic acids by the sulphonation of monosulphonic acids; and six trisulphonic acids by the sulphonation of disulphonic acids. For the sulphonation of β-naphthylamine, sulphuric acid is used, but for that of the monosulphonic acids 20 p.c. anhydro-acid, and for that of the disulphonic acids 40 p.c. anhydro-acid are required, the end of the di- or tri-sulphonation being ascertained either by the solubility of the product or by the behaviour of the diazotised acid with R-salt. The effects of concentration of the acid, of temperature and of duration of the reaction on the nature of the product correspond with those traced out in other cases of sulphonation. It should be noted that sulphonation in the 1-position occurs only when at least one other sulphonic group is present in the molecule, and that the 1-sulphonic group when present is the first to be eliminated by hydrolysis.

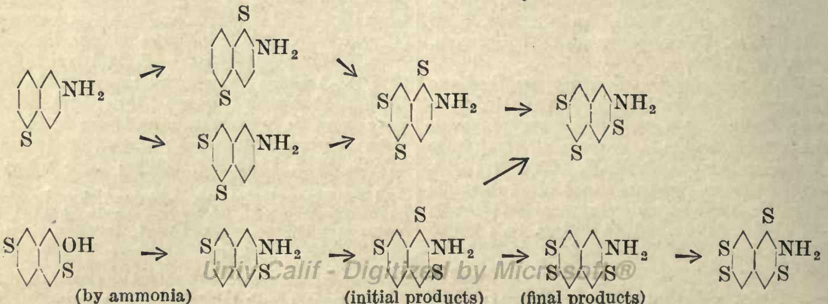
To illustrate the order in which sulphonic groups are introduced, the following examples of di- and of tri-sulphonation may be given:—

(*a*) When β-naphthylamine-7-sulphonic acid is sulphonated with 4 times its weight of 25 p.c. anhydro-acid at 15°, the products and their percentage amounts are—



(25 p.c.) (25 p.c.) (50 p.c.)

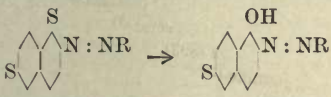
(*b*) When β-naphthylaminedisulphonic acids are sulphonated with 40 p.c. anhydro-acid at 140°, trisulphonic acids are formed, the nature of which depends on the duration of the reaction. In the scheme, two examples of the effect of prolonged heating are shown, the changes which the 1 : 3 : 7-trisulphonic acid undergoes in the presence of the anhydro-acid being particularly noteworthy—



(by ammonia) (initial products) (final products) β-Naphthylaminemonosulphonic acids are very sparingly soluble in water. The di- and tri-sulphonic acids dissolve easily in water, but their acid salts are less soluble, and are precipitated instead of the acids when a mineral acid is added to solutions of their alkali salts.

As sources of azo- dyes, the β-naphthylaminesulphonic acids are less important than the α- compounds. Many of the dyes obtained by coupling them with tetrazo- derivatives are of little value (*cf.* Cassella, D. R.-P. 46711 of 1888), and, moreover, the β-acids cannot be used as middle components in polyazo- dyes, as the NH_2 radicle, after coupling has taken place in the *ortho-* position relatively to it, does not admit of being itself diazotised (*cf.* Bayer, D. R.-P. 79816; Eng. Pat. 9972 of 1893).

β-Naphthylaminesulphonic acids containing either 1- or 8-sulphonic groups do not form azo-dyes, but diazoamino- compounds when coupled with diazotised bases. Those containing a 1-sulphonic group exchange it for hydroxyl, giving 2-diazo-α-naphthol-derivatives when diazotised and afterwards warmed at 50°–60° with excess (2 mols.) of sodium carbonate solution:



β-Naphthylaminesulphonic acids containing a 4-sulphonic group, like the *meta*-sulphonic acids from α-naphthylamine, yield hydroxytoluic acids by prolonged heating with caustic alkali solution at 280°, but, unlike them, are not converted into diaminonaphthalenes when heated under pressure with ammonia.

Unlike α-naphthylaminesulphonic acids which, when digested with caustic alkali solution, exchange the NH_2 for an OH radicle, β-naphthylaminesulphonic acids, under similar conditions, retain the amino- group, exchanging a SO_3H for the OH radicle, thus furnishing aminonaphtholsulphonic acids of which they are an important source.

β-Naphthylaminemonosulphonic Acids.[1]

(i.) β - **Naphthylamine - 1 - sulphonic acid** (Tobias's acid) is obtained when sodium β-naphthol-1-sulphonate is heated with 4–5 times its weight of 15–20 p.c. aqueous ammonia for 20 hours at 220°–230°. The β-naphthylamine, also formed, is removed from the cold product by filtration, and the acid separated from unchanged β-naphtholsulphonate by precipitation with hydrochloric acid (Tobias, D. R.-P. 74688; Eng. Pat. 15404 of 1893). The formation of β-naphthylamine can be avoided if the naphtholsulphonate be heated with 40 p.c. ammonium sulphite solution and 20 p.c. ammonia at 100°–150° until the reaction is complete, and the product afterwards acidified (Bucherer, J. pr. Chem. 1904, [ii.] 70, 357; Badische, D. R.-P. 117471 of 1899; Eng. Pat. 1387 of 1900).

Identification.—The *acid* separates in sparingly soluble anhydrous scales from hot, or in efflorescent hydrated needles from cold water; the *sodium* salt $NaA+H_2O$, in easily soluble scales which give a non-fluorescent solution (Tobias, *l.c.*). It is convertible into *β-chloronaphthalene-1-sulphonyl chloride*, m.p. 76° (Armstrong and Wynne, Chem. Soc. Proc. 1895, 11, 238), and into 1 : 2-*dichloronaphthalene* (Tobias, *l.c.*; Armstrong and Wynne, *l.c.*).

Reactions.—(1) From its sparingly soluble, crystalline *diazo-* compound, *β-naphthol-1-sulphonic acid* (Tobias) and *azo-* dyes (Badische, D. R.-P. 112833; Eng. Pat. 25511 of 1899) have been obtained.

(2) When heated at 230° in a dry, neutral atmosphere, the sodium salt is converted into *sodium β-naphthylsulphamate* (Tobias, *l.c.*).

(3) On sulphonation with 20 p.c. anhydro-acid it yields *β-naphthylamine-1 : 5-disulphonic acid* (Armstrong and Wynne, *l.c.*).

(ii.) β-**Naphthylamine-4-sulphonic acid** is obtained when β-naphthol-4-sulphonic acid is heated with ammonia under pressure (Kalle, D. R.-P. 78603 of 1893).

Identification.—The *acid* $HA+H_2O$ crystallises in sparingly soluble, long, white needles; the *potassium* salt $KA+1\frac{1}{2}H_2O$ in small needles; and the *sodium* salt $NaA+4H_2O$ in scales. The solution of the sodium salt shows violet fluorescence.

Reaction.—When heated with 60 p.c. caustic soda solution at 230°–280° under pressure, it is converted into *o-toluic acid* (Kalle, D. R.-P. 79028 of 1893).

(iii.) β-**Naphthylamine-5-sulphonic acid** ([γ-] acid; Dahl acid) constitutes about 40 p.c. of the product obtained when β-naphthylamine is heated with 3 times its weight of sulphuric acid at 100°–105° (*v.* 8-acid); about 55 p.c. of that obtained when β-naphthylamine sulphate is sulphonated at 15°–20° with 3 times its weight of sulphuric acid (Dahl, D. R.-P. 32276 of 1884); and 68–70 p.c. of that obtained when β-naphthylamine is sulphonated with 3 times its weight of 20 p.c. anhydro-acid at 70°–80° Dahl, D. R.-P. 29084; Eng. Pat. 7712 of 1884). It is also obtained when acet-β-naphthalide is sulphonated at 20°–30° with 5 times its weight of sulphuric acid, and the product deacetylated by boiling it with water (Kinzlberger & Co., D. P. Anm. K. 5732 of 1887).

Preparation.—β-Naphthylamine sulphate is stirred with 3 times its weight of sulphuric acid at 15°–20° during 48–70 hours until sulphonated. The product, converted into sodium salt, is extracted by boiling 90–95 p.c. alcohol; the alcoholic filtrate evaporated; and the residue, which contains small quantities of the 6- and 7-salts in addition to the 5-salt, is freed from these by conversion into and fractional crystallisation of the barium salts. As the barium or calcium salt of the 5-acid is easily soluble, a partial separation can be effected previous to the extraction with alcohol by converting the sulphonation product into the barium or calcium salt, and allowing the 6-, 7-, and 8-salts to separate, as far as possible, from the concentrated solution (Dahl, D. R.-P. 32271 of 1884).

Identification.—The *acid* HA forms needles or scales, soluble in 260 parts of boiling or 1300 parts of cold water. The salts crystallise well, dissolve easily in water, and, like the acid, show reddish-blue fluorescence in dilute solution.

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[1] In every case where the constitution of a β-naphthylaminesulphonic acid is given, the NH_2 group is supposed to be in the position '2.'

The *barium* salt $BaA_2+2\frac{1}{2}H_2O$ forms granular aggregates; the *calcium* salt CaA_2+11H_2O, needles soluble in 11 parts of cold water, the *potassium* salt $KA+H_2O$, small rhombohedra, the *sodium* salt $NaA+5H_2O$, prisms, soluble in 10 parts of boiling 95 p.c. alcohol, the *ammonium* salt, plates (*cf.* Forsling, 1887, Ber. 20, 2103). It is convertible into *β-chloronaphthalene-5-sulphonyl chloride*, m.p. 70°, and into 1 : 6-*dichloronaphthalene* (Armstrong and Wynne, Chem. Soc. Proc. 1889, 5, 48; Cleve, Ber. 1892, 25, 2481; Forsling, *l.c.*).

Reactions.—(1) From the sparingly soluble *diazo-* compound, *β-naphthol-5-sulphonic acid* (Dahl, D. R.-P. 29084; Eng. Pat. 7712 of 1884), and *azo-* dyes (Dahl, D. R.-P. 30640; Eng. Pat. 11002 of 1884; Badische, D. R.-P. 120322; Eng. Pat. 2784 of 1900) have been obtained.

(2) Fusion with caustic potash at 260°–270° converts it into 2-*amino-5-naphthol* (Bayer, D. P. Anm. F. 7372; Eng. Pat. 5267 of 1894).

(3) When sulphonated with 4 times its weight of 20 p.c. anhydro-acid in the cold, it yields as chief product *β-naphthylamine-5* : 7-*disulphonic acid* (Armstrong and Wynne, Chem. Soc. Proc. 1890, 6, 128); and with 40 p.c. anhydro-acid, finally at 100°, *β-naphthylamine-1 : 5 : 7-trisulphonic acid* (Bayer, D. R.-P. 80878; Eng. Pat. 20580 of 1893).

(iv.) **β-Naphthylamine-6-sulphonic acid** ([β-] acid; Brönner acid) occurs to the extent of about 5 p.c. in the product obtained when β-naphthylamine is heated with 3 times its weight of sulphuric acid at 100°–105° for 6 hours (*v.* 8-acid), and of about 50 p.c. in that formed when β-naphthylamine sulphate, or β-naphthylamine-5- or 8-sulphonic acid, is heated with 3 times its weight of sulphuric acid at 160°–170° for 2 hours (*v.* 7-acid). It is also produced, mixed with a small proportion of the 7-acid (Bayer and Duisberg, Ber. 1890, 23, 1914), when an intimate mixture of β-naphthylamine and sulphuric acid, in the proportion necessary to form β-naphthylamine hydrogen sulphate, is baked at 200°–210° for 2 hours (Liebmann, D. P. Anm. L. 3205 of 1885); or when β-naphthylamine is heated with 3 times its weight of potassium bisulphate at about 230° (Bischoff and Brodsky, Ber. 1890, 23, 1914).

Preparation.—(1) β-Naphthylamine-6-sulphonic acid and its salts, being much less soluble in water than the 7- compounds (*q.v.*), can be separated without much difficulty by fractional crystallisation from the products obtained either by sulphonating β-naphthylamine under the conditions just described, or by heating β-naphthol-6-sulphonic acid, containing the 7-isomeride (*cf.* Green, Chem. Soc. Trans. 1889, 55, 37; Eng. Pat. 15849 of 1888), with ammonia. As with the 7-isomeride, the purity of the 6-acid can be judged from the appearance of its crystals, or of those of its ammonium salt, as they separate from solution (Green, *l.c.*).

(2) The pure acid[1] is obtained when ammonium or sodium β-naphthol-6-sulphonate is heated with aqueous ammonia at 180° under pressure (Brönner, D. R.-P. 22547; Eng. Pat. 3724 of 1882; *cf.* Landshoff, D. R.-P. 27378 of 1883; Ber. 1883, 16, 1932); or with 40 p.c. ammonium bisulphite solution and 20 p.c. ammonia at 100°–150°, the product afterwards being acidified (Badische, D. R.-P. 115335, 117471, of 1899; Eng. Pat. 1387 of 1900).

Identification.—The *acid* $HA+H_2O$ crystallises in scales soluble in 630 parts of boiling water (Weinberg, Ber. 1887, 20, 2909), and, like its salts, shows blue fluorescence in solution. The *lead* salt PbA_2+2H_2O forms scales soluble in 670 parts of water at 1°; the *barium* salt BaA_2+6H_2O, long needles soluble in 450 parts of cold water; the *calcium* salt CaA_2+6H_2O, scales soluble in 225 parts of water at 5°; the *potassium* salt $KA+H_2O$, silky needles, soluble in 40–45 parts of cold water; the *sodium* salt $NaA+2H_2O$, silky needles, soluble in about 40 parts of cold water, and easily in hot 90 p.c. alcohol (*cf.* Forsling, Ber. 1887, 20, 77; Limpricht, quoted by Schultz, Chemie des Steinkohlenth, 3rd ed. 1, 209). The *ammonium* salt NH_4A+H_2O, large thin plates, is the least soluble of the ammonium β-naphthylaminesulphonates in cold water (Green, *l.c.*). It is convertible into *β-chloronaphthalene-6-sulphonyl chloride*, m.p. 109° (Forsling, *l.c.*), and into 2 : 6-*dichloronaphthalene* (Forsling, *l.c.*; Armstrong and Wynne, Chem. Soc. Proc. 1889, 5, 52).

Reactions.—(1) From its moderately soluble, yellow *diazo-* compound *azo-* dyes have been obtained (*cf.* Badische, D. R.-P. 120322 of 1900).

(2) When it is boiled with a large excess of 40 p.c. sodium bisulphite solution and the product acidified, *β-naphthol-6-sulphonic acid* is formed (Badische, D. R.-P. 134401 of 1899).

(3) On sulphonation with 4 times its weight of 20 p.c. anhydro-acid at 20°, it yields a mixture of *β-naphthylamine-1* : 6-*disulphonic acid* with about 20 p.c. of *β-naphthylamine-6* : 8-*disulphonic acid* (Armstrong and Wynne, Chem. Soc. Proc. 1890, 6, 130; *cf.* Forsling, Ber. 1888, 21, 3495).

(v.) **β-Naphthylamine-7-sulphonic acid** ([δ-] acid; F-acid). This acid, mixed with about an equal quantity of β-naphthylamine-6-sulphonic acid (Schultz, Ber. 1887, 20, 3159), constitutes the product obtained when β-naphthylamine is heated with 6 times its weight of sulphuric acid at temperatures above 150° (Bayer, D. R.-P. 39925; Eng. Pat. 5846 of 1886), when β-naphthylamine sulphate is heated with 3 times its weight of sulphuric acid at 160°–170° (Bayer, D. R.-P. 41505 of 1886); or when β-naphthylamine-5- or 8-sulphonic acid is heated with 3 times its weight of sulphuric acid at 160°–170° for about 2 hours (Bayer, D. R.-P. 42272, 42273 of 1887; Weinberg, Ber. 1887, 20, 3354; Erdmann, *ibid.* 1888, 21, 637). It has been isolated (5 p.c.) from the mixture of acids formed when β-naphthylamine is heated with sulphuric acid at 100°–105° (*v.* 8-acid). It is also obtained when acet-β-naphthalide is heated with 6 times its weight of sulphuric acid at 150°–160° for 1–1½ hours, and the product deacetylated by pouring the hot melt into water (Kinzlberger & Co., D. P. Anm. K. 5732 of 1887).

Preparation.—(1) When β-naphthylamine

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[1] The second naphthylaminesulphonic acid—characterised by its solubility in water, the solubility of its sodium salt in alcohol, and the redder shade of its azo-dyes—which is stated by the Farbfabrik vorm. Brönner (*l.c.*) to occur in the Brönner product, doubtless owed its origin to impurity in the Schaeffer acid employed (*cf.* Bayer and Duisberg, Ber. 1887, 20, 1427).

sulphate is heated with 3 times its weight of sulphuric acid at 160°–170° for about 2 hours, and the product poured on to ice, the precipitated acid consists of the 6- and 7-isomerides. From this mixture the 6-acid can be isolated with little trouble, but the separation of pure 7-acid is much more difficult. Fractional crystallisation of the mixed acids from water at about 80° (Schultz, Ber. 1887, 20, 3159), or of the mixed copper salts (Aktienges., D. R.-P. 44248; Eng. Pat. 687 of 1888), or lead salts (Aktienges., D. R.-P. 44249; Eng. Pat. *l.c.*), the 7-compound being in each case the more soluble, can be employed, but is probably not attempted on the large scale. The purity of the 7-acid obtained by direct sulphonation can be judged from the appearance of its crystals (Schultz, *l.c.*), or of those of its ammonium salt (Green, Chem. Soc. Trans. 1889, 55, 36), as they separate from solution.

(2) Pure β-naphthylamine-7-sulphonic acid is obtained without difficulty when sodium β-naphthol-7-sulphonate is heated with twice its weight of 20 p.c. ammonia at 250° for 6 hours under pressure (Cassella, D. R.-P. 43740 of 1886; Bayer and Duisberg, Ber. 1887, 20, 1432; Weinberg, *ibid.* 2908); or with 40 p.c. ammonium bisulphite solution and 20 p.c. ammonia at 100°–150°, the product finally being acidified (Badische, D. R.-P. 117471 of 1899; Eng. Pat. 1387 of 1900).

Identification.—The *acid* $HA+H_2O$ forms slender, voluminous needles soluble in 350 parts of boiling water. When boiled with a quantity of water insufficient to dissolve it, the crystalline acid changes into a very sparingly soluble, anhydrous, sandy powder. The *barium* salt BaA_2+5H_2O forms thin scales soluble in 400 parts of cold water; the *calcium* salt CaA_2+6H_2O, scales soluble in 270 parts of cold water; the *potassium* salt, needles soluble in 40 parts of cold water; the *ammonium* salt, small plates; the *sodium* salt $NaA+4H_2O$, small needles soluble in 70 parts of cold water, and in hot 90 p.c. alcohol (*cf.* Bayer and Duisberg, *l.c.*; Weinberg, *l.c.*; Schultz, *l.c.*). The solutions of the salts show reddish-violet fluorescence. It is convertible into *β-chloronaphthalene*-7-*sulphonyl chloride*, m.p. 86° (Armstrong and Wynne, Chem. Soc. Proc. 1889, 5, 49; Cleve, Ber. 1892, 25, 2484), and into 2 : 7-*dichloronaphthalene* (Erdmann, Ber. 1888, 21, 638; Armstrong and Wynne, *l.c.*).

Reactions.—(1) From its orange-red *diazo*-compound, *β-naphthol*-7-*sulphonic acid* (Bayer and Duisberg, *l.c.*; Schultz, *l.c.*); and *azo-* dyes (*cf.* Cassella, D. R.-P. 43740 of 1886) have been obtained.

(2) When heated with 20 p.c. sodium bisulphite solution (1 mol.) at 90°–100° for 24 hours, sodium β-naphthylamine-7-sulphonate (2 mols.) is converted into sodium *ββ′-dinaphthylamine*-7 : 7′-*disulphonate* (Bayer, D. R.-P. 114974; Eng. Pat. 22804 of 1899).

(3) Fusion with 50 p.c. caustic soda solution at 260°–300° converts it into 2-*amino*-7-*naphthol* (Gesellsch., D. R.-P. 47816 of 1888).

(4) When sulphonated with 4 times its weight of 20–25 p.c. anhydro-acid at the ordinary temperature, it yields three *β-naphthylamine-disulphonic acids*, viz. the 1 : 7-, 4 : 7-, and 5 : 7-isomerides (Bayer, D. R.-P. 79243 of 1894; Dressel and Kothe, Ber. 1894, 27, 1194; Armstrong and Wynne, Chem. Soc. Proc. 1890, 6, 130).

(vi.) **β-Naphthylamine-8-sulphonic acid** ([α-] acid; Badische acid). When β-naphthylamine is heated with 3 times its weight of sulphuric acid at 100°–105° for about 6 hours, it yields a product (Badische, D. R.-P. 20760 of 1881) which contains the four heteronucleal β-naphthylaminesulphonic acids in the approximate proportion of 50 p.c. of the 8-acid, 40 p.c. of the 5- acid, 5 p.c. each of the 6- and the 7-acids (Dahl, D. R.-P. 29084; Eng. Pat. 7712 of 1884; Green, Chem. Soc. Trans. 1889, 55, 36). The proportion of the 8-acid does not exceed 45 p.c. when β-naphthylamine sulphate is sulphonated with 3 times its weight of sulphuric acid at 15°-20° (*v.* 5-acid), diminishing at higher temperatures until at 160°–170° the product contains only the 6- and 7-acids (Schultz, Ber. 1887, 20, 3159),[1] while it amounts only to 30 p.c. when β-naphthylamine is sulphonated with 3 times its weight of 20 p.c. anhydro-acid at 70°–80° (Dahl, *l.c.*; Green, *l.c.*).

Preparation.—(1) The product obtained by sulphonating β-naphthylamine with 3 times its weight of sulphuric acid at 100°–105° is converted into sodium salt, which, as a dry powder, is extracted with 90–95 p.c. alcohol to remove the isomeric salts, the residue consisting of the pure sodium β-naphthylamine-8-sulphonate (Dahl, *l.c.*; Green, *l.c.*). Fractional crystallisation of the mixed calcium salts can be used to effect a partial separation (*v.* 5-acid).

(2) The pure acid is obtained when sodium β-naphthol-8-sulphonate is heated with ammonia under pressure (Bayer, D. R.-P. 42273 of 1887; Pfitzinger and Duisberg, Ber. 1889, 22, 397), or with 40 p.c. ammonium bisulphite solution and 20 p.c. ammonia at 100°–150°, the product finally being acidified (Badische, D. R.-P. 117471 of 1899; Eng. Pat. 1387 of 1900).

Identification.—The *acid* forms slender needles, soluble in 200 parts of boiling or in 1700 parts of cold water. The salts crystallise well, and like the acid, show blue fluorescence in dilute solution (*cf.* Forsling, Ber. 1887, 20, 2100). The *barium* salt BaA_2+4H_2O forms prisms soluble in 23 parts of cold water; the *calcium* salt CaA_2+6H_2O, prisms soluble in 11 parts of cold water; the *potassium* salt $KA+\frac{1}{2}H_2O$, six-sided prisms; the *sodium* salt NaA (Erdmann, Annalen, 1893, 275, 281), large prisms insoluble in alcohol; the *ammonium* salt (Green, *l.c.*), large, solid prisms. It is convertible into *β-chloronaphthalene*-8-*sulphonyl chloride*, m.p. 129°, and into 1 : 7-*dichloronaphthalene* (Armstrong and Wynne, Chem. Soc. Proc. 1888, 4, 105; 1889, 5, 53; Forsling, *l.c.*; Ber. 1888, 21, 2803; 1889, 22, 619).

Reactions.—(1) From its sparingly soluble *diazo-* compound, *β-naphthol*-8-*sulphonic acid* (Dahl, *l.c.*) and *azo-* dyes (*cf.* Badische, D. R.-P. 120322; Eng. Pat. 2784 of 1900; D. R.-P.

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[1] Forsling's statement that the sulphonation product at 140° consists almost entirely of a mixture of the 5- and 8-acids (Ber. 1887, 20, 2100), must be regarded as incorrect in view of the fact that the product at 120° compared with that at 100° contains a smaller proportion of the 8-acid and a considerably increased yield of the 6- and 7-acids (Dahl, *l.c.*; Bayer, D. R.-P. 42273 of 1887; Weinberg, Ber. 1887, 20, 3354).

176640 of 1905; Eng. Pat. 7287 of 1906) have been obtained.

(2) By interaction with diazotised bases, it forms not azo- dyes but soluble yellow *diazo-amino-* compounds (Bayer and Duisberg, Ber. 1887, 20, 1428; Witt, *ibid.* 1888, 21, 3483; Erdmann, *l.c.*).

(3) When it is boiled with a large excess of 40 p.c. sodium bisulphite solution, and the product acidified, *β-naphthol-*8-*sulphonic acid* is formed (Badische, D. R.-P. 134401 of 1899).

(4) Fusion with caustic potash at 260°–270° converts it into 2-*amino-*8-*naphthol* (Bayer, D. P. Anm. F. 7335; Eng. Pat. 5148 of 1894).

(5) When sulphonated in the cold with 20 p.c. anhydro-acid, it gives *β-naphthylamine-*6 : 8-*disulphonic acid* as chief product (Armstrong and Wynne, Chem. Soc. Proc. 1890, 6, 128).

β-Naphthylaminedisulphonic Acids.

(i.) **β-Naphthylamine- 1 : 5 -disulphonic acid** is obtained when β-naphthylamine-1-sulphonic acid is sulphonated with 20 p.c. anhydro-acid in the cold (Armstrong and Wynne, Chem. Soc. Proc. 1895, 11, 238); *or* (as minor product) mixed with the 5 : 7-acid when β-naphthylamine-5-sulphonic acid is sulphonated under similar conditions (Armstrong and Wynne, *ibid.* 1890, 6, 129).

Identification.—The *normal potassium* salt is moderately soluble in water, and is convertible into *β-chloronaphthalene-*1 : 5-*disulphonyl chloride*, m.p. 158°, and into 1 : 2 : 5-*trichloronaphthalene* (Armstrong and Wynne, *l.c.*).

Reactions.—(1) Its sparingly soluble, colourless *diazo-* compound gives *azo-* dyes (*cf.* Badische, D. R.-P. 139909; Eng. Pat. 7153 of 1902), or, with excess (1–2 mols.) of sodium carbonate solution at 50°–60°, yields 2-*diazo-α-naphthol-*5-*sulphonic acid* (Badische, D. R.-P. 145906; Eng. Pat. 6615 of 1902).

(2) When fused with caustic alkali at 210°–230°, it gives 2-*amino-*5-*naphthol-*1-*sulphonic acid* (Kalle, D. R.-P. 242052 of 1909).

(3) On sulphonation with 40 p.c. anhydro-acid at 100°, it is converted into *β-naphthylamine-*1 : 5 : 7-*trisulphonic acid* (Bayer, D. R.-P. 80878; Eng. Pat. 20580 of 1893).

(ii.) **β-Naphthylamine- 1 : 6 -disulphonic acid** is obtained as chief product, with about 20 p.c. of the 6 : 8-acid, when β-naphthylamine-6-sulphonic acid is sulphonated with 20 p.c. anhydro-acid at a temperature below 20° (Armstrong and Wynne, Chem. Proc. Soc. 1890, 6, 130; *cf.* Forsling, Ber. 1888, 21, 3495); *or*, pure, by heating sodium β-naphthol-1 : 6-disulphonate with 40 p.c. ammonium sulphite solution and 20 p.c. ammonia at 100°–150°, and afterwards acidifying the product (Badische, D. R.-P. 117471 of 1899; Eng. Pat. 1387 of 1900).

Identification.—The *normal potassium* salt K_2A+2H_2O in large crystals, the *sodium* salt in long needles, and the *ammonium* salt $(NH_4)_2A+H_2O$ in triclinic forms, are very soluble; but the *acid potassium* salt $KHA+H_2O$ and *acid sodium* salt $NaHA+2H_2O$ in long needles, are only sparingly soluble and in dilute solution show blue fluorescence (Forsling, *l.c.*). It is convertible into *naphthalene-*1 : 6-*disulphonic acid* (Armstrong and Wynne, *l.c.*); into *β-chloronaphthalene-*1 : 6-*disulphonyl chloride*, m.p. 124·5°; and into 1 : 2 : 6-*trichloronaphthalene* (Forsling, *l.c.*; Armstrong and Wynne, *l.c.*).

Reaction.—Its sparingly soluble, crystalline *diazo-* compound, when warmed with excess of sodium carbonate solution, yields 2-*diazo-α-naphthol-*6-*sulphonic acid* (Badische, D. R.-P. 148882; Eng. Pat. 6615 of 1902).

(iii.) **β-Naphthylamine-1 : 7-disulphonic acid** is formed (25 p.c.) together with the 4 : 7- and 5 : 7-disulphonic acids, when β-naphthylamine-7-sulphonic acid is sulphonated in the cold with 20–25 p.c. anhydro-acid. It is separated by converting the product into normal potassium salt, and collecting the least soluble portion by fractional crystallisation (Bayer, D. R.-P. 79243 of 1894; Dressel and Kothe, Ber. 1894, 27, 1194). It is also obtained when potassium β-naphthol-1 : 7-disulphonate is heated either with ammonium chloride and ammonia solution at 180°–200° (Bayer, D. P. Anm. F. 7274; D. R.-P. 77596 of 1893; Eng. Pat. 1063 of 1894; Dressel and Kothe, *l.c.* 1206), or with ammonium sulphite solution and ammonia at 100°–150°, the product afterwards being acidified (Badische, D. R.-P. 117471 of 1899; Eng. Pat. 1387 of 1900).

Identification.—The *normal barium* salt, moderately soluble needles; the *potassium* salt K_2A+3H_2O, large monosymmetric crystals; and the *acid potassium* salt, sparingly soluble slender needles, give solutions showing violet-blue fluorescence (Dressel and Kothe, *l.c.*). The acid in acetic acid solution does not couple with diazobenzene (Bayer, D. P. Anm. F. 7274 of 1893).

Reactions.—(1) From the easily soluble *diazo-* compound *naphthalene-*1 : 7-*disulphonic acid* (Bayer, D. R.-P. 77596 of 1893); *β-naphthol-*1 : 7-*disulphonic acid* (Dressel and Kothe, *l.c.*); and 2-*diazo-α-naphthol-*7-*sulphonic acid* (Badische, D. R.-P. 148882; Eng. Pat. 6615 of 1902), have been obtained.

(2) Prolonged boiling with 20 p.c. hydrochloric acid converts it into *β-naphthylamine-*7-*sulphonic acid* (Dressel and Kothe, *l.c.*).

(iv.) **β-Naphthylamine-3 : 6-disulphonic acid** (β-naphthylamine-[α-]disulphonic acid; amino-R-acid) is obtained by heating sodium β-naphthol-3 : 6-disulphonate either with ammonia under pressure (Pfitzinger and Duisberg, Ber. 1889, 22, 398; *cf.* Landshoff, D. R.-P. 27378 of 1883); or with ammonium bisulphite solution and ammonia at 100°–150°, the product afterwards being acidified (Badische, D. R.-P. 117471 of 1899; Eng. Pat. 1387 of 1900). It is also formed when sodium β-naphthylamine-3 : 6 : 8-trisulphonate is boiled with zinc dust and dilute caustic soda solution (Kalle, D. R.-P. 233934 of 1909).

Reactions.—(1) Its sparingly soluble, yellow *diazo-* compound gives *azo-* dyes (*cf.* Bayer, D. R.-P. 157508 of 1903; Eng. Pat. 12512 of 1904), and from it *naphthalene-*2 : 7-*disulphonic acid* (Pfitzinger and Duisberg, *l.c.*), *β-chloronaphthalene-*3 : 6-*disulphonyl chloride*, m.p. 165°, and 2 : 3 : 6-*trichloronaphthalene* (Armstrong and Wynne, Chem. Soc. Proc. 1890, 6, 12), have been obtained.

It couples with diazotised bases, yielding many *monoazo-* dyes, or, if end component, *polyazo-* dyes (*cf.* Cassella, D. R.-P. 39029; Eng. Pat. 9214 of 1885).

(2) When fused with caustic soda at 230°–250° it yields 2-*amino*-3-*naphthol*-6-*sulphonic acid* (Höchst, D. R.-P. 53076; Eng. Pat. 15176 of 1889; Friedlaender and Zakrzewski, Ber. 1894, 27, 763).

(v.) **β-Naphthylamine-3 : 7-disulphonic acid** (β-naphthylamine-[δ-]disulphonic acid) is formed when sodium β-naphthol-3 : 7-disulphonate is heated either with 25 p.c. ammonia solution under pressure at 200° (Cassella, D. R.-P. 46711 of 1888); or with ammonium bisulphite solution and ammonia at 100°–150°, the product being afterwards acidified (Badische, D. R.-P. 117471 of 1899; Eng. Pat. 1387 of 1900); *or* when β-naphthylamine-1 : 3 : 7-trisulphonic acid is boiled with dilute mineral acids (Dressel and Kothe, Ber. 1894, 27, 1199).

Identification.—The *acid barium* salt forms very sparingly soluble microscopic crystals; the *acid potassium* salt, sparingly soluble scales; the *acid sodium* salt dissolves in 12·5 parts of boiling water, or in 50 parts of water at 20°, the solutions showing blue fluorescence (Dressel and Kothe, *l.c.*). It is convertible into β-*chloronaphthalene*-3 : 7-*disulphonyl chloride*, m.p. 176°, and into 2 : 3 : 7-*trichloronaphthalene* (Armstrong and Wynne, Chem. Soc. Proc. 1890, 6, 127).

Reactions.—(1) From the sparingly soluble, yellow *diazo*- compound, *naphthalene*-2 : 6-*disulphonic acid* (Armstrong and Wynne, *l.c.*), and *azo*- dyes (Cassella, D. R.-P. 50907; Eng. Pat. 18425 of 1888) have been obtained.

(2) On sulphonation with 40 p.c. anhydro-acid at 80°–90°, it is converted into β-*naphthylamine*-1 : 3 : 7-*trisulphonic acid* (Bayer, D. P. Anm. F. 7036 of 1893; Dressel and Kothe, *l.c.*).

(vi.) **β-Naphthylamine-4 : 7-disulphonic acid** (Andresen's acid) is obtained when β-nitronaphthalene-4 : 7-disulphonic acid is reduced (Schultz, Ber. 1890, 23, 77); *or* (25 p.c.) when β-naphthylamine-7-sulphonic acid is sulphonated with 20–25 p.c. anhydro-acid in the cold, and, after removal of the 1 : 7-disulphonic acid as potassium salt, is separated as normal sodium salt from the more soluble 5 : 7-disulphonic acid (Bayer, D. R.-P. 79243 of 1894; Dressel and Kothe, Ber. 1894, 27, 1196).

Identification.—The normal *barium* and *sodium* salts form crystalline crusts; the *acid sodium* salt $NaHA+H_2O$, needles, which in solution show intense blue fluorescence (Dressel and Kothe, *l.c.*). It is convertible into β-*chloronaphthalene*-4 : 7-*disulphonyl chloride*, m.p. 147°, and into 1 : 3 : 6-*trichloronaphthalene* (Armstrong and Wynne, Chem. Soc. Proc. 1891, 7, 27).

Reactions.—(1) From its moderately soluble, yellow *diazo*- compound, *naphthalene*-1 : 6-*disulphonic acid* has been obtained (Armstrong and Wynne, *l.c.*).

(2) By digestion with 35 p.c. caustic potash solution at 180°–200° under pressure, it gives 2-*amino*-4-*naphthol*-7-*sulphonic acid* (Bayer, D. P. Anm. F. 7978; Eng. Pat. 25214 of 1894).

(3) When heated with aniline and aniline hydrochloride at 150°–170° it yields *diphenyl*-1 : 3-*diaminonaphthalene*-6-*sulphonic acid* (Bayer, D. R.-P. 77866; Eng. Pat. 16780 of 1893).

(vii.) **β-Naphthylamine-4 : 8-disulphonic acid** (C-acid) is obtained by the reduction of β-nitronaphthalene-4 : 8-disulphonic acid (Cassella, D. R.-P. 65997 of 1890; Fischer, *cf.* J. Soc. Chem. Ind. 1898, 17, 837).

Identification.—The *acid* forms prisms; the *acid barium* salt, minute needles; the *acid sodium* salt needles, easily soluble in hot water. The alkaline solutions show deep blue fluorescence. It does not couple with diazotised bases to form azo- dyes (Cassella, *l.c.*).

Reactions.—(1) From the moderately soluble, yellow *diazo*- compound, *naphthalene*-1 : 5-*disulphonic acid* and β-*naphthol*-4 : 8-*disulphonic acid* have been obtained (Cassella, *l.c.*).

(2) By partial hydrolysis with water or with 10 p.c. sulphuric acid at 170°–185°, it yields β-*naphthol*-4-*sulphonic acid* (Kalle, D. R.-P. 78603 of 1893).

(3) When boiled with zinc dust and 35 p.c. caustic soda solution it gives a mixture of β-*naphthylamine*-4- and 8-*sulphonic acids* (Kalle, D. R.-P. 233934 of 1909); reduced electrolytically, it gives the 8-*sulphonic acid* (Bayer, Fr. Pat. 439010 of 1912; *v.* p. 592, footnote 1); and with sodium amalgam it yields β-*naphthylamine* (Friedlaender and Lucht, Ber. 1893, 26, 3033).

(4) By digestion with 80 p.c. caustic potash solution at 215° it is converted into 2-*amino*-4-*naphthol*-8-*sulphonic acid* (Bayer, D. P. Anm. F. 8070; D. R.-P. 85241; Eng. Pat. 3580 of 1895).

(5) When heated with aniline and aniline hydrochloride at 150°–170° it yields *diphenyl*-1 : 3-*diaminonaphthalene*-5-*sulphonic acid* (Bayer, D. R.-P. 77866; Eng. Pat. 16780 of 1893).

(6) On sulphonation with 40 p.c. anhydro-acid at 80°–120° it forms β-*naphthylamine*-4 : 6 : 8-*trisulphonic acid* (Bayer, D. R.-P. 89242 of 1895).

(viii.) **β-Naphthylamine-5 : 7-disulphonic acid** is obtained as chief product when β-naphthylamine-5-sulphonic acid is sulphonated with 20 p.c. anhydro-acid below 20°, remaining in the mother liquor from which the 1 : 5-disulphonate has been separated as normal potassium salt (Armstrong and Wynne, Chem. Soc. Proc. 1890, 6, 129). It is also the chief (50 p.c.) and most soluble product of the sulphonation of β-naphthylamine-7-sulphonic acid (*v.* 1 : 7- and 4 : 7- acids) with 20–25 p.c. anhydro-acid (Bayer, D. R.-P. 79243 of 1894; Dressel and Kothe, Ber. 1894, 27, 1197; *cf.* Armstrong and Wynne, *l.c.* 131).

Identification.—The *acid potassium* salt is easily soluble, and is convertible into *naphthalene*-1 : 3-*disulphonic acid*; β-*chloronaphthalene*-5 : 7-*disulphonyl chloride*, m.p. 156°; and 1 : 3 : 6-*trichloronaphthalene* (Armstrong and Wynne, *l.c.*).[1] From its *diazo*- compound *azo*- dyes can be obtained (*cf.* Kalle, D. R.-P. 162180 of 1904).

Reactions.—(1) When digested with 50 p.c. caustic soda solution under pressure at 180°–195° it yields 2-*amino*-5-*naphthol*-7-*sulphonic acid* (Badische, D. P. Anm. B. 14154; D. R.-P. 75469; Eng. Pat. 2614 of 1893).

(2) On sulphonation with 40 p.c. anhydro-acid at 100° it is converted into β-*naphthylamine*-1 : 5 : 7-*trisulphonic acid* (Bayer, D. R.-P. 80878; Eng. Pat. 20580 of 1893).

(ix.) **β-Naphthylamine-6 : 8-disulphonic acid** (β-naphthylamine-[γ-]disulphonic acid; amino-G-acid) is formed as chief product when β-naphthylamine sulphate is heated with 20–30 p.c. anhydro-acid at 110°–140°, *or* when crude β-naphthylamine-8-sulphonic acid is heated

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[1] For reduction product, *v.* p. 592, footnote 1.

with 10 p.c. anhydro-acid at 100° (Gans & Co., D. R.-P. 35019; Eng. Pat. 816 of 1884); also as chief product when β-naphthylamine-8-sulphonic acid is sulphonated with 20 p.c. anhydro-acid below 20° (Armstrong and Wynne, Chem. Soc. Proc. 1890, 6, 128), *or* as minor product (20 p.c.) when the 6-acid is sulphonated with 20 p.c. anhydro-acid below 20° (Armstrong and Wynne, *ibid.* 130).

Preparation.—The pure acid is obtained by heating sodium β-naphthol-6 : 8-disulphonate either with ammonia solution under pressure (*cf.* Landshoff, D. R.-P. 27378 of 1883); or with ammonium bisulphite solution and ammonia at 100°–150°, the product afterwards being acidified (Badische, D. R.-P. 117471 of 1899; Eng. Pat. 1387 of 1900; Bucherer, J. pr. Chem. 1904, [2] 70, 358).

Identification.—The acid and salts are easily soluble. It is convertible into *β-chloronaphthalene*-6 : 8-*disulphonyl chloride*, m.p. 170°, and into 1 : 3 : 7-*trichloronaphthalene* (Armstrong and Wynne, *ibid.* 13). It does not couple with diazotised bases (Schultz, Ber. 1888, 21, 3487).

Reactions.—(1) From its easily soluble, yellow *diazo-* compound, *naphthalene*-1 : 3-*disulphonic acid* (Armstrong and Wynne, *l.c.*); *β-naphthol*-6 : 8-*disulphonic acid* (Gans & Co., *l.c.*); and *azo-* dyes (*cf.* Bayer, D. R.-P. 160172 of 1903; Badische, D. R.-P. 176640 of 1905; Eng. Pat. 7287 of 1906) have been obtained.

(2) When fused with caustic soda at 200°–230° it is converted into 2-*amino*-8-*naphthol*-6-*sulphonic acid* (Höchst, D. R.-P. 53076; Eng. Pat. 15176 of 1889; Cassella, D. P. Anm. C. 3063; Eng. Pat. 16699 of 1889), but at 270°–280° into *hydroxytoluic acid* (Höchst, D. R.-P. 81281 of 1893).

(3) On sulphonation with 40 p.c. anhydro-acid at 80°–90°, it yields *β-naphthylsulphamino*-6 : 8-*disulphonic acid*, but at 120°–130°, *β-naphthylamine*-3 : 6 : 8-*trisulphonic acid* (Dressel and Kothe, Ber. 1894, 27, 2152).

β-NAPHTHYLAMINETRISULPHONIC ACIDS.

(i.) **β-Naphthylamine-1 : 3 : 7-trisulphonic acid** is formed when β-naphthylamine-3 : 7-disulphonic acid is sulphonated with 40 p.c. anhydro-acid at 80°–90° (Bayer, D. P. Anm. F. 7036 of 1893; Dressel and Kothe, Ber. 1894, 27, 1199); also when β-naphthol-1 : 3 : 7-trisulphonic acid is heated with 25 p.c. ammonia solution under pressure at 190° (Bayer, D. P. Anm. F. 7003; Eng. Pat. 17141 of 1893; Dressel and Kothe, *l.c.*).

Salts.—The *acid barium* salt and *acid sodium* salt Na_2HA+4H_2O in scales, are easily soluble, and in solution show violet-blue fluorescence.

Reactions.—(1) When boiled with dilute mineral acids it yields *β-naphthylamine*-3 : 7-*disulphonic acid* (Dressel and Kothe, *l.c.*).

(2) On sulphonation with 40 p.c. anhydro-acid at 130° it is converted into a mixture of the 3 : 5 : 7- and 3 : 6 : 7-*trisulphonic acids* with the 1 : 3 : 6 : 7-*tetrasulphonic acid* (Bayer, D. R.-P. 81762; Eng. Pat. 17141A of 1893; Dressel and Kothe, *l.c.*).

(ii.) **β-Naphthylamine-1 : 5 : 7-trisulphonic acid** is formed when β-naphthylamine-5-sulphonic, or 1 : 5-disulphonic or 5 : 7-disulphonic acid is sulphonated with 40 p.c. anhydro-acid at 100° (Bayer, D. R.-P. 80878; Eng. Pat. 20580 of 1893).

Salts.—The *barium*, *acid potassium*, and *acid sodium* salts dissolve easily, giving solutions which show blue fluorescence.

Reactions.—(1) From its easily soluble *diazo-* compound, with excess of sodium carbonate, 2-*diazo-α-naphthol*-5 : 7-*disulphonic acid* has been obtained (Höchst, D. P. Anm. F. 16863; Eng. Pat. 23993 of 1902). It does not couple with diazotised bases.

(2) When boiled with dilute mineral acids it is partially hydrolysed, forming *β-naphthylamine*-5 : 7-*disulphonic acid* (Bayer, *l.c.*)

(3) By digestion with 65 p.c. caustic soda solution under pressure at 160°–220° it is converted into 2-*amino*-5-*naphthol*-1 : 7-*disulphonic acid* (Bayer, D. R.-P. 80878; Eng. Pat. 20580 of 1893).

(4) When heated with 30 p.c. anhydro-acid at 140°–160° it undergoes change into the isomeric *β-naphthylamine*-3 : 5 : 7-*trisulphonic acid* (Bayer, D. R.-P. 90849 of 1895).

(iii.) **β-Naphthylamine-3 : 5 : 7-trisulphonic acid** is formed, together with the 3 : 6 : 7-trisulphonic, and the 1 : 3 : 6 : 7-tetrasulphonic acids, when β-naphthylamine-3 : 7-disulphonic acid is heated with 40 p.c. anhydro-acid at 130°. By boiling the product with water, the tetrasulphonic acid is hydrolysed to 3 : 6 : 7-trisulphonic acid, which is then converted into sodium salt, and, after acidification, separated as the sparingly soluble acid sodium salt. From the concentrated mother liquor the easily soluble acid sodium salt of the 3 : 5 : 7-isomeride can be separated (Bayer, D. R.-P. 81762; Eng. Pat. 17141A of 1893; Dressel and Kothe, Ber. 1894, 27, 1201). It is the sole product of the change which occurs when β-naphthylamine-1 : 5 : 7-trisulphonic acid is heated with 30 p.c. anhydro-acid at 140°–160° (Bayer, D. R.-P. 90849 of 1895).

Salts. — The *sodium* salt $Na_3A+5\frac{1}{2}H_2O$ from dilute alcohol, the *acid sodium* salt Na_2HA, and the *acid barium* salt are very soluble, and in solution show intense green fluorescence.

Reactions.—From the very soluble *diazo-* compound, *naphthalene*-1 : 3 : 7-*trisulphonic acid*, *β-naphthol*-3 : 5 : 7-*trisulphonic acid*, and, with R-salt, an easily soluble red *azo-* dye, have been obtained (Bayer, D. R.-P. 81762; Eng. Pat. 17141A of 1893; Dressel and Kothe, *l.c.*).

(iv.) **β-Naphthylamine-3 : 6 : 7-trisulphonic acid** is formed when β-naphthylamine-3 : 7-disulphonic acid is sulphonated with 40 p.c. anhydro-acid at 130°, being separated by means of its sparingly soluble acid sodium salt from the 3 : 5 : 7-trisulphonic acid, also produced; *or* when β-naphthylamine-1 : 3 : 6 : 7-tetrasulphonic acid is boiled with dilute mineral acids (Bayer, D. R.-P. 81762; Eng. Pat. 17141A of 1893); *or* when β-naphthol-3 : 6 : 7-trisulphonic acid is heated with 25 p.c. ammonia solution under pressure at 190° (Bayer, D. P. Anm. F. 7019; Eng. Pat. 17141 of 1893; Dressel and Kothe, Ber. 1894, 27, 1209).

Salts.—The *sodium* salt is easily, the *barium* salt and *acid sodium* salt Na_2HA+3H_2O in long silky needles are sparingly soluble in cold water, the solutions showing intense blue fluorescence.

Reactions.—(1) From the sparingly soluble, yellow, crystalline *diazo-* compound, *naphthalene*-2 : 3 : 6-*trisulphonic acid*, β-*naphthol*-3 : 6 : 7-*trisulphonic acid*, and, with R-salt, a sparingly soluble red *azo-* dye, have been obtained (Dressel and Kothe, *l.c.*).

(2) When heated with 65 p.c. caustic soda solution under pressure at 180°–240°, it is converted into 2-*amino*-7-*naphthol*-3 : 6-*disulphonic acid* (Bayer, D. P. Anm. F. 7019; D. R.-P. 80878; Eng. Pats. 17141, 20580 of 1893.

(3) On sulphonation with 40 p.c. anhydro-acid at 100°–130°, it yields β-*naphthylamine*-1 : 3 : 6 : 7-*tetrasulphonic acid* (Dressel and Kothe, *l.c.*).

(v.) **β-Naphthylamine - 3 : 6 : 8 - trisulphonic acid** is obtained when β-naphthol-3 : 6 : 8-trisulphonic acid is heated with ammonia at 200°–250° (Landshoff, D. R.-P. 27378 of 1883); *or* when β-naphthylamine-6 : 8-disulphonic acid is heated with 40 p.c. anhydro-acid at 120°–130° (Dressel and Kothe, Ber. 1894, 27, 2153); *or* when sodium α-nitronaphthalene-3 : 6 : 8-trisulphonate is heated with ammonia solution under pressure at 150°–170°, nitrogen being eliminated (Kalle, D. R.-P. 176621 of 1905).

Salts.—The *acid potassium* $K_2HA+1\frac{1}{2}H_2O$ salt forms needles, soluble in 40 parts of water at 20°; the *acid sodium* salt, easily soluble needles; the solutions show intense sky-blue fluorescence.

Reactions.—(1) From its yellow *diazo-* compound *azo-* dyes (*cf.* Kalle, D. R.-P. 162180 of 1904) and *naphthalene*-1 : 3 : 6-*trisulphonic acid* (Dressel and Kothe, *l.c.*) have been obtained.

(2) When boiled with zinc dust and dilute caustic soda solution, it yields α-*naphthylamine*-3 : 6-*disulphonic acid* (Kalle, D. R.-P. 233934 of 1909).

(3) By fusion with caustic soda at 230°, it is converted into 2-*amino*-8-*naphthol*-3 : 6-*disulphonic acid* (Höchst, D. R.-P. 53023; Eng. Pat. 15175 of 1889).

(vi.) **β-Naphthylamine - 4 : 6 : 8 - trisulphonic acid** is obtained when sodium β-naphthylamine-4 : 8-disulphonate is heated with 40 p.c. anhydro-acid at 80°–90°, and finally at 120° (Bayer, D. P. Anm. F. 8154; D. R.-P. 89242 of 1895).

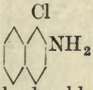
Reaction.—When heated with 60 p.c. caustic soda solution under pressure at 170°–180°, it is converted into 2-*amino*-4-*naphthol*-6 : 8-*disulphonic acid* (Bayer, *l.c.*).

β-NAPHTHYLAMINETETRASULPHONIC ACID.

β-Naphthylamine-1 : 3 : 6 : 7-tetrasulphonic acid occurs in the product formed when β-naphthylamine-3 : 7-disulphonic acid is heated with 40 p.c. anhydro-acid at 130°. It is obtained when β-naphthylamine-3 : 6 : 7-trisulphonic acid is heated with 40 p.c. anhydro-acid at 100°–130° (Dressel and Kothe, Ber. 1894, 27, 1203), *or* when sodium β-naphthol-1 : 3 : 6 : 7-tetrasulphonate is heated with 25 p.c. ammonia solution under pressure (Bayer, D. P. Anm. F. 7003; Eng. Pat. 17141 of 1893).

Salts.—The *barium* salt Ba_2A+6H_2O, in sparingly soluble, microscopic crystals, and the easily soluble *sodium* salt show, in dilute solution, violet-blue fluorescence. Acid salts have not been obtained, and acid solutions when boiled undergo partial hydrolysis giving rise to β-*naphthylamine*-3 : 6 : 7-*trisulphonic acid* (Dressel and Kothe, *l.c.*).

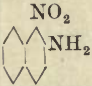
CHLORO-β-NAPHTHYLAMINE.



1 - Chloro - β - naphthylamine, obtained by chlorinating acet-β-naphthalide in acetic acid solution, and hydrolysing the product with hot hydrochloric acid, forms needles, m.p. 59°, and is convertible into 1 : 2-*dichloronaphthalene*. The *hydrochloride* $B\cdot HCl+H_2O$ forms needles; the *acetyl* derivative, needles, m.p. 147° (Cleve, Ber. 1887, 20, 1989).

1-Chloro-β-naphthylaminesulphonic acids.—When sulphonated with 2 p.c. anhydro-acid at 70°, 100°, and 160°, it yields as chief products successively the 1-*chloro*-β-*naphthylamine*-5-, 6-, and 7-*sulphonic acids* (Armstrong and Wynne, Chem. Soc. Proc. 1889, 5, 36, 48). These acids when diazotised and heated in solution with excess (2 mols.) of sodium carbonate at 50°–60°, exchange chlorine for hydroxyl, being converted into the corresponding 2-*diazo*-α-*naphtholsulphonic acids* (Badische, D. R.-P. 145906, 148882; Eng. Pat. 6615 of 1902).

NITRO-β-NAPHTHYLAMINES.



(i.) **1 - Nitro - β - naphthylamine** is obtained when acet-β-naphthalide is nitrated in acetic acid solution, and the resulting nitroacet-β-naphthalide deacetylated by heating it with alcoholic caustic potash. It forms orange-yellow needles, m.p. 126°–127°, and dissolves moderately in hot water, readily in alcohol (Jacobson, Ber. 1881, 14, 1792; Liebermann and Jacobson, Annalen, 1882, 211, 64). The *acetyl* derivative, m.p. 123·5°, is converted into 2-*amino*-1-*naphthol* when boiled with aqueous caustic soda (Jacobson, *ibid.* 806).

(ii.) **5-Nitro-β-naphthylamine** is formed as chief product, together with the 8-isomeride, when β-naphthylamine nitrate is stirred into ten times its weight of sulphuric acid below 5°, and 20 p.c. anhydro-acid is added gradually. Poured into water, the nitration product yields the less soluble 5-nitro- derivative as sulphate, the more soluble sulphate of the 8-isomeride being present in the mother liquor (Hirsch, D. R.-P. 57491; Eng. Pat. 9768 of 1890; Friedlaender and Szymanski, Ber. 1892, 25, 2076). It forms red needles, m.p. 143·5°; its *acetyl* derivative yellow needles, m.p. 185·5°.

Reactions.—From its *diazo-* compound 5-*nitro*-β-*naphthol*, yellow needles, m.p. 147°, has been obtained; by reduction it yields 1 : 6-*diaminonaphthalene*, needles, m.p. 77·5° (Friedlaender and Szymanski, *l.c.*); and when boiled with sodium sulphite or bisulphite solution it is converted into a 1 : 6-*diaminonaphthalenesulphonic acid* (Read, Holliday & Sons, Eng. Pat. 26020 of 1896).

(iii.) **8-Nitro-β-naphthylamine** (*v.* 5-nitro-β-naphthylamine) forms red needles, m.p. 103·5°, and its *acetyl* derivative, yellow needles, m.p. 195·5°. From its *diazo-* compound 8-*nitro*-β-*naphthol*, yellow needles, m.p. 142°, can be obtained, and it gives 1 : 7-*diaminonaphthalene*, scales, m.p. 117·5°, on reduction (Friedlaender and Szymanski, Ber. 1892, 25, 2081).

(iv.) **6-Nitro - β - naphthylamine - 8 - sulphonic**

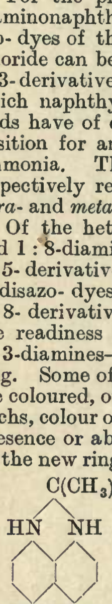
acid, obtained by nitrating β-naphthylamine-8-sulphonic acid dissolved in sulphuric acid (Immerheiser, D. R.-P. 57023 of 1890), gives a *barium* salt $BaA_2+4\frac{1}{2}H_2O$, and *ammonium* salt NH_4A, in red crystals (Jacchia, Annalen, 1902, 323, 119), and yields 2 : 6-*diaminonaphthalene* on reduction with sodium amalgam (Friedlander and Lucht, Ber. 1893, 26, 3033).

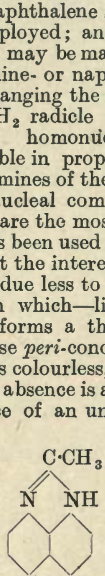
V. DIAMINO- DERIVATIVES.

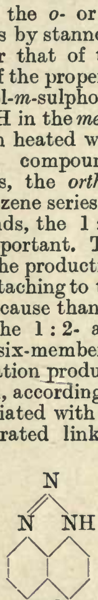
Introductory.—The existence of ten diaminonaphthalenes is to be expected on theoretical grounds, and all ten are known, having been made by methods which involve either replacement of OH by NH_2 in aminonaphthols or dihydroxynaphthalenes, or reduction of dinitronaphthalenes or nitronaphthylamines.

For the preparation of the 1 : 2- or 1 : 4-diaminonaphthalene, reduction of the *o*- or *p*-azo- dyes of the naphthalene series by stannous chloride can be employed; and for that of the 1 : 3-derivative use may be made of the property which naphthylamine- or naphthol-*m*-sulphonic acids have of exchanging the SO_3H in the *meta*-position for an NH_2 radicle when heated with ammonia. These homonucleal compounds respectively resemble in properties, the *ortho*-, *para*- and *meta*-diamines of the benzene series.

Of the heteronucleal compounds, the 1 : 5- and 1 : 8-diamines are the most important. The 1 : 5- derivative has been used for the production of disazo- dyes, but the interest attaching to the 1 : 8- derivative is due less to this cause than to the readiness with which—like the 1 : 2- and 2 : 3-diamines—it forms a third six-membered ring. Some of these *peri*-condensation products are coloured, others colourless, and, according to Sachs, colour or its absence is associated with the presence or absence of an unsaturated linking in the new ring:

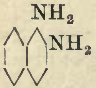

Colourless.


Green.


Red.

The diaminonaphthalenes crystallise well, but, as a rule, are less stable, and therefore less suitable for the production of dye-stuffs, than the respective diaminonaphthalenesulphonic acids. With nitrous acid, the 2 : 3- and 1 : 8- diamines furnish azimides, but the other bases if homonucleal are not diazotised, and if heteronucleal give tetrazo- derivatives.

DIAMINONAPHTHALENES.



(i.) 1 : 2-**Diaminonaphthalene** is obtained by reducing azo- compounds, formed by coupling diazotised bases with β-naphthylamine (Griess, Ber. 1882, 15, 2193; Lawson, *ibid.* 1885, 18, 800, 2423; Sachs, *ibid.* 3128; Witt, *ibid.* 1886, 19, 2795; 1888, 21, 3482); *or* [β-]naphthaquinonedioxime (Koreff, *ibid.* 1886, 19, 179); *or* 2-nitro-α-naphthylamine (Lellmann and Remy, *ibid.* 803); *or* 1-nitro-β-naphthylamine (Lawson, *l.c.*; Lellmann and Remy, *l.c.*) with stannous chloride in hydrochloric acid solution. It can also be obtained from 1 : 2-diaminonaphthalene-4-sulphonic acid (Friedlaender and Kielbasinski, Ber. 1896, 29, 1978) or 3- or 5-sulphonic acid (Gattermann and Schulze, *ibid.* 1897, 30, 53, 55) by interaction with sodium amalgam.

Preparation.—On the laboratory scale, 10 grams of benzeneazo-β-naphthylamine, dissolved in 300 grams of boiling acetic acid (1 : 5), are reduced by adding zinc-dust in small quantities until the colour of the solution changes to bright yellow. The sulphate, obtained by filtering the boiling solution into dilute sulphuric acid, is then boiled with sodium carbonate solution until dissolved (Bamberger and Schieffelin, Ber. 1889, 22, 1376).

Identification.—It separates from hot water in silvery rhombic scales, m.p. 95°–96°, and is oxidised rapidly, becoming brown on exposure to the air.[1] The *hydrochloride*, $B\cdot 2HCl$ forms short prisms easily soluble in water, and with ferric chloride gives an olive-green colouration, changing to brown and yellow; the *sulphate* $B_2\cdot H_2SO_4$, scales; the *diacetyl* compound, needles, m.p. 234° (Lawson, *l.c.*). With benzil, [β-]naphthaquinone, phenanthraquinone (Lawson, *l.c.*; Witt, *l.c.*), or glyoxal (Hinsberg, Ber. 1890, 23, 1394) it yields *quinoxalines.*

The 1-*acetyl* derivative has been obtained, not by acetylation but mixed with the 1 : 4-compound, by nitration and reduction of acet-α-naphthalide (Dahl, D. P. Anm. D. 6503 of 1894).

Aryl derivatives.—The 2-phenyl derivative, broad needles or scales, m.p. 138°–140°, forming sparingly soluble salts (Witt, Ber. 1887, 20, 573, 1184; Zincke and Lawson, *ibid.* 1170); and the 2-*p*-tolyl derivative, needles, m.p. 146°–147° (Fischer, *ibid.* 1892, 25, 2846), have been obtained by reduction of azo- derivatives of phenyl- and *p*-tolyl-β-naphthylamine.

(ii.) 1 : 3-**Diaminonaphthalene** is formed when 1 : 3-dinitronaphthalene is reduced with tin and hydrochloric acid (Urban, Ber. 1887, 20, 973). It is also produced when sodium α-naphthylamine- or α-naphthol-3-sulphonate is heated with ammonium chloride and 22 p.c. ammonia under pressure at 160°–180° (Kalle, D. R.-P. 89061 of 1894; Eng. Pat. 9103 of 1895); *or* when 1-amino-3-naphthol (Friedlaender, Ber. 1895, 28, 1953), or 1 : 3-dihydroxynaphthalene (Friedlaender and Rüdt, *ibid.* 1896, 29, 1612), is heated with concentrated aqueous ammonia under pressure at 150°; *or* when 1 : 3-diaminonaphthalene-2-carboxylic acid is heated at 100° (Atkinson and Thorpe, Chem. Soc. Trans. 1906, 89, 1922).

Identification.—It crystallises from water in scales, m.p. 96°; its *hydrochloride* $B\cdot 2HCl$ and *sulphate* in easily soluble needles, which in solution give a dark brown colouration with ferric chloride; the *diacetyl* compound in sparingly soluble needles, m.p. 263°. With diazotised bases it gives chrysoïdines (Friedlaender, *l.c.*), and with nitrous acid a deep yellow colouration (Urban, Ber. 1887, 20, 974).

Aryl derivatives.—Diphenyl-1:3-diaminonaphthalene is obtained when α-naphthylamine-3-sulphonic acid (Bayer, D. R.-P. 75296; Eng Pat. 8898 of 1893), phenyl-α-naphthylamine-3-sulphonic acid (Bayer, D. R.-P. 78854; Eng. Pat. 19623 of 1893), or α-naphthol-3-sulphonic

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[1] Coupled with an oxidising agent, it has been used as a hair dye (Aktienges., D. R.-P. 154652 of 1903).

acid (Bayer, D. R.-P. 77866; Eng. Pat. 16780 of 1893) is heated with aniline and aniline hydrochloride at 150°–170°. It is insoluble in, and its *hydrochloride* is decomposed by water. The corresponding ditolyl, dixylyl and phenyl tolyl derivatives have been prepared (*l.c.*). By condensation of these aryl derivatives with nitrosodimethylaniline hydrochloride, basic blue dyes of the *azine* class are formed (Bayer, D. R.-P. 78497; Eng. Pat. 8898 of 1893).

(iii.) 1 : 4-**Diaminonaphthalene** is formed by reducing azo- derivatives of *α*-naphthylamine (Perkin, Chem. Soc. Journ. 1865, 18, 173; Griess, Ber. 1882, 15, 2192; Friedlaender, *ibid.* 1889, 22, 590) with stannous chloride dissolved in hydrochloric acid, or with sodium hyposulphite (Grandmougin, *ibid.* 1906, 39, 3561); *or* by reducing 4-nitro-*α*-naphthylamine with tin and hydrochloric acid (Liebermann and Dittler, Annalen, 1876, 183, 238). It is also formed by hydrolysing 1 : 4-diaminonaphthalene-6-sulphonic acid (Cassella, D. R.-P. 74177; Eng. Pat. 15444 of 1893).

Preparation.—On the laboratory scale, benzeneazo-*α*-naphthylamine is boiled with zinc dust and water, the colourless solution filtered into dilute sulphuric acid, and the crystalline sulphate warmed with aqueous sodium carbonate for about 5 minutes (Bamberger and Schieffelin, Ber. 1889, 22, 1381).

Identification.—It crystallises from water in needles or small prisms, m.p. 120°, which when moist rapidly become coloured green, and decompose. The *hydrochloride* $B\cdot 2HCl$ forms readily soluble scales, and in neutral solution with ferric chloride gives a green colouration, changing to a brown precipitate of impure [*α*-]naphthaquinone (Griess, *l.c.*); the *sulphate* $B\cdot H_2SO_4$, sparingly soluble needles; the *diacetyl* derivative, needles, m.p. 305° (Kleemann, Ber. 1886, 19, 334; Bamberger and Schieffelin, *l.c.*).

Reactions.—(1) By nitrous acid (Dahl, *l.c.*; Grandmougin and Michel, Ber. 1892, 25, 977), or by dilute chromic acid solution, or ferric chloride, it is oxidised to [*α*-] *naphthaquinone*.

(2) When its hydrochloride is heated with *α*-naphthylamine and *α*-aminoazonaphthalene at 130°–140°, *Magdala red* is obtained (Witt, D. R.-P. 40868 of 1886, *v.* Azines).

(3) On reduction in boiling amyl alcohol solution with sodium it yields, as sole product, ar.-*tetrahydro*-1 : 4-*diaminonaphthalene* (Bamberger and Schieffelin, *l.c.*).

Monoacetyl-1:4-diaminonaphthalene, with its *hydrochloride* (Liebermann and Dittler, *l.c.*) and *sulphate* (Dahl, D. P. Anm. D. 6503 of 1894), has been prepared, and, as the one amino- group can be diazotised and coupled before the other is deacetylated, it is of importance in the production of *disazo-* dyes (*cf.* Höchst, D. R.-P. 67426, 79952; Eng. Pat. 18783 of 1891; Bayer, D. R.-P. 117972 of 1897; Eng. Pat. 18572 of 1898; Leonhardt, D. R.-P. 121667; Eng. Pat. 23615 of 1898), owing to the fact that the diamine itself cannot easily be diazotised (*cf.* Dahl, D. R.-P. 65273 of 1891; Eng. Pat. 4109 of 1892).

Alkyl and Aryl derivatives.—*unsymm.*-Dimethyl-1 : 4-diaminonaphthalene, an oil (Friedlaender and Welmans, Ber. 1888, 21, 3124); and the ethyl-, m.p. 152° (Kock, Annalen, 1888, 243, 312; Bamberger and Goldschmidt, Ber. 1891, 24, 2471); phenyl-, m.p. 148° (Wacker, Annalen, 1888, 243, 302; Fischer, *ibid.* 1895, 286, 183); and *α*-naphthyl-diamino- derivatives (Wacker, *l.c.*) have been described.

(iv.) 1 : 5-**Diaminonaphthalene** ([*α*-]diaminonaphthalene; semi-naphthalidam) is obtained from 1 : 5-dinitronaphthalene by reduction with ammonium sulphide (Zinin, Annalen, 1844, 52, 361; 1853, 85, 329), with tin and hydrochloric acid (Hollemann, Zeitsch. Chem. 1865, [2] 1, 556; Ladenburg, Ber. 1878, 11, 1651; Erdmann, Annalen, 1888, 247, 360), with stannous chloride and alcoholic hydrochloric acid (Meyer and Müller, Ber. 1897, 30, 773), or with phosphorus iodide and water (Aguiar, *ibid.* 1870, 3, 32; 1874, 7, 306). It is also formed when 1 : 4-dihydroxynaphthalene is heated either with ammonia under pressure at 250°–300° (Ewer and Pick, D. R.-P. 45549 of 1887), or with ammonium bisulphite solution and ammonia at 125° (Badische, D. R.-P. 117471 of 1899; Eng. Pat. 1387 of 1900); *or* when 1 : 5-diaminonaphthalene-2-sulphonic acid is heated with dilute mineral acid (Friedlaender and Kielbasinski, Ber. 1896, 29, 1983); *or* when *α*-naphthylamine is heated with naphthalene and sodamide at 230° (Sachs, Ber. 1906, 39, 3021).

Identification.—It crystallises in needles, m.p. 189·5°, sublimes without decomposition, and with ferric chloride gives an intense bluish-violet colouration. The *hydrochloride* $B\cdot 2HCl$ and the *sulphate* $B\cdot H_2SO_4$ form moderately soluble needles; the *tetrazo-* compound is convertible into 1 : 5-*dichloronaphthalene* (Erdmann, *l.c.*).

Reactions.—(1) When reduced in boiling amyl alcohol solution with sodium, it is converted into *tetrahydro*-1 : 5-*diaminonaphthalene*, which is both an *ac-* and an *ar-* base (Bamberger, Abrahall and Bammann, Ber. 1889, 22, 943, 951).

(2) When boiled with 27 p.c. sodium bisulphite solution it yields as chief product 1-*amino*-5-*naphthyl sulphite*, or, if subsequently heated with alkali, 1-*amino*-5-*naphthol* (Bucherer, J. pr. Chem. 1904, [2] 69, 57, 84).

(3) *Disazo-* dyes have been obtained from its tetrazo- compound (Badische, D. R.-P. 39954; Eng. Pat. 14625 of 1886; D. R.-P. 130475; Eng. Pat. 9287 of 1900), and *azo-* or *disazo-* dyes by coupling it with diazotised primuline (Badische, D. R.-P. 93304 of 1896; Eng. Pat. 2874 of 1897), oxamine dyes (Badische, D. R.-P. 140955 of 1902), or other bases (*cf.* Cassella, D. R.-P. 71329 of 1891; Badische, D. R.-P. 75743; Eng. Pat. 18317 of 1893).

(v.) 1 : 6-**Diaminonaphthalene**, prepared by heating 1 : 6-dihydroxynaphthalene with ammonia under pressure at 150°–300° (Ewer and Pick, D. R.-P. 45788 of 1887), *or* *β*-naphthylamine with sodamide and naphthalene at 230° (Sachs, Ber. 1906, 39, 3022), can be obtained pure by reducing either 5-nitro-*β*-naphthylamine with iron and acetic acid (Friedlaender and Szymanski, Ber. 1892, 25, 2080; *cf.* Hirsch, D. R.-P. 57491 of 1890; Dawson and Hirsch, Eng. Pat. 9768 of 1890), *or* 1 : 6-dinitronaphthalene with tin and hydrochloric acid (Kehrmann and Matis, Ber. 1898, 31, 2149). It is also formed by acting on 1 : 6-diaminonaphthalene-4-sulphonic acid with sodium amalgam (Friedlaender and Lucht, Ber. 1893, 26, 3034).

Identification.—It crystallises from water in short needles, m.p. 77·5°, darkens on exposure to the air, shows blue fluorescence in solution, and gives with ferric chloride a dark brownish-violet colouration. The *hydrochloride*, needles, is easily, but the *sulphate*, $B\cdot H_2SO_4$, needles, only sparingly soluble in water; the *diacetyl* derivative, needles, m.p. 257°, dissolves sparingly in alcohol; the *tetrazo-* compound is convertible into 1 : 6-*dichloronaphthalene* (Friedlaender and Szymanski, *l.c.*).

(vi.) **1 : 7-Diaminonaphthalene** is prepared by reducing 8-nitro-β-naphthylamine in alcoholic solution with tin and hydrochloric acid (Friedlaender and Szymanski, Ber. 1892, 25, 2082), *or* by heating 1 : 7-dihydroxy-β-naphthoic acid with ammonia under pressure at 200°–210° (Friedlaender and Zinberg, Ber. 1896, 29, 40).

Identification.—It crystallises from water in needles, m.p. 117·5°, gives with ferric chloride a violet colouration, and forms a *diacetyl* derivative, rhombohedra, m.p. 213°. The *tetrazo-* compound is convertible into 1 : 7-*dichloronaphthalene* (Friedlaender and Szymanski, *l.c.*).

(vii.) **1 : 8-Diaminonaphthalene** ([β-]diaminonaphthalene) can be obtained by reducing 1 : 8-dinitronaphthalene either with phosphorus iodide and water (Aguiar, Ber. 1874, 7, 306; Meyer and Müller, *ibid.* 1897, 30, 775), or with tin and hydrochloric acid (Ladenburg, *ibid.* 1878, 11, 1651; Erdmann, Annalen, 1888, 247, 363); *or* by reducing 4 : 5-dinitro-α-naphthoic acid (m.p. 265°) with tin and hydrochloric acid (Ekstrand, Ber. 1887, 20, 1353). It is also formed when 1 : 8-dihydroxynaphthalene is heated with ammonia under pressure at 250°–300° (Erdmann, *l.c.*).

Identification.—It crystallises from aqueous alcohol in needles, m.p. 67°, and in aqueous solution gives with ferric chloride a dark chestnut-brown colouration. The *hydrochloride* $B\cdot 2HCl$ forms very soluble scales, m.p. 280° (Ekstrand, *l.c.*); the *sulphate* $B\cdot H_2SO_4$, sparingly soluble needles; the *dibenzoyl* derivative, needles, m.p. 311°–312° (Sachs, Ber. 1906, 39, 3027); and the *oxalate*, either needles, m.p. 271° (Meyer and Müller, *l.c.*); or $BA+2H_2O$, decomp. 270°; B_2A, m.p. 205° (Sachs, Annalen, 1909, 365, 101).

Reactions.—(1) Many condensation products can be obtained from this diamine. For example, with acetic anhydride it forms a green *anhydro-* compound, m.p. 210° (Sachs, Ber. 1906, 39, 3027); with ethyl oxalate, a red crystalline *perimidine-* derivative (Aguiar, *ibid.* 1874, 7, 306; Meyer and Müller, *l.c.*; Sachs, Annalen 1909, 365, 69, 96); with phthalic anhydride a yellow *perimidylbenzoic acid* or red *phthaloperinone*, needles, m.p. 227°–228° (Sachs, *ibid.* 117; Bayer, D. R.-P. 202354 of 1906; Eng. Pat. 7575 of 1908); with nitrous acid a red *azimide* (Aguiar, *l.c.* Erdmann, *l.c.*); with acetone a colourless *dimethyldihydroperimidine* (Badische, D. R.-P. 122475 of 1900; *cf.* Sachs, *l.c.* 151); with phosgene or alkyl carbonates, colourless *perimidones* (Sachs, *l.c.* 135).

(2) When heated with dilute hydrochloric acid under pressure at 180°, it is converted into 1 : 8-*dihydroxynaphthalene* (Aktienges., D. P. Anm. A. 4028 of 1894).

(3) When boiled with sodium bisulphite solution it yields as chief product 1-*amino*-8-*naphthyl sulphite*, convertible by heating with alkali into 1-*amino*-8-*naphthol* (Badische, D. R.-P. 115335 of 1899; Eng. Pat. 1387 of 1900; Bucherer, J. pr. Chem. 1904, [ii.] 69, 58).

(4) *Azo-* dyes are produced by coupling it with diazotised primuline (Badische, D. R.-P. 94074; Eng. Pat. 2874 of 1897), oxamine dyes (Badische, D. R.-P. 140955 of 1902), and other bases (*cf.* Cassella, D. R.-P. 71329 of 1891; Badische, D. P. Anm. B. 31919; Eng. Pat. 20000 of 1902).

(viii.) **2 : 3-Diaminonaphthalene** is obtained by heating 2 : 3-dihydroxynaphthalene either with 30 p.c. ammonia solution under pressure at 250° (Höchst, D. R.-P. 73076 of 1893; Friedlaender and Zakrzewski, Ber. 1894, 27, 764), or with 30 p.c. ammonium sulphite solution and 20 p.c. ammonia at 80°, the product afterwards being acidified (Badische, D. R.-P. 117471 of 1899; Eng. Pat. 1387 of 1900).

Identification.—It crystallises from water in scales, m.p. 191°, and gives no colouration with ferric chloride. The *hydrochloride* is easily, but the *sulphate* only sparingly, soluble. The *diacetyl* derivative forms needles, m.p. 247°, convertible by prolonged boiling with acetic acid into an *anhydride*, m.p. 168°.

Reactions.—(1) With nitrous acid it yields an *azimide*, yellow needles, m.p. 187°, and with diazotised bases (1 mol.) it couples giving red *azo-* dyes (Friedlaender and Zakrzewski, *l.c.*).

(2) It condenses with α- or *o*-diketones, forming *quinoxalines*, behaving, therefore, as an *o*-diamine (Friedlaender and Zakrzewski, *l.c.*).

(ix.) **2 : 6-Diaminonaphthalene** is obtained when 2 : 6-dihydroxynaphthalene is heated with ammonia under pressure at 150°–300° (Ewer & Pick, D. R.-P. 45788 of 1887), or with ammonia and ammonium chloride at 200°–250° (Lange, Chem. Zeit. 1888, 12, 856); or with ammonia-calcium chloride at 270° (Jacchia, Annalen, 1902, 323, 132). It is also formed by the interaction of 2 : 6-diaminonaphthalene-8-sulphonic acid with sodium amalgam (Friedlaender and Lucht, Ber. 1893, 26, 3033).

Identification.—It crystallises in scales, m.p. 216°, darkens on exposure to the air, and with ferric chloride gives a green colouration, which changes to blue when the solution is warmed. The *sulphate* is sparingly soluble; the *diacetyl* derivative forms needles.

Aryl derivative.—The diphenyl derivative, m.p. 210°, obtained by heating 2 : 6-dihydroxynaphthalene with aniline and aniline hydrochloride at 170°, yields green *azine-* dyes by interaction with nitrosodimethylaniline hydrochloride (Leonhardt, D. R.-P. 54087 of 1889; Eng. Pat. 3098 of 1890), or with quinonedichlorodiimide (Leonhardt, D. R.-P. 56990. 58576 of 1890).

(x.) **2 : 7-Diaminonaphthalene** is obtained when 2 : 7-dihydroxynaphthalene is heated with ammonia under pressure at 150°–300° (Ewer & Pick, D. R.-P. 45788 of 1887), or with ammonia and ammonium chloride at 200°–250° (Lange, Chem. Zeit. 1888, 12, 856), or with ammonia-calcium chloride at 260°–270° (Bamberger and Schieffelin, Ber. 1889, 22, 1384); *or* boiled with ammonium sulphite solution and ammonia (Franzen and Deibel, J. pr. Chem. 1908, [ii.] 78, 155). It is also formed when 2-amino-7-naphthol is heated with 40 p.c. ammonium sulphite solution and 20 p.c.

ammonia under pressure at 130°–140°, the product afterwards being acidified (Bucherer, J. pr. Chem. 1904, [ii.] 69, 89).

Identification.—It crystallises from water in scales, m.p. 161°, and gives no colouration with ferric chloride. Its salts and *tetrazo-* compound are easily soluble.

Aryl derivatives.—Diphenyl-2 : 7-diaminonaphthalene, formed when 2 : 7-dihydroxynaphthalene is heated with aniline and aniline hydrochloride at 140°–180° (Durand & Huguenin, D. R.-P. 40886 of 1886; Annaheim, Eng. Pat. 14283 of 1886; Ber. 1887, 20, 1372), forms scales m.p. 163°-164°; its *diacetyl* derivative, small crystals, m.p. 197·5° (Clausius, *ibid.* 1890, 23, 528); and its *tetramethyl*-p-*diamino-* compound, obtained by interaction of *p*-aminodimethylaniline and 2 : 7-dihydroxynaphthalene at 200°–220°, ill-defined crystals, m.p. 180° (Aktienges., D. R.-P. 75044 of 1893). From the diphenyl-derivative blue or violet *azine-* dyes are obtained by interaction with nitrosodimethylaniline or with quinonedichlorodiimide (Durand, Huguenin & Co., *l.c.*; D. R.-P. 58371 of 1891).

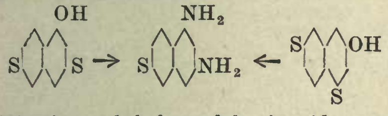
The *o*-tolyl, m.p. 106°; *p*-tolyl, m.p. 236°–237°; and *m*-xylyl, m.p. 130°, derivatives have been prepared (Durand & Huguenin, *l.c.*).

DIAMINONAPHTHALENESULPHONIC ACIDS.

The methods by which sulphonic acids of the heteronucleal diaminonaphthalenes can be obtained do not lend themselves to generalisation; those for homonucleal diaminonaphthalenesulphonic acids can be summarised—

(i.) For 1 : 2- or 1 : 4-diaminosulphonic acids: Reduction of azo- dyes formed by coupling diazotised bases with the appropriate *β*- or *α*-naphthylaminesulphonic acids (*cf.* Witt, Ber. 1888, 21, 3485; Reverdin and de la Harpe, *ibid.* 1892, 25, 1403; 1893, 26, 1281).

(ii.) For 1 : 3-diaminosulphonic acids Interaction of *α*- or *β*-naphthylamine-, or naphthol-*m*-sulphonic acids with ammonia at high temperatures (*cf.* Kalle, D. R.-P. 89061 of 1894; Eng. Pat. 9103 of 1895; Bayer, D. R.-P. 78854; Eng. Pat. 19623 of 1893).



Diaminonaphthalenesulphonic acids are used technically for two purposes—the production of azo- dyes and azine dyes.

For azo- dyes.—In addition to furnishing tetrazo- derivatives, diaminonaphthalenesulphonic acids, if derived from the—

1 : 3- diamine (*cf.* Kalle, D. R.-P. 90905, 90906, 92654, 93595; Eng. Pat. 9103 of 1895);

1 : 5- diamine (*cf.* Cassella, D. R.-P. 61174; Eng. Pat. 15346 of 1890);

1 : 8- diamine (*cf.* Cassella, D. R.-P. 77425; Eng. Pat. 24714 of 1893); or the

2 : 7- diamine (*cf.* Aktienges., D. R.-P. 79780, 80070, 82724; Eng. Pat. 3844 of 1894); can be coupled with diazotised bases.

Sulphonic acids derived from the 1 : 4-diamine do not couple. With nitrous acid, they are usually oxidised, but azo- dyes can be made from them by diazotising one amino-group at a time. Except for the 2-sulphonic acid (*cf.* Levinstein, D. R.-P. 102160; Eng. Pat. 17064 of 1896), this is achieved by employing sulphonic acids of 4-aminoacet-*α*-naphthalide in which the one amino- group can be diazotised and coupled before the other is deacetylated (*cf.* Dahl, D. R.-P. 66354 of 1891; Cassella, D. R.-P. 74177, 78831, 79910; Eng. Pat. 15444 of 1893; D. R.-P. 127362; Eng. Pat. 23615 of 1898).

1 : 8 -Diaminonaphthalenesulphonic acids, like the 2 : 3- derivatives, form azimides with nitrous acid. They couple with diazotised bases forming *azo-* dyes, but a marked increase in the purity of shade, and fastness is obtained if the acetone condensation products (dimethyldihydroperimidines) of these acids are used for coupling (Badische, D. R.-P. 121228, 122475; Eng. Pat. 12819 of 1900), or if the azo- dyes, formed by coupling 1 : 8- diaminosulphonic acids with diazotised bases, are converted into azimides (Cassella, D. R.-P. 77425; Eng. Pat. 24714 of 1893; D. R.-P. 139908; Eng. Pat. 26147 of 1901; Bayer, D. R.-P. 222928 of 1909; *cf.* Höchst, D. R.-P. 143387 of 1902; Eng. Pat. 953 of 1903).

For azines.—The sulphonic acids employed in the production of azine dyes have been those derived from the diaryl- 1 : 3- diaminonaphthalenes (Bayer, D. R.-P. 78497, 79189, 80778, 86223, 86224; Eng. Pats. 8898, 11892 of 1893), and from the diaryl-2 : 6- and diaryl- 2 : 7-diaminonaphthalenes (Leonhardt, D. R.-P. 54087 of 1889; Eng. Pat. 3098 of 1890).

The sources and general characters of the diaminonaphthalenesulphonic acids are summarised in the following tables, references to fluorescence, usually green in colour, or non-fluorescence of solutions of the alkali salts being omitted, for want of room :—

Diaminonaphthalenemonosulphonic Acids.

Constitution.	Preparation.	Acids, Salts and Reactions.
N : N : S		
1 : 2 : 3	Reduction of azo-derivatives of *α*-naphthylamine-3-sulphonic acid (Gattermann and Schulze, Ber. 1897, 30, 54).	*Acid* HA, broad needles. Gives intense emerald-green colouration with ferric chloride.
1 : 2 : 4	Reduction of azo-derivatives of naphthionic acid (Witt, Ber. 1886, 19, 1720); *or* of congo-red (Friedlaender and Kielbasinski, Ber. 1896, 29, 1978).	*Acid* sp. soluble needles. Is decomposed by nitrous acid and does not couple. *Acetyl* derivative converted into ethenyl compound by mineral acids or heat (Lange, D. R.-P. 57942 of 1890).
1 : 2 : 5	Reduction of azo-derivatives of *α*-naphthylamine-5-sulphonic acid (Gattermann and Schulze, Ber. 1897, 30 53); *or* of *β*-naphthylamine-5-sulphonic acid (Witt, Ber. 1888, 21, 3486).	*Acid* HA, sparingly soluble leaflets. Is decomposed by nitrous acid and does not couple with diazotised bases.

Constitution.	Preparation.	Acids, Salts and Reactions.
N : N : S		
1 : 2 : 6	Reduction of azo-derivatives of β-naphthylamine-6-sulphonic acid (Witt, Ber. 1888, 21, 3484).	*Acid* sparingly soluble needles; *sodium* salt, scales. Is decomposed by nitrous acid and does not couple with diazotised bases.
1 : 2 : 7	Reduction of azo-derivatives of β-naphthylamine-7-sulphonic acid (Witt, Ber. 1888, 21, 3485).	*Acid* grey powder. Is decomposed by nitrous acid and does not couple with diazotised bases.
1 : 3 : 5	(1) α-Naphthol-3 : 5-disulphonic acid heated with ammonia under pressure at 175° (Kalle, D. R.-P. 94075 of 1895). (2) β-Naphthylamine-4 : 8-disulphonic acid heated with 30 p.c. ammonia under pressure at 215° (Bayer, D. P. Anm. F. 8845 of 1896; but *cf.* Kalle, D. R.-P. 89061 of 1894; Eng. Pat. 9103 of 1895).	*Acid* readily soluble. Gives no colouration with ferric chloride, but faintly yellow solution with nitrous acid. Couples with diazotised bases. For *diaryl* derivatives, *cf.* Bayer, D. R.-P. 77866, 78854; Eng. Pats. 16780, 19623 of 1893.
1 : 3 : 6	α-Naphthylamine- or α-naphthol-3 : 6-disulphonic acid heated with ammonia under pressure at 160°–180° (Kalle, D. R.-P. 89061 of 1894; Eng. Pat. 9103 of 1895; Friedlaender and Taussig, Ber. 1897, 30, 1462).	*Acid* sparingly; *sodium* salt, readily soluble. Forms yellow *diazo*-compound. Couples with diazotised bases (*cf.* Kalle, D. R.-P. 92654. 93595; Eng. Pat. 9103 of 1895. For *diaryl* derivatives, *cf.* Bayer, D. R.-P. 76414, 77866; Eng. Pats. 8898, 16780 of 1893.
1 : 3 : 7	α-Naphthylamine- or α-naphthol-3 : 7-disulphonic acid heated with ammonia under pressure at 160°–180° (Kalle, D. R.-P. 89061 of 1894; Eng. Pat. 9103 of 1895).	*Acid* very sparingly soluble needles. Gives reddish-brown colouration with ferric chloride. For *diaryl* derivatives, *cf.* Bayer, D. R.-P. *l.c.*, 78854; Eng. Pats. *l.c.*, 19623 of 1893.
1 : 3 : 8	α-Naphthylamine- or α-naphthol-3:8-disulphonic acid heated with ammonia under pressure at 160°–180° (Kalle, D. R.-P. 89061 of 1894; Eng. Pat. 9103 of 1895.	*Acid* very sparingly soluble; *alkali* salts show green fluorescence in solution. Gives reddish-brown colouration with ferric chloride. For *diaryl* derivatives, *cf.* Bayer, D. R.-P. *l.c.*; Eng. Pats. *l.c.*
1 : 4 : 2	(1) Reduction of azo-derivatives of α-naphthylamine-2-sulphonic acid (Levinstein, D. P. Anm. C. 5939; Eng. Pat. 2946 of 1896). (2) Action of sodium bisulphite on [α]-naphthaquinonedichlordiimide (Friedlaender and Oesterreich; *cf.* J. Soc. Chem. Ind. 1898, 17, 836).	*Acid* very sparingly soluble. Gives dark green colouration with ferric chloride. Forms *aminodiazonaphthalenesulphonic acid* with nitrous acid (1 mol.), but second amino-group can be diazotised after first has been coupled (Levinstein, D. R.-P. 102160; Eng. Pat. 2946 of 1896).
1 : 4 : 5	Reduction of 4-nitro-α-naphthylamine-5-sulphonic acid (Bayer, D. R.-P. 133951 of 1899; Levinstein, Eng. Pat. 13178 of 1899).	*Acid* greyish needles, rapidly oxidised in alkaline solution.
1 : 4 : 6	(1) Sulphonation of acetyl-1 : 4-diaminonaphthalene with 20 p.c. anhydro-acid at 25°–50° and subsequent deacetylation (Dahl, D. R.-P. 66354 of 1891; Ammelburg, J. pr. Chem. 1893, [ii.] 48, 286). (2) Reduction of azo-derivatives (Cassella, D. R.-P. 116922 of 1898) or of nitro-derivatives (Levinstein, Eng. Pat. 12119 of 1898) of α-naphthylamine-6- *or* 7-sulphonic acid.	*Acid* very sparingly soluble needles; *potassium* salt KA, and *barium* salt BaA_2+7H_2O, easily soluble. Forms [α]-*naphthaquinone* with nitrous acid or ferric chloride. For *monacetyl* derivatives, *cf.* Cassella, D. R.-P. 74177; Eng. Pat. 15444 of 1893; Bayer, D. R.-P 109609 of 1898.
1 : 5 : 2	(1) Nitration and reduction of α-naphthylamine-2-sulphonic acid (Cassella, D. R.-P. 70890 of 1892; Friedlaender and Kielbasinski, Ber. 1896, 29, 1983). (2) Sulphonation of 1 : 5-diaminonaphthalene sulphate with 5 p.c. anhydro-acid at 100° (Bucherer and Uhlmann, J. pr. Chem. 1909, [ii.] 80, 213).	*Acid* sparingly soluble small needles; *sodium* salt readily; *barium* salt, BaA_2, sparingly soluble. Forms an easily soluble yellow *tetrazo*-compound. Couples with 1 or 2 mols. of a diazotised base.
1 : 5 : 3	Nitration and reduction of α-nitronaphthalene-7-sulphonic acid (Cassella, D. R.-P. 85058 of 1894), *or*, mixed with 1 : 8 : 3-acid, of naphthalene-β-sulphonic acid (Cassella, D. R.-P. 67017, Eng. Pat. 6972 of 1891).	*Acid* sparingly, salts readily soluble; *hydrochloride* prisms. Forms a *tetrazo*-compound.
1 : 5 : 4	(1) Nitration, reduction, and deacetylation of acetylnaphthionic acid (Nietzki and Zübelen, Ber. 1889, 22, 451; Bucherer and Uhlmann, J. pr. Chem. 1909, [ii.] 80, 255). (2) 1 : 5-Dihydroxynaphthalene-4-sulphonic acid heated with ammonium sulphite solution and ammonia (Bucherer and Uhlmann, *l.c.*).	*Acid* very sparingly soluble. Forms a *tetrazo*-compound. Couples with diazotised bases.

Constitution.	Preparation.	Acids, Salts and Reactions.
N : N : S		
1 : 6 : 4	1-Amino-6-naphthol-4-sulphonic acid heated with ammonia under pressure at 170°–180° (Dahl, D. R.-P. 65834, 71157 of 1892; Friedlaender and Kielbasinski, Ber. 1896, 29, 1979).	*Acid* very sparingly soluble needles; *sodium* and *barium* salts easily soluble. Forms a *tetrazo*-compound which decomposes at 0° into a *diazonaphtholsulphonic acid.* Couples with diazotised bases.
1 : 8 : 3	Nitration and reduction of α-nitronaphthalene-6-sulphonic acid (Cassella, D. R.-P. 85058 of 1894), *or*, mixed with 1 : 5 : 3-acid, of naphthalene-β-sulphonic acid (*ibid.*, D. R.-P. 67017; E. P. 6972 of 1891).	*Acid* sparingly soluble needles; *alkali* salts readily soluble; *hydrochloride* needles. Forms an *azimide.* Couples with 1 or 2 mols. of diazotised bases.
1 : 8 : 4	(1) Nitration and reduction of α-nitronaphthalene-5-sulphonic acid (Cassella, D. R.-P. 70019 of 1892; E. P. 4613 of 1893). (2) Acid sulphate of 1 : 8-diaminonaphthalene 'baked' above 100° in a vacuum (Bayer, D. R.-P. 216075 of 1908).	*Acid* almost insoluble; *sodium* salt readily sol.; *hydrochloride* and *sulphate* crystallise well. Forms an *azimide* (*cf.* Cassella D. R.-P. 77425; Eng. Pat. 24714 of 1893). Couples with 1 or 2 mols. of diazotised bases.
2 : 3 : 6	2-3-Dihydroxynaphthalene-6-sulphonic acid *or* 2-amino-3-naphthol-6-sulphonic acid, heated with ammonia under pressure at 150°–220° (Aktienges., D. P. Anm. A. 3676 of 1893; Eng. Pat. 8381 of 1894; Friedlaender and Oesterreich; *cf.* J. Soc. Chem. Ind. 1898, 17, 836).	*Acid* sparingly soluble; *sodium* salt leaflets, showing blue fluorescence in solution; *barium* salt, BaA_2. Gives dark yellow colouration with ferric chloride. Forms an *azimide* (Aktienges., *l.c.*). Couples with 2 mols. of diazotised bases (*cf.* Aktienges., D. R.-P. 84461 of 1894).
2 : 6 : 4	Nitration and reduction of β-naphthylamine-8-sulphonic acid (Friedlaender and Lucht, Ber. 1893, 26, 3033).	*Acid* sparingly soluble flat prisms. Gives emerald-green colouration with ferric chloride (Jacchia, Annalen, 1902, 323, 130).

Diaminonaphthalenedisulphonic Acids.

Constitution.	Preparation.	Acids, Salts and Reactions.
N : N : S : S		
1 : 2 : 3 : 6	Reduction of azo-derivatives of β-naphthylamine-3 : 6-disulphonic acid (Witt, Ber. 1888, 21, 3487).	*Acid* sp. sol.; *acid sodium* salt NaHA, needles. Gives emerald-green coln. with ferric chloride. Decomposed by nitrous acid. Does not couple in acid solution (Cassella, D. R.-P. 72584 of 1892).
1 : 2 : 3 : 8	Reduction of azo-derivatives of α-naphthylamine-3 : 8-disulphonic acid (Bernthsen, Ber. 1890, 23, 3094).	*Acid sodium* salt $NaHA+3H_2O$, needles. *Anhydride* (sultam) ($+2H_2O$), sparingly soluble long needles.
1 : 3 : (5) : 7	α-Naphthol-3 : 5 : 7-trisulphonic acid heated with ammonia and ammonium chloride under pressure at 160°–180° (Kalle, D. R.-P. 90906; Eng. Pat. 9103 of 1895).	*Acid* very sparingly soluble needles. Gives yellowish-red colouration with ferric chloride, and brown with nitrous acid. Couples with diazotised bases.
1 : 3 : 6 : 8	α-Naphthol- or α-naphthylamine-3 : 6 : 8-trisulphonic acid heated with ammonia and ammonium chloride at 160°–180° (Kalle, D. R.-P. 90905, E. P. 9103 of 1895).	*Acid* sparingly soluble leaflets. Gives intense green colouration with ferric chloride and brown with nitrous acid. Couples with diazotised bases. For 1-3-*diaryl* derivatives, *v.* 8-monosulphonic acid.
1 : 5 : 3 : 7	Dinitration and reduction of naphthalene-2 : 6-disulphonic acid (Cassella, D. R.-P. 61174, Eng. Pat. 15346 of 1890; *cf.* Oehler, D. P. Anm. O. 1430 of 1890; Bayer, D. R.-P. 126198 of 1900).	*Acid* very sparingly soluble leaflets; *sodium* and *barium* salts sparingly soluble. Forms an insol. *tetrazo*-compound (*cf.* Cassella, D. R.-P. 62075; Eng. Pat. 15346 of 1890). Couples with diazotised bases.
1 : 5 : 4 : (8)	1 : 5-Dinitronaphthalene heated with sodium bisulphite solution in reflux apparatus or under pressure (Fischesser & Co., D. R.-P. 79577; Eng. Pat. 13156 of 1894).	*Acid* readily soluble; *acid barium* salt $Ba(HA)_2+10H_2O$, moderately soluble. Gives a reddish-blue colouration with ferric chloride. Forms a *tetrazo*-compound, and couples.
1 : 6 : 3 : 8	Nitration and reduction of α-nitronaphthalene-3:8-disulphonic acid (Friedlaender and Kielbasinski, Ber. 1896, 29, 1982; *cf.* 2574).	*Acid* sparingly soluble, showing green fluorescence in solution.
1 : 6 : 4 : 8	Dinitration and reduction of naphthalene-1 : 5-disulphonic acid (Kalle, D. R.-P. 72665 of 1893; Friedlaender and Kielbasinski, Ber. 1896, 29, 1980; *cf.* 2574).	*Acid* sp. sol.; *sodium* salt, Na_2A, easily sol. needles Gives cherry-red coln. with ferric chloride. Forms a sparingly soluble *tetrazo*-compound. Couples with diazotised bases.
1 : 8 : (2) : 5	1 : 8-Diaminonaphthalene-4-sulphonic acid sulphonated with 8 p.c. anhydro-acid at 80° (Cassella, D. R.-P 72584 of 1892).	*Acid* and *sodium* salt readily soluble. Forms an *azimide.* Couples readily with 1 mol., less readily with 2 mols., of diazotised bases.
1 : 8 : 3 : 6	Dinitration and reduction of naphthalene-2 : 7-disulphonic acid (Cassella, D. R.-P. 61174; Eng. Pat. 13346 of 1890; Oehler, D. P. Anm. O. 1430 of 1890; *cf.* Alén, Förhandl. 1883, 3, 17).	*Acid potassium* salt $KHA+3H\ O$, needles; *acid barium* salt $Ba(HA)_2+6H_2O$, sp. sol. needles. Gives reddish-brown coln. with ferric chloride. Forms an *azimide* (Cassella, D. R.-P. 69963 of 1891). Couples with diazotised bases.

Constitution.	Preparation.	Acids, Salts and Reactions.
N:N:S:S 2:3:6:8	2-Amino-3-naphthol-6:8-disulphonic acid heated with 30 p.c. ammonia under pressure at 185°–190° (Aktienges., D. R.-P. 86448; Eng. Pat. 8645 of 1895).	*Acid* sparingly soluble needles; *sodium* salt readily soluble.
2:6:?:?	2:6-Dihydroxynaphthalenedisulphonic acid heated with ammonia and ammonium chloride under pressure at 200° (Jacchia, Annalen, 1902, 323, 131).	*Acid*, $H_2A + 4\frac{1}{2}H_2O$, leaflets.
2:7:3:6	2:7-Dihydroxynaphthalene-3:6-disulphonic acid heated with ammonia under pressure at 200°–220° (Aktienges., D. P. Anm. A. 3686 of 1893; Eng. Pat. 3844 of 1894).	*Acid*, sparingly, *sodium* salt, readily soluble. Gives faint brown colouration with ferric chloride. Forms a sparingly soluble *tetrazo*-compound. Couples with diazotised bases.

1:8-Diaminonaphthalene-2:4:(7 or 6)-trisulphonic acid, obtained when 1·8-dinitronaphthalene is heated with sodium bisulphite solution (Fischesser & Co., D. R.-P. 79577, Eng. Pat. 13156 of 1894), gives *acid sodium* salt $Na_2HA + 2H_2O$, readily, but *acid barium* salt $BaHA + 2H_2O$ only sparingly soluble. The colouration with ferric chloride is yellowish-brown. It forms an *azimide*, and couples with 1 mol. of a diazotised base.

TRIAMINONAPHTHALENES.

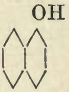
1:2:6-Triaminonaphthalene, obtained by reduction of 1:6-dinitro-β-naphthylamine (*cf.* Kehrmann and Matis, Ber. 1898, 31, 2419), forms a *triacetyl* derivative, needles, m.p. 280°, and gives the reactions of an *o*-diamine (Loewe, Ber. 1890, 23, 2544). 1:3:6-Triaminonaphthalene, obtained by heating 1:6-dihydroxynaphthalene-3-sulphonic acid with ammonia under pressure at 160°–180° (Kalle, D. R.-P. 89061 of 1894; Eng. Pat. 9103 of 1895); and 1:3:7-triaminonaphthalene, prepared similarly from 1:7-dihydroxy-3-sulphonic or 2-amino-6-naphthol-8-sulphonic acid (Kalle, D. R.-P. 90905; Eng. Pat. 9103 of 1895) form sparingly soluble *sulphates* and give brown solutions with nitrous acid.

VI. HYDROXY- DERIVATIVES.

Introductory.—α-Naphthol, β-naphthol, several of the α- and β-naphtholsulphonic acids, and the greater number of the dihydroxynaphthalenes, are obtained on the large scale from the appropriate naphthalenesulphonic acids by fusion with caustic potash or soda. An alternative method, also of wide application, for the production of hydroxy-derivatives is that in which naphthylaminesulphonic acids are used, the exchange of the amino- group for hydroxyl being effected by the diazo- reaction, by the bisulphite method, or by water at a high temperature.

In general, the hydroxynaphthalenes resemble the hydroxybenzenes in chemical behaviour and properties, and the resemblance is complete when, by hydrogenation of the non-substituted ring, *ar.*- derivatives are formed from them (*cf.* Bamberger, Annalen, 1890, 257, 10). Nevertheless, in certain directions, differences—one of them of much technical importance—exist between the two series, as may be illustrated by reference to the two naphthols. These compounds, and β-naphthol more readily than α-naphthol, are converted into naphthylamines when heated with ammonia under pressure (Badische, D. R.-P. 14612; Eng. Pat. 2516 of 1880), into alkyl ethers when heated with alcohol and hydrochloric acid at 150° (Liebermann and Hagen, Ber. 1882, 15, 1427), and into naphthyl ethers when boiled with dilute sulphuric acid (Graebe, *ibid* 1880, 13, 1850), whereas phenol under similar conditions yields, at most, only traces of the corresponding products. Similar differences can be recognised when the dihydroxynaphthalenes are compared with the dihydroxybenzenes.

HYDROXYNAPHTHALENES.



(i.) α-**Naphthol** occurs in very small amount in coal tar fractions of high boiling-point (Schulze, Annalen, 1885, 227, 150). It was first obtained from α-naphthylamine by the diazo- reaction (Griess, Proc. Roy. Soc. 1867, 12, 419), but on the large scale is prepared either by fusing sodium naphthalene-α-sulphonate with caustic soda or potash (*cf.* Schaeffer, Annalen, 1869, 152, 281); or, free even from traces of β-naphthol, by heating α-naphthylamine with water under pressure.

Preparation.—The process adopted in the manufacture of α-naphthol from sodium naphthalene-α-sulphonate is practically identical with that described under β-naphthol (*q.v.*; *cf.* Levinstein, Eng. Pat. 2300 of 1883). Alternatively, α-naphthylamine hydrochloride or sulphate is heated with 5 times its weight of water under pressure at 200° for 1–4 hours, and the product distilled to remove small quantities of impurities of high boiling point (Höchst, D. R.-P. 74879; Eng. Pat. 14301 of 1892); *or* α-naphthylamine is heated with sodium bisulphate, phosphoric acid, or zinc chloride and water at 210° (Höchst, D. R.-P. 76595 of 1892).

Properties.—α-Naphthol crystallises in lustrous monoclinic needles (*cf.* Groth, Annalen, 1869, 152, 284), m.p. 94°, b.p. 278°–280° (Schaeffer, *l.c.*), sp.gr. 1·224 at 4° (Schröder, Ber. 1879, 12, 1613), and dissolves readily in alcohol, organic solvents, or in solutions of caustic alkalis, but only very sparingly in hot water. Its odour is phenolic and it volatilises readily with steam.

Reactions.—(1) It is converted into *α-dinaphthylene oxide* $(C_{10}H_6)_2O$ when boiled for some time in the air, when distilled with litharge, or, mixed with naphthalene and other products, when heated in a tube at 350°–400° (Graebe, Knecht, and Unzeitig, Annalen, 1881, 209, 134; Merz and Weith, Ber. 1881, 14, 195).

(2) With nitrous acid it forms a mixture of 2-*nitroso*- and 4-*nitroso-α-naphthol* (*v. Naphtha-*

quinoneoximes), the former as chief product (Fuchs, Ber. 1875, 8, 626), or, in ethereal solution, 2 : 4-*dinitro-α-naphthol* (Schmidt, *ibid.* 1900, 33, 3245).

(3) By nitration 2 : 4-*dinitro-α-naphthol* (Martius, J. pr. Chem. 1867, 102, 442), but by oxidation with nitric acid *phthalic acid* can be obtained from it. With potassium permanganate it is oxidised in acid solution to *phthalic acid*, and in alkaline solution to *phthalonic acid* (Henriques, Ber. 1888, 21, 1608).

(4) The action of ammonia, acetamide, and aniline on α-naphthol is described in connection with α-naphthylamine (*q.v.*).

(5) On reduction with sodium in amyl alcohol solution it is converted into ar.- *tetrahydro-α-naphthol*, as sole product (Bamberger and Bordt, Ber. 1890, 23, 215).

(6) By interaction of its dry sodium compound[1] with carbon dioxide 2-*hydroxy-α-naphthoic acid* is obtained (Schmitt and Burkard, Ber. 1887, 20, 2699).

Colour reactions.—Bleaching-powder solution added to an aqueous solution of α-naphthol gives first a dark-violet colouration and then a flocculent precipitate of the same colour. Ferric chloride added to an aqueous solution produces a milky opalescence, which changes to a violet flocculent precipitate of *αα′-dinaphthol* (Schaeffer, *l.c.*; Dianin, Ber. 1873, 6, 1252; 1874, 7, 487). Like β-naphthol (*q.v.*), it develops a Prussian-blue colouration with chloroform and caustic potash solution, but, unlike β-naphthol, it gives a deep violet turbid liquid when mixed in aqueous solution with sodium hypoiodite (Jorissen, Ann. Chim. anal. 1901, 7, 217).

Tests.—Commercial α-naphthol should be colourless, have a melting-point very nearly that of the pure compound, and leave only a small residue on extraction with caustic alkali solution.

Estimation.—The *picrate*, m.p. 189°–190°, which is almost insoluble in water (Marchetti, Gazz. chim. ital. 1882, 12, 503), can be employed in the quantitative estimation of α-naphthol. The sample is heated with N/20 picric acid solution in a closed vessel, and the excess of picric acid afterwards determined by titration with N/10 baryta, lacmoid being the indicator (Küster, Ber. 1894, 27, 1104).

α-Naphthyl methyl ether (α-methoxynaphthalene) is formed by heating sodium α-naphtholate with methyl chloride and methyl alcohol under pressure at 100° (Bayer, Eng. Pat. 1168 of 1879); *or* by passing methyl chloride through sodium α-naphtholate at 280° (Vincent, Bull. Soc. chim. 1883, [2] 40, 107); *or* by leading a solution of α-naphthol in methyl alcohol into naphthalene-β-sulphonic acid at 140°–145° (Krafft & Roos, D. R.-P. 76574 of 1893; Eng. Pat. 6190 of 1894); *or* by heating α-naphthylamine with methyl alcohol and zinc chloride at 180°–200° (Hantzsch, Ber. 1880, 13, 1347). It is conveniently prepared by heating α-naphthol (5 pts.) with absolute methyl alcohol (5 pts.) and sulphuric acid (2 pts.) at 140° in a reflux apparatus provided with a small mercury column (Gattermann, Annalen, 1888, 244, 72). It is an oil with an orange-like odour, b.p. 269°, sp.gr. 1·0974 at 15°, and is volatile with steam.

α-Naphthyl ethyl ether, obtained by methods similar to those described for the methyl ether (*cf.* Schaeffer, *l.c.*; Liebermann and Hagen, Ber. 1882, 15, 1427; Gattermann, *l.c.*), can be prepared by heating α-naphthol (72 grms.) with 36 p.c. caustic potash (85 c.c.) and potassium ethyl sulphate (90 grms.) for 6 hours under pressure at 150°, any unchanged α-naphthol being removed by coupling with diazotised sulphanilic acid (Witt and Schneider, Ber. 1901, 34, 3173). It is an oil of peculiar odour, m.p. 5·5°, b.p. 276°, and is volatile with steam.

Reactions.—On sulphonation it yields *ethoxy-α-naphthol-4-sulphonic acid*, from which by nitration 2 : 4-*dinitro-α-naphthol*, 4-*nitro-α-naphthyl ethyl ether*, and 2-*nitroethoxy-α-naphthol*-4-*sulphonic acid* are formed (Witt and Schneider, *l.c.*).

α-Naphthyl carbonate, formed by the interaction of phosgene and sodium α-naphtholate, is a crystalline powder, m.p. 129°–130° (Höchst, D. R.-P. 80888, 80889; Eng. Pat. 14134 of 1894).

α-Naphthyl acetate, prepared by heating α-naphthol with acetic acid at 200° (Graebe, Annalen, 1889, 209, 151), forms broad needles or tables, m.p. 49° (Miller, Annalen, 1881, 208, 248), and is hydrolysed by boiling with water.

α-NAPHTHOLSULPHONIC ACIDS.

Introductory.—The general methods employed in the preparation of α-naphtholsulphonic acids are :—

(1) Sulphonation of α-naphthol;

(2) Exchange of the amino- group in α-naphthylaminesulphonic acids for hydroxyl by the diazo- reaction, or by the bisulphite reaction, or by interaction with water at a high temperature;

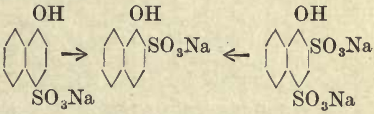
(3) Exchange of chlorine in α-chloronaphthalenesulphonic acids for hydroxyl by fusion with caustic alkali;

(4) Exchange of one sulphonic group in naphthalenepolysulphonic acids for hydroxyl by fusion with caustic alkali.

In addition to these processes, which are of technical importance, others of more limited application or value are known, such as—

(*a*) The partial hydrolysis of α-naphtholpolysulphonic acids by interaction either with dilute acids at a high temperature or with sodium amalgam;

(*b*) The change (*cf.* α-naphthylamine-4-sulphonic acid) which sodium α-naphthol-4-sulphonate and 2 : 4-disulphonate undergo when heated at 170° :—



The α-naphtholsulphonic acids and their salts are more soluble and less well-defined than the related α-naphthylaminesulphonic derivatives; they are less easy, therefore, to recognise in or to isolate from mixtures containing them. The zinc salt, although easily soluble, has been used for the purpose of identifying monosulphonic acids, and it has been found that the qualitative

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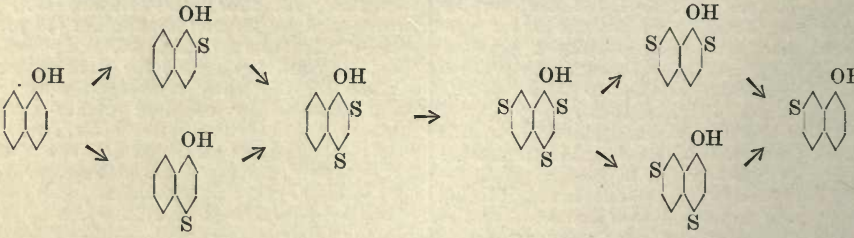
[1] Crystalline sodium α-(or β-)naphtholate can be obtained by dissolving the naphthol (1 pt.) in boiling 7·5 p.c. caustic soda solution to which, afterwards, common salt (1 pt.) is added (König, D. R.-P. 216596 of 1908).

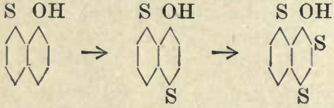
composition of a sulphonation product can be determined largely by means of nitrous acid (giving rise to *o*- or *p*-nitroso- derivatives), nitric acid (producing naphthol yellows), or diazotised bases (leading to the formation of *o*- or *p*-azo-dyes): reagents which interact with some isomerides but not with others.

The course of the sulphonation of α-naphthol, as traced by the application of these analytical methods, is shown in the scheme—



from which it will be seen that three of the acids owe their formation to partial hydrolysis of the trisulphonic acid—effected by relatively dilute sulphuric acid at the highest temperature employed in these sulphonations.

The scheme also shows that acids containing the SO_3H radicle in the 3-, 5-, or 8- position are not formed by the action of sulphuric acid on α-naphthol. Neither are they formed by the sulphonation of α-naphtholsulphonic acids obtained in other ways, for example—



and to obtain them recourse must be had to the second general method with α-naphthylaminesulphonic acids of the desired orientation.

As in the case of the corresponding α-naphthylaminesulphonic acids, it is found that α-naphtholsulphonic acids with a sulphonic group in the 3- position give 1 : 3-diaminonaphthalene derivatives with ammonia; those containing it in the 8- position give *peri*-anhydrides (*sultones*); and those in which it occurs in the 3-, 4-, or 5- position give *ortho*-azo-dyes.

α-Naphtholmonosulphonic Acids.[1]

(i.) **α-Naphthol-2-sulphonic acid** (Schaeffer's acid) has not been obtained pure by the sulphonation of α-naphthol. The earliest process for its preparation, by heating α-naphthol with twice its weight of sulphuric acid on a water-bath until sulphonation is complete (Schaeffer, Annalen, 1869, 152, 293; Darmstaedter and Wichelhaus, Eng. Pat. 89 of 1869), has been shown by Conrad and Fischer (Annalen, 1893, 273, 109), and by Bender (Ber. 1889, 22, 999), to give rise to a product containing much 4-mono- and 2 : 4-di-sulphonic acids.[2] If α-naphthol be heated only for a short time with an equal weight of sulphuric acid at 60°–70°, so that sulphonation is incomplete, the yield is increased from 23 p.c. under Schaeffer's conditions to 50 p.c., and the product can be separated as potassium salt by the addition of potassium chloride to the melt diluted slightly with water (Friedlaender and Taussig, Ber. 1897, 30, 1457).

Preparation.—It can be prepared either from α-naphthol by Friedlaender and Taussig's method (*l.c.*), or from α-naphthylamine-2-sulphonic acid by the diazo- reaction (Cleve, Ber. 1881, 24, 3476); or the sodium salt, in 70–80 p.c. yield, by heating sodium α-naphthol-4-sulphonate or 2 : 4-disulphonate, mixed with twice its weight of naphthalene or paraffin, during 3–4 hours at 160°–170° (Bayer, D. R.-P. 237396; Eng. Pat. 2355 of 1911).

Salts.—The *acid* forms small rhombic prisms and differs from its isomerides in being sparingly soluble in dilute mineral acids. The *lead* salt PbA_2+H_2O in scales; *barium* salt $BaA_2+1\frac{1}{2}H_2O$ in needles; and *calcium* salt CaA_2+H_2O(?) in scales, are sparingly soluble (Cleve, *l.c.*): the *potassium* salt $KA+\frac{1}{2}H_2O$, in prisms, is soluble in 37 parts of water at 18°, but almost insoluble in saturated potassium chloride solution (Conrad and Fischer, *l.c.*).

Reactions.—(1) Nitrous acid reacts with it in the cold forming 4-*nitroso-α-naphthol-2-sulphonic acid*, which does not give a naphthol green with iron salts,[3] but like α-naphthol-2-sulphonic acid yields 2 : 4-*dinitro-α-naphthol* when warmed with dilute nitric acid (*cf.* Bender, *l.c.*; Conrad and Fischer, *l.c.*).

(2) By further sulphonation it is converted successively into α-*naphthol*-2 : 4-*disulphonic* and 2 : 4 : 7-*trisulphonic acids* (*cf.* Bender, *l.c.*).

(ii.) **α-Naphthol-3-sulphonic acid** is obtained when naphthalene-1 : 3-disulphonic acid is fused with caustic alkalis at 200°–300° (Badische, D. R.-P. 57910; Eng. Pat. 9537 of 1890); *or* when diazotised α-naphthylamine-3-sulphonic acid is boiled with 10 p.c. sulphuric acid (Friedlaender, Ber. 1895, 28, 1952) or water (Gattermann and Schulze, *ibid.* 1897, 30, 54); *or* when diazotised 2-amino-8-naphthol-6-sulphonic acid is boiled with alcohol (Badische, *l.c.*; Friedlaender and Taussig, Ber. 1897, 30, 1458); *or* when α-naphthol-3 : 8-disulphonic acid is reduced electrolytically (Bayer, Fr. Pat. 439010 of 1912, *v.* p. 592, footnote 1).

Salts.—The *zinc* salt $ZnA_2+8\frac{1}{2}H_2O$ forms long needles and, like the *barium* salt, is easily soluble (Friedlaender and Taussig, *l.c.*).

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[1] In every case where the constitution of an α-naphtholsulphonic acid is given, the OH radicle is supposed to be in the position '1.'

[2] Mixed products also are formed by the methods employed by Claus and Oehler (Ber, 1882, 15, 312; *cf.* Armstrong and Wynne, Chem. Soc. Proc. 1890, 6, 80), by Claus and Knyrim (Ber. 1885, 18, 2924), and by Baum (D. P. Anm. B. 4197; Eng. Pat. 3498 (prov.) of 1883), in which sulphuric acid, chlorosulphonic acid, or anhydro-acid is employed, the methods themselves being valueless (*cf.* Conrad and Fischer, *l.c.*).

[3] The production of a naphthol green with iron salts serves to distinguish *ortho*- from *para*-nitroso-derivatives.

Reactions.—(1) When coupled with diazotised bases it yields *ortho*-azo- dyes (Gattermann and Schulze, *l.c.*).

(2) When heated with ammonia under pressure at 160°–180° it is converted into 1 : 3-*diaminonaphthalene* (Kalle, D. R.-P. 89061 of 1894; Eng. Pat. 9103 of 1895); and with aniline and its hydrochloride at 150°–170° into *diphenyl*-1 : 3-*diaminonaphthalene* (Bayer, D. R.-P. 77866; Eng. Pat. 16780 of 1893).

(3) Digestion with 60 p.c. caustic soda under pressure at 180° converts it into o-*toluic acid* (Kalle, D. R.-P. 79028 of 1894).

(iii.) α-**Naphthol-4-sulphonic acid** (Nevile and Winther's acid). This acid is found in the sulphonation product obtained from α-naphthol by Schaeffer's method (*v.* 2-acid), and can be separated from the 2-acid either by converting the product into sodium salt, from which it is extracted by boiling 90 p.c. alcohol (Verein, D. R.-P. 26012; Eng. Pat. 2237 of 1883), or by precipitation as zinc salt (Friedlaender and Taussig, Ber. 1897, 30, 1458).

Preparation.—From naphthionic acid: By boiling the diazo- compound with 10 p.c. sulphuric acid (Nevile and Winther, Chem. Soc. Trans. 1880, 37, 632; Dahl, Eng. Pat. 2296 of 1883; Erdmann, Annalen, 1888, 247, 341); *or* by heating the sodium salt with 50 p.c. caustic soda solution under pressure at 240°–260°, and boiling the solution of the product in water to expel ammonia (Aktienges., D. R.-P. 46307 of 1888); *or*, pure and in almost quantitative yield, by digesting the sodium salt with 40 p.c. sodium bisulphite solution at 80°–90°, boiling the product with alkali to expel ammonia, and then acidifying it to remove sulphurous acid (Bayer, D. R.-P. 109102; Eng. Pat. 16807 of 1899).

It can also be obtained by digesting α-chloronaphthalene-4-sulphonic acid with 25 p.c. caustic soda solution under pressure at 200°–220° (Oehler, D. R.-P. 77446 of 1893); *or* by heating α-methoxynaphthalene-4-sulphonic acid with 50 p.c. caustic soda solution under pressure at 240° (Dahl, D. R.-P. 88843 of 1896); *or* by stirring α-naphthyl carbonate into monohydrate at 10°–20°, pouring the solution on to ice, salting out the disulpho-α-naphthyl carbonate, and boiling this product with water at 60°–70° (Höchst, D. R.-P. 80889; Eng. Pat. 14135 of 1894; Reverdin, Ber. 1894, 27, 3460).

Salts.—The *acid* and salts are easily soluble. The *zinc* salt ZnA_2+8H_2O forms prisms; the *sodium* salt, which can be salted out from solution, forms columnar crystals (Friedlaender and Taussig, *l.c.*), is soluble in 90 p.c. alcohol, and gives with ferric chloride a blue or bluish-green colouration (Dahl, *l.c.*; Erdmann, *l.c.*).

Reactions.—(1) The ortho-*azo*- dyes which it yields by coupling with diazotised bases are of much technical importance on account of the purity of their shades (*cf.* Verein, *l.c.*; Bayer, D. R.-P. 35341; Eng. Pat. 9510 of 1885; Gesellsch., D. R.-P. 66838 of 1892).

(2) Nitrous acid reacts with it in the cold forming 2-*nitroso-α-naphthol*-4-*sulphonic acid* (Witt and Kaufmann, Ber. 1891, 24, 3160), which gives a *naphthol green* with iron salts (Gans & Co. D. R.-P. 28065; Eng. Pat. 2269 of 1884; Hoffmann, Ber. 1885, 18, 46), and, like α-naphthol-2 : 4-sulphonic acid, yields 2 : 4-*dinitro-α-naphthol* when warmed with dilute nitric acid (*cf.* Bender, Ber. 1889, 22, 997).

(3) When heated at 160°–170°, the sodium salt is converted into *sodium α-naphthol*-2-*sulphonate* (Bayer, D. R.-P. 237396; Eng. Pat. 2355 of 1911).

(4) By digestion with ammonium sulphite solution and ammonia at 100°–150°, it is converted into *naphthionic acid* (Badische, D. R.-P. 117471 of 1899; Eng. Pat. 1387 of 1900).

(5) On further sulphonation it yields successively *α-naphthol*-2 : 4-*disulphonic acid* (Armstrong, *priv. comm.*), and *α-naphthol*-2 : 4 : 7-*trisulphonic acid* (*cf.* Friedlaender and Taussig, *l.c.* 1463).

(iv.) α-**Naphthol-5-sulphonic acid** (Cleve's acid; L- acid) is obtained by boiling diazotised α-naphthylamine-5-sulphonic acid with 10 p.c. sulphuric acid (Verein, D. R.-P. 26012; Eng. Pat. 2237 of 1883; *cf.* Gaess, D. P. Anm. G. 2393 of 1883; Schöllkopf, Eng. Pat. 15781 of 1885). It is also formed when sodium naphthalene-1 : 5-disulphonate is fused with caustic soda at 160°–190°; the sparingly soluble sodium α-naphthol-5-sulphonate being obtained by acidifying the aqueous solution of the melt with hydrochloric acid (Ewer & Pick, D. R.-P. 41934 of 1887); *or* when α-chloronaphthalene-5-sulphonic acid is heated with 8 p.c. caustic soda solution under pressure at 240°–250° (Oehler, D. R.-P. 77446 of 1893).

Identification.—The *acid* forms a semi- crystalline deliquescent mass (Erdmann, Annalen, 1888, 247, 343); the *zinc* salt $ZnA_2+8\frac{1}{2}H_2O$, easily soluble long needles (Friedlaender and Taussig, Ber. 1897, 30, 1460); the *sodium* salt dissolves readily in warm alcohol, and gives with ferric chloride a violet-red colouration (Gaess, *l.c.*).

Reactions.—(1) Diazotised bases couple with it forming ortho-*azo*- dyes, but these are of little value (*cf.* Gesellsch., D. R.-P. 66838 of 1892).

(2) Nitrous acid reacts with it in the cold forming 2-*nitroso-α-naphthol*-5-*sulphonic acid*, which crystallises well, and gives a *naphthol green* with iron salts (Friedlaender and Taussig, *l.c.*).

(3) Fusion with caustic soda at 220°–260° converts it into 1 : 5-*dihydroxynaphthalene* (Ewer and Pick, *l.c.*; Schultz, Ber. 1887, 20, 3161).

(v.) α-**Naphthol-6-sulphonic acid** is obtained from α-naphthylamine-6-sulphonic acid either by the diazo- reaction (*cf.* Erdmann and Süvern, Annalen, 1893, 275, 304); or by digestion with 40 p.c. sodium bisulphite solution at 120°–150°, the product being boiled to expel ammonia and then acidified to remove sulphurous acid (Bayer, D. R.-P. 109102; Eng. Pat. 16807 of 1899). It is also formed when sodium naphthalene-1 : 6-disulphonate is fused with caustic soda (*cf.* Bucherer, J. pr. Chem. 1904, [ii.] 70, 346).

This acid is technically unimportant, and of its properties little is known.

(vi.) α-**Naphthol-7-sulphonic acid** is probably the chief product when the mixed barium salt from the acids (mainly α-naphthol-2 : 7-, and 4 : 7-disulphonic, and 2 : 4 : 7-trisulphonic acids) obtained by heating α-naphthol with 4 times its weight of sulphuric acid at 130° for an hour, is boiled with hydrochloric or diluted sulphuric acid (Liebmann and Studer, D. P. Anm. L. 4327; Eng. Pat. 7812 of 1887).

In the pure form it can be obtained either from α-naphthylamine-7-sulphonic acid by the bisulphite method (*cf.* Bucherer, J. pr. Chem. 1904, [ii.] 70, 347); *or*, from 2-carboxy-α-naphthol-7-sulphonic acid by heating it with a small quantity of water at 120° (Friedlaender and Taussig, Ber. 1897, 30, 1461).

Identification.—The *acid*, a crystalline mass, gives with ferric chloride a brownish-violet colouration, and like the salts is easily soluble. The *zinc* salt ZnA_2+8H_2O forms radiate groups of needles; the *barium* salt needles (Friedlaender and Taussig, *l.c.*).

Reactions.—(1) Coupled with diazotised bases in acetic acid solution it gives *monoazo-* and in alkaline solution *disazo-* dyes (Bender, *l.c.*; Friedlaender and Taussig, *l.c.*).

(2) Nitrous acid reacts with it forming a *nitroso-α-naphthol*-7-*sulphonic acid*, which is converted into *naphthol yellow S* when warmed with dilute nitric acid (Bender, Ber. 1889, 22, 996).

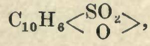
(3) By digestion with sodium bisulphite solution and ammonia at 100°–110°, followed by acidification, it is converted into α-naphthylamine-7-sulphonic acid (Badische, D. R.-P. 117471 of 1899; Eng. Pat. 1387 of 1900).

(vii.) **α-Naphthol-8-sulphonic acid** (S-acid). Unlike its isomerides, diazotised α-naphthylamine-8-sulphonic acid when boiled with water or dilute sulphuric acid is not converted into α-naphthol-8-sulphonic acid but into *naphthasultone*, the *peri*-anhydride of this acid (Schultz, Ber. 1887, 20, 3162; Erdmann, Annalen, 1888, 247, 344). The acid can be obtained from the sultone by heating it with alcoholic ammonia at 130°, adding lead acetate, and decomposing the precipitated lead salt with hydrogen sulphide (Erdmann, *l.c.*); *or* from α-naphthylamine-8-sulphonic acid either by heating it with water under pressure at 180°–220° (Höchst, D. R.-P. 74644; Eng. Pat. 14301 of 1892), or by the bisulphite method (*cf.* Bucherer, J. pr. Chem. 1904, [ii.] 70, 347).

Salts.—The *acid* $HA+H_2O$ is crystalline, m.p. 106°–107°, and very soluble. It does not lose the water of crystallisation below 180°, and shows little tendency to pass into the anhydride even in the presence of dehydrating agents. The *potassium* salt KA in scales; the *basic sodium* salt $Na_2A+1\frac{1}{2}H_2O$ in small needles; and the *ammonium* salt NH_4A in scales, are easily soluble, and like the acid give with ferric chloride a dark green colouration, changing rapidly to red (Erdmann, *l.c.*).

Reactions.—(1) With nitrous acid a sparingly soluble *nitroso-* compound is obtained, which yields 2:4-*dinitro-α-naphthol*-8-*sulphonic acid* (*brilliant yellow*) when warmed with nitric acid (Schöllkopf, D. R.-P. 42304 of 1886).

(2) When fused with caustic potash at 220° it is converted into 1:8-*dihydroxynaphthalene* (Erdmann, Annalen. 1888, 247, 356).

Naphthasultone  $C_{10}H_6<\substack{SO_2\\O}>$, first described as naphtholsulphonic acid S (Schöllkopf, D. R.-P. 40571; Eng. Pat. 15775 of 1885; *v.* S-acid), is obtained almost quantitatively by boiling diazotised α-naphthylamine-8-sulphonic acid with alcohol, water, or dilute sulphuric acid (Karpeles, *cf.* J. Soc. Chem. Ind. 1898, 17, 837). It crystallises from alcohol in large prisms, m.p. 154°, distils above 360° with only slight decomposition, and is almost insoluble in water.

Reactions.—(1) It yields salts of α-naphthol-8-sulphonic acid when boiled with aqueous caustic alkalis or alcoholic ammonia, but does not react with these in the cold (Schultz, Ber. 1887, 20, 3162; Erdmann, Annalen, 1888, 247, 345).

(2) When heated with sulphuric acid at 80°–90° it is converted into *α-naphthol*-4:8-*disulphonic acid* (Schöllkopf, *l.c.*; Bernthsen, Ber. 1890, 23, 3090), and with 25 p.c. anhydro- acid at temperatures below 100° into *α-naphthol*-2:4:8-*trisulphonic acid* (Bayer, D. P. Anm. F. 4569; Eng. Pat. 3397 of 1890; Dressel and Kothe, Ber. 1894, 27, 2143).

α-NAPHTHOLDISULPHONIC ACIDS.

(i.) **α-Naphthol-2:4-disulphonic acid** is formed by the sulphonation of α-naphthol or of α-naphthol-2- or 4-sulphonic acid at temperatures below 100°,[1] and is separated from mono- or disulphonic acids in the product by removing these either with nitrous acid as sparingly soluble nitroso- compounds, or with diazotised bases as insoluble azo- dyes. When α-naphthol (5 pts.) is heated with sulphuric acid (9 pts.) for 2 hours at 50°, the product consists of the 2:4-disulphonic acid mixed with about 5 p.c. (Conrad and Fischer, Annalen, 1893, 273, 105), or about 30 p.c. (Friedlaender and Taussig, Ber. 1897, 30, 1457), of α-naphthol-2-sulphonic acid.

Identification.—The *potassium* salt K_2A in solution gives with ferric chloride a deep blue colouration, but is not precipitated by lead acetate or barium chloride, and yields neither azo- dyes nor a nitroso- compound (Conrad and Fischer, *l.c.*).

Reactions.—(1) When warmed with nitric acid, pure 2:4-*dinitro-α-naphthol* (*Martius yellow*) is obtained (Bender, *l.c.*).

(2) When the potassium salt is heated at 170°–180° (Conrad and Fischer, *l.c.* 111), or the sodium salt, suspended in naphthalene, is heated at 150°–160° (Bayer, D. R.-P. 237396; Eng. Pat. 2355 of 1911) it is converted into potassium *α-naphthol*-2-*sulphonate.*

(3) By further sulphonation it is converted into *α-naphthol*-2:4:7-*trisulphonic acid* (*cf.* Friedlaender and Taussig, *l.c.* 1463).

(ii.) **α-Naphthol-2:5-disulphonic acid** is prepared by heating α-naphthol-5-sulphonic acid with sulphuric acid or with 20 p.c. anhydro-acid below 100° (Bayer, D. R.-P. 68344 of 1889; Eng. Pat. 3397 of 1890).

Identification.—The *sodium* salt which crystallises in prisms, does not form a nitroso- derivative (Bayer, *l.c.*) or couple with diazotised bases (Gattermann and Schulze, Ber. 1897, 30, 55).

Reaction.—By digestion with 60 p.c. caustic soda solution at 250° it gives 1:5-*dihydroxynaphthalene*-2-*sulphonic acid* (Bayer, *l.c.*).

(iii.) **α-Naphthol-2:7-disulphonic acid** occurs among the products formed when α-naphthol is heated with sulphuric acid at temperatures above 100° for several hours, and is probably the

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[1] According to Bender (Ber. 1889, 22, 998), the product obtained by heating α-naphthol with 2½ times its weight of sulphuric acid at 100°–105° for three hours, contains in addition to the 2:4-acid about 45 p.c. of a second disulphonic acid, having a sulphonic group in each nucleus, and some trisulphonic acid, its composition being estimated from the results obtained (*a*) by nitration, (*b*) by precipitation with diazotised xylidine.

chief constituent of the mixture of acids obtained by sulphonating α-naphthol with 2–3 times its weight of 'about 93 p.c.' sulphuric acid ('65°–66°B.') at 125°–130° for about 2 hours (Leonhardt, Eng. Pat. 11318 of 1887; *cf.* Friedlaender and Taussig, Ber. 1897, 30, 1463).[1] A method for isolating the constituents of the mixture has not been described.

It can be obtained from α-naphthylamine-2 : 7-disulphonic acid by the diazo- reaction (*cf.* Reverdin and de la Harpe, Ber. 1892, 25, 1405); *or* from α-chloronaphthalene-2 : 7-disulphonic acid by digestion with 30 p.c. caustic soda solution at 200°–210° (Oehler, D. R.-P. 74744 of 1893); *or* from α-naphthol-2 : 4 : 7-trisulphonic acid by interaction with sodium amalgam (Friedlaender and Lucht, Ber. 1893, 26, 3031).

Identification.—Little is known of the properties of the pure acid. It forms a soluble *zinc* salt ZnA (Friedlaender and Lucht, *l.c.*), and gives a blue colouration with ferric chloride; para-*azo*-dyes by coupling with diazotised bases (Oehler, *l.c.*); and a *nitroso*- derivative which does not form a naphthol green with iron salts (Friedlaender and Taussig, *l.c.*).

(iv.) α-**Naphthol-3 : 6-disulphonic acid** obtained when sodium naphthalene-1 : 3 : 6-trisulphonate is heated with 50 p.c. caustic soda solution at 170°–180° (Gürke and Rudolph, D. R.-P. 38281; Eng. Pat. 15716 of 1885), can be prepared from α-naphthylamine-3 : 6-disulphonic acid either by the diazo-reaction (Freund, D. R.-P. 27346; Eng. Pat. 1069 of 1883)[2] or by heating its acid sodium salt with water under pressure at 180° (Cassella, D. P. Anm. C. 4375 of 1892).

Identification.—The *acid barium* salt BaH_2A_2 is sparingly soluble; the *acid sodium* salt NaHA dissolves readily in water or alcohol, gives with ferric chloride a blue colouration, and with diazotised bases ortho-*azo-* dyes (Freund, *l.c.*; *cf.* Friedlaender and Taussig, Ber. 1897, 30, 1462).

Reactions.—When heated with ammonia under pressure at 160°–180° it is converted into 1 : 3-*diaminonaphthalene-6-sulphonic acid* (Kalle, D. R.-P. 89061 of 1894; Eng. Pat. 9103 of 1895), or with aniline and aniline hydrochloride at 150°–170° into the *diphenyl*-derivative of this acid (Bayer, D. R.-P. 77866; Eng. Pat. 16780 of 1893).

(v.) α-**Naphthol-3 : 7-disulphonic acid** can be prepared from α-naphthylamine-3 : 7-disulphonic acid, either by the diazo- reaction (Freund, D. R.-P. 27346; Eng. Pat. 1069 of 1883)[2] or by heating its acid sodium salt with water under pressure at 180° (Cassella, D. P. Anm. C. 5069 of 1892).

Reactions.—Of its properties or salts little is known, but it resembles the 3 : 6-acid (*q.v.*) in its behaviour towards ferric chloride, diazotised bases (Freund, *l.c.*) ammonia (Kalle, D. R.-P. 89061 of 1894; Eng. Pat. 9103 of 1895), and aniline (Bayer, D. R.-P. 77866; Eng. Pat. 16780 of 1893).

(vi.) α-**Naphthol-3 : 8-disulphonic acid** (α-naphthol-[ε-]disulphonic acid) is prepared from α-naphthylamine-3 : 8-disulphonic acid either by heating its acid sodium salt with water under pressure at 180° (Höchst, D. R.-P. 71494; Eng. Pat. 14301 of 1892), or by boiling its diazo- compound with dilute sulphuric acid[3] (Aktienges., D. R.-P. 45776; Eng. Pat. 4625 of 1888; Bernthsen, Ber. 1889, 22, 3330).

Identification.—The *sodium* salt Na_2A+6H_2O forms long prisms soluble in about 5·5 parts of cold water, gives with ferric chloride a deep blue colouration and yields, not a naphthol yellow, but oxidation products with nitric acid (Aktienges., *l.c.*; Bernthsen, *l.c.*).

Reactions.—(1) It couples with diazotised bases forming ortho-*azo-* dyes (Aktienges., D. R.-P. 57444; Eng. Pat. 6932 of 1890; D. R.-P. 63951; Eng. Pat. 17333 of 1888).

(2) By digestion with 50 p.c. caustic soda solution at 170°–210° it forms 1 : 8-*dihydroxynaphthalene-3-sulphonic acid* (Kalle, D. R.-P. 82422 of 1894). Electrolytically, it is reduced to the 3-*sulphonic acid* (*v.* p. 592, footnote 1).

(3) When heated with ammonia under pressure at 160°–180° it is converted into 1 : 3-*diaminonaphthalene - 8 - sulphonic acid* (Kalle, D. R.-P. 89061 of 1894; Eng. Pat. 9103 of 1895), or with aniline and aniline hydrochloride at 150°–170° into the *diphenyl-* derivative of this acid (Bayer, D. R.-P. 77866; Eng. Pat. 16780 of 1893).

(4) Dehydrating agents, *ex. gr.* sulphuric acid at 100°, or phosphoric oxide, or phosphoric chloride, convert it into *naphthasultone-3-sulphonic acid* (Badische, D. R.-P. 55094 of 1889).

The *peri*-anhydride, naphthasultone-3-sulphonic acid (naphthasultonesulphonic acid-ε; ζ-naphtholdisulphonic acid), forms readily soluble silky needles; the *barium* salt sparingly soluble long needles; the *sodium* salt $NaA+3H_2O$ long needles soluble in about 93 parts of cold water. It gives no colouration with ferric chloride, and is readily convertible into α-naphthol-3 : 8-disulphonic acid by mineral acids or by alkalis (Ewer and Pick, D. R.-P. 52724 of 1888; Badische, *l.c.*; Bernthsen, *l.c.*). Ammonia reacts with it forming the half amide: α-Naphthol-8-sulphonamide-3-sulphonic acid (ε- or ζ-naphtholsulphamidesulphonic acid), $OH{\cdot}C_{10}H_5(SO_2NH_2){\cdot}SO_3H$, which crystallises in moderately soluble needles. Its *barium* salt BaA_2+5H_2O and *sodium* salt $NaA+H_2O$, needles, are moderately soluble; its *sodium ammonium* salt NaA,NH_3+H_2O ($3H_2O$ in D. R.-P. 53934) forms very soluble small prisms, and from each salt when boiled with dilute acids α-naphthol-3 : 8-disulphonic acid is obtained

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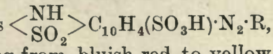
[1] Bearing in mind the conclusions reached by Bender (Ber. 1889, 22, 998; *cf.* Aktienges., D. R.-P. 45776; Eng. Pat. 4625 of 1888), and by Friedlaender and Taussig (Ber. 1897, 30, 1463), it is probable that the Patents dealing with the prolonged sulphonation of α-naphthol may be divided into two groups:

(*a*) Those in which anhydro-acid or a relatively large proportion of sulphuric acid is used at 100°, or at temperatures below 100°, leading mainly to the production of α-naphthol-2 : 4-di- and 2 : 4 : 7-tri-sulphonic acids (*cf.* Seltzer, D. R.-P. 20716 of 1882; Durand and Huguenin, Eng. Pat. 2591 (prov. spec.) of 1883; Vignon & Co., Eng. Pat. 9808 (prov. spec.) of 1884).

(*b*) Those in which a relatively small proportion of sulphuric acid at 100°–130° is used leading to the production of α-naphthol-2 : 7-disulphonic acid mixed with varying proportions of the 4 : 7-di-, and 2 : 4 : 7-trisulphonic acids (*cf.* Badische, D. R.-P. 10785; Eng. Pat. 5305 of 1879; Levinstein, Eng. Pat. 5692 of 1882; Vignon, D. R.-P. 32291; Eng. Pat. 6872 of 1884; Leonhardt, Eng. Pat. 11318 of 1887; Read, Holliday and Sons, Eng. Pat. 5103 of 1891).

[2] In this Patent the product is considered to be a β-naphtholdisulphonic acid on account of the fastness to acids shown by the derived azo-dyes, but these are now known to be *ortho*-azo-dyes (Cassella, *l.c.*).

[3] If the boiling be stopped directly nitrogen ceases to be evolved, the solution will contain the *peri*-anhydride, which by continued boiling furnishes the naphtholdisulphonic acid (Bernthsen, *l.c.*).

(Badische, D. R.-P. 53934 of 1889; Bernthsen, *l.c.*). It couples with diazotised bases, forming ortho-*azo*- dyes (*cf.* Badische, D. R.-P. 57484, 57907 of 1889; Geigy, D. R.-P. 139287 of 1902), which when boiled for a short time with alkali hydroxides or carbonates are converted into *peri*-anhydrides  $<\genfrac{}{}{0pt}{}{NH}{SO_2}>C_{10}H_4(SO_3H){\cdot}N_2{\cdot}R$, the colour changing from bluish-red to yellow (Bernthsen, Ber. 1890, 23, 3094).

(vii.) α-**Naphthol-4 : 6-disulphonic acid** can be prepared from α-naphthylamine-4 : 6-disulphonic acid either by the diazo- reaction (Dahl, D. R.-P. 41957 of 1886), or by the bisulphite method (Bucherer, J. pr. Chem. 1904, [ii.] 70, 347); *or*, mixed with the 4 : 7- acid, from tetrasulpho-αα′-dinaphthyl carbonate, by heating the product of the sulphonation of αα′-dinaphthyl carbonate with dilute acid at 60°–70° to eliminate carbon dioxide, the 4 : 7-disulphonic acid being removed by salting out (Höchst, D. R.-P. 80888; Eng. Pat. 14134 of 1894).

Reactions.—It yields *azo*- dyes when coupled with diazotised bases, and a *naphthol yellow* when boiled with nitric acid (Dahl, *l.c.*).

(viii.) α-**Naphthol-4 : 7-disulphonic acid** occurs in varying amounts in the products obtained by the sulphonation of α-naphthol under conditions which lead also to the formation of the 2 : 7- acid (*q.v.*; *cf.* Friedlaender and Taussig, Ber. 1897, 30, 1463).

It can be prepared from α-naphthylamine-4 : 7-disulphonic acid either by the diazo-reaction (Dahl, D. R.-P. 41957 of 1886), or by the bisulphite method (Bucherer, J. pr. Chem. 1904, [2] 70, 347); *or* from α-chloronaphthalene-4 : 7-disulphonic acid by digestion with 30 p.c. caustic soda solution at 200°–210° (Oehler, D. R.-P. 74744 of 1893); *or* by boiling with dilute acid either tetrasulpho-αα′-dinaphthyl carbonate (*v.* 4 : 6-acid; Höchst, D. R.-P. 80888; Eng. Pat. 14134 of 1894), or 2-carboxy-α-naphthol-4 : 7-disulphonic acid (Friedlaender and Taussig, *l.c.*; *cf.* Seidler, D. R.-P. 56328 of 1889).

Identification.—The *barium* salt $BaA+4H_2O$ and *sodium* salt Na_2A+4H_2O are crystalline. The sodium salt in solution gives with ferric chloride a blue colouration (Oehler, *l.c.*).

Reactions.—(1) Ortho-*azo* dyes are obtained by coupling it with diazotised bases (*cf.* Dahl, *l.c.*; Oehler, *l.c.*).

(2) Nitrous acid reacts with it forming a very soluble *nitroso*- compound which, like the acid, yields 2 : 4-*dinitro-α-naphthol*-7-*sulphonic acid* (naphthol yellow S) when warmed with nitric acid (Armstrong and Wynne, Chem. Soc. Proc. 1890, 6, 17; Dahl, *l.c.*).

(3) When boiled with 65 p.c. sulphuric acid or with hydrochloric acid it is hydrolysed not to α-naphthol, but only to α-*naphthol*-7-*sulphonic acid* (Liebmann and Studer, D. P. Anm. L. 4327; Eng. Pat. 7812 of 1887; *cf.* Friedlaender and Taussig, *l. c.*).

(ix.) α-**Naphthol-4 : 8-disulphonic acid** (α-naphtholdisulphonic acid S; α-naphthol-[δ]-disulphonic acid) is obtained when naphthasultone (so-called α-naphtholsulphonic acid S of D. R.-P. 40571) is heated with sulphuric acid at 80°–90° until soluble in water (Schöllkopf, D. R.-P. 40571; Eng. Pat. 15775 of 1885; Bernthsen, Ber. 1890, 23, 3090). It is also formed from α-naphthylamine-4 : 8-disulphonic acid either by the diazo- reaction (Schöllkopf, *l.c*), or by the bisulphite method (Bucherer, J. pr. Chem. 1904, [ii.] 69, 80; *cf.* Badische, D. R.-P. 115335 of 1899; Eng. Pat. 1387 of 1900).

Identification.—The *barium* salt is sparingly soluble, the *sodium* salt Na_2A+H_2O forms very soluble scales (Aktienges., D. R.-P. 45776; Eng. Pat. 4625 of 1888), and with ferric chloride gives a deep blue colouration (Bernthsen, *l.c.*).

Reactions.—(1) It couples with diazotised bases forming ortho-*azo*- dyes (Schöllkopf, *l.c.*; Aktienges., D. R.-P. 57444; Eng. Pat. 6932 of 1890; D. R.-P. 60921 of 1891).

(2) Nitrous acid converts it into the 2-*nitroso*-derivative (Dressel and Kothe, Ber. 1894, 27, 2145) which, when warmed with nitric acid, forms 2 : 4-*dinitro-α-naphthol*-8-*sulphonic acid* (the *brilliant yellow* of D. R.-P. 40571).

(3) When fused with caustic soda at 250° it yields 1 : 8-*dihydroxynaphthalene*-4-*sulphonic acid* (Bayer, D. R.-P. 54116, 67829; Eng. Pat. 13655, 18517 of 1889).

(4) By the bisulphite reaction, it can be converted into α-*naphthylamine*-4 : 8-*disulphonic acid* (Badische, D. R.-P. 117471 of 1899; Eng. Pat. 1387 of 1900).

(5) With 5 p.c. anhydro- acid in the cold, it yields the anhydride, *naphthasultone*-4-*sulphonic acid* (Badische, D. R.-P. 57388 of 1889; Bernthsen, *l.c.*), but with 25 p.c. anhydro- acid below 100° it gives α-*naphthol*-2 : 4 : 8-*trisulphonic acid* (Bayer, D. P. Anm. F. 4569; Eng. Pat. 3397 of 1890; Dressel and Kothe, *l.c.*).

The *peri*-anhydride, naphthasultone-4-sulphonic acid (naphthasultonesulphonic acid-δ) forms an easily soluble *barium* salt. The *sodium* salt $NaA+3H_2O$, in moderately soluble scales, is converted readily into sodium α-naphthol-4 : 8-disulphonate by alkalis, boiling with 5 p.c. sulphuric acid, or prolonged boiling with water, and gives neither a colouration with ferric chloride nor azo- dyes with diazotised bases (Bernthsen, *l.c.*; *cf.* Badische, D. R.-P. 57388 of 1889). Dissolved in concentrated ammonia it gives with hydrochloric acid a precipitate of α-Naphthol-8-sulphonamide-4-sulphonic acid (δ-acid), the half amide, as *sodium* salt $OH{\cdot}C_{10}H_5(SO_2NH_2){\cdot}SO_3Na+2H_2O$, which crystallises in rhomb-like scales, regenerates the sultone or α-naphthol-4 : 8-disulphonic acid when boiled with dilute acids (Badische, D. R.-P. 57856 of 1889; Bernthsen, *l.c.*), and couples with diazotised bases forming ortho-*azo*- dyes which closely resemble those obtained from the 8-sulphonamide-3-sulphonic-acid (*cf.* Badische, D. R.-P. 60777, 64065 of 1889; Geigy, D. R.-P. 139287 of 1902).

(x.) α-**Naphthol-5 : 7-disulphonic acid** has not been described, but is mentioned in connection with the bisulphite reaction as producible from and convertible into α-*naphthylamine*-5 : 7-*disulphonic acid* (Badische, D. R.-P. 115335, 117471 of 1899; Eng. Pat. 1387 of 1900).

(xi.) α-**Naphthol-5 : 8-disulphonic acid** is obtained from α-naphthylamine-5 : 8-disulphonic acid by the diazo- reaction, the sultone first formed being converted by alkali into the naphtholdisulphonic acid (Bayer, D. R.-P. 70857 of 1892).

The *peri*-anhydride, naphthasultone-5-sulphonic acid, forms a *sodium* salt $NaA+\frac{1}{2}H_2O$ in moderately soluble long needles (Gattermann, Ber. 1899, 32, 1158), and, like the disulphonic acid, when heated with 40 p.c. caustic soda solution under pressure at 170°–200°, yields 1 : 8-*dihydroxynaphthalene*-4-*sulphonic acid* (Bayer, D. R.-P. 80667 of 1892 ; Eng. Pat. 1227 of 1894).

(xii.) α-**Naphthol-6 : 8-disulphonic acid** has been prepared from α-naphthylamine-6 : 8-disulphonic acid either by the diazo- reaction, the sultone first formed being converted into the naphtholdisulphonic acid by alkali (Bayer, D. R.-P. 75084 of 1893) or by the bisulphite reaction (Bucherer, J. pr. Chem. 1904, [ii.] 70, 347). It is also formed when α-naphthylamine-4 : 6 : 8-trisulphonic acid (Kalle, D. R.-P. 82563 of 1893), or α-naphthol-4 : 6 : 8-trisulphonic acid (Kalle, D. P. Anm. K. 11397 of 1894) is heated with dilute (2 p.c.) acid at 180°–200°.

Identification.—The *acid sodium* salt forms easily soluble short needles, which with ferric chloride gives a fleeting green colouration, and with nitrous acid a *nitroso-* derivative not convertible into a naphthol yellow by nitric acid (Kalle, *l.c.*). The naphthasultone-6-sulphonic acid and α-naphthol-8-sulphonamide-6-sulphonic acid have not been fully characterised (Bayer, *l.c.*).

Reaction.—When heated with 50 p.c. caustic soda solution at 170°–210°, it is converted into 1:8-*dihydroxynaphthalene*-6-*sulphonic acid* (Kalle, D. R.-P. 82422 of 1894).

α-NAPHTHOLTRISULPHONIC ACIDS.

(i.) α-**Naphthol-2 : 4 : 7-trisulphonic acid** is the chief product of the sulphonation of α-naphthol either with 25 p.c. anhydro- acid at 100°–110° or with 45 p.c. anhydro- acid at 40°–50° (Badische, D. R.-P. 10785 ; Eng. Pat. 5305 of 1879),[1] and can be isolated by means of the characteristic barium salt (Friedlaender and Taussig, Ber. 1897, 30, 1463). It is also obtained when diazotised α-naphthylamine-2 : 4 : 7-trisulphonic acid is boiled with acidified water (*cf.* Höchst, D. R.-P. 22545 ; Eng. Pat. 2178 of 1882), *or* when α-chloronaphthalene-2 : 4 : 7-trisulphonic acid is heated with 12 p.c. caustic soda solution at 150° (Oehler, D. R.-P. 77996 of 1893).

Identification.—The *barium* salt $Ba_3A_2+3H_2O$ in glistening minute crystals, is almost insoluble when once separated from water ; the other salts are easily soluble (Friedlaender and Taussig, *l.c.*). The *sodium* salt gives a blue colouration with ferric chloride, but yields neither azo- dyes nor a nitroso- compound.

Reactions.—(1) When warmed with nitric acid it yields 2 : 4-*dinitro-α-naphthol*-7-*sulphonic acid* (naphthol yellow S; *cf.* Badische, *l.c.* ; Höchst, *l.c.* ; Lauterbach, Ber. 1881, 14, 2028).

(2) When heated with hydrochloric acid or 65 p.c. sulphuric acid it is partially hydrolysed, forming *α-naphthol*-7-*sulphonic acid* (*cf.* Liebmann and Studer, D. P. Anm. L. 4327 ; Eng. Pat. 7812 of 1887). With sodium amalgam it furnishes *α-naphthol*-2 : 7-*disulphonic acid* (Friedlaender and Taussig, *l.c.*).

(ii.) α-**Naphthol-2 : 4 : 8-trisulphonic acid** has been prepared by sulphonating α-naphthol-4 : 8-disulphonic acid or its sultone with 25 p.c. anhydro- acid below 100° (Bayer, D. P. Anm. F. 4569 ; Eng. Pat. 3397 of 1890 ; Dressel and Kothe, Ber. 1894, 27, 2143).

Identification.—The *sodium* salt $Na_3A+1\frac{1}{2}H_2O$ is a readily soluble crystalline powder, shows green fluorescence in solution, gives with ferric chloride a blue colouration, and does not couple with diazotised bases (Dressel and Kothe, *l.c.*).

Reactions.—(1) With nitro-sulphuric acid at 20° it gives 2 : 4-*dinitro-α-naphthol*-8-*sulphonic acid* (brilliant yellow ; Dressel and Kothe, *l.c.*).

(2) By fusion with caustic soda at 210°, it is converted into 1 : 8-*dihydroxynaphthalene*-2 : 4-*disulphonic acid* (*ibid.* ; *cf.* Bayer, D. R.-P. 57021 ; Eng. Pat. 3397 of 1890).

(iii.) α-**Naphthol-3 : 5 : 7-trisulphonic acid** can be obtained either from naphthalene-1 : 3 : 5 : 7-tetrasulphonic acid by digestion with 15 p.c. caustic soda solution under pressure at 180° (Bayer, D. R.-P. 79054 ; Eng. Pat. 25074 of 1893), or from α-naphthylamine-3 : 5 : 7-trisulphonic acid by the diazo- reaction (Kalle, D. P. Anm. K. 12732 of 1895).

Reactions.—(1) When heated with ammonia under pressure at 160°–180° it is converted into 1 : 3-*diaminonaphthalene*-5 : 7-*disulphonic acid* (Kalle, D. R.-P. 90906 ; Eng. Pat. 9103 of 1895).

(2) On digestion with 50 p.c. caustic soda solution at 150°–160°, it yields 1 : 5-*dihydroxynaphthalene*-3 : 7-*disulphonic acid* (Kalle, D. P. Anm. K. 12732 of 1895), or with 60 p.c. solution at 200°, a mixture of this acid with 1 : 3-*dihydroxynaphthalene*-5 : 7-*disulphonic acid* (Bayer, D. R.-P. 79054 ; Eng. Pat. 25074 of 1893).

(iv.) α-**Naphthol-3 : 6 : 8-trisulphonic acid** is formed from α-naphthylamine-3 : 6 : 8-trisulphonic acid either by the diazo- reaction, the sultone being an intermediate product (Koch, D. R.-P. 56058 ; Eng. Pat. 9258 of 1890), *or* by heating it with water under pressure at 180°–250° (Höchst, D. R.-P. 71495 ; Eng. Pat. 14301 of 1892).

Reactions.—(1) By digestion with 60 p.c. caustic soda solution at 170°–220° it yields 1 : 8-*dihydroxynaphthalene* - 3 : 6 - *disulphonic acid* (Höchst, D. R.-P. 67563 of 1890).

(2) When heated with ammonia under pressure at 160°–180° it is converted into 1 : 3-*diaminonaphthalene*-6 : 8-*disulphonic acid* (Kalle, D. R.-P. 90905 ; Eng. Pat. 9103 of 1895), or with aniline and aniline hydrochloride at 150°–170° into the *diphenyl-* derivative of this acid (Bayer, D. R.-P. 77866 ; Eng. Pat. 16780 of 1893).

Its sultone gives yellow solutions with alkalis. When dissolved in ammonia the sodium salt of the sultone with hydrochloric acid yields sodium α-naphthol-8-sulphonamide-3 : 6-disulphonate (Koch, *l.c.* ; Höchst, D. R.-P. 69518 of 1890), which couples with diazotised bases forming *azo-* dyes (*cf.* Koch, D. R.-P. 58076 ; Höchst, D. R.-P. 65143 ; Eng. Pat. 9258 of 1890 ; Geigy, D. R.-P. 139287 of 1902).

(v.) α-**Naphthol-4 : 6 : 8-trisulphonic acid** has been obtained from α-naphthylamine-4 : 6 : 8-trisulphonic acid either by the diazo- reaction,

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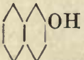
[1] The acid formed by heating α-naphthol with three times its weight of sulphuric acid at 110°–115° for twelve to fifteen hours (Badische, *l.c.*), and serving as a source of naphthol yellow S, would probably contain a large proportion of the 2 : 7- and 4 : 7-disulphonic acids (*cf.* p. 619, footnote 1).

the sultone formed being dissolved in alkali (Bayer, D. P. Anm. F. 7006; *cf.* D. R.-P. 80741; Eng. Pat. 17141c of 1893), or by the bisulphite reaction (Bucherer, J. pr. Chem. 1904, [ii.] 70, 347).

Reactions.—(1) By digestion with 70 p.c. caustic soda solution under pressure at 170°–190°, it yields 1 : 8-*dihydroxynaphthalene*-3 : 5-*disulphonic acid* (Bayer, D. P. Anm. 7004; Eng. Pat. 17141c of 1893).

(2) When heated with 2 p.c. hydrochloric acid under pressure at 160°–200° it is partially hydrolysed, forming *α-naphthol*-6 : 8-*disulphonic acid* (Kalle, D. P. Anm. K. 11397 of 1894).

Its sultone is easily soluble, forming colourless non-fluorescent solutions which with alkalis become deep yellow; the corresponding α-naphthol-8-sulphonamide-4 : 6-disulphonic acid couples with diazotised bases giving ortho-*azo-* dyes (*cf.* Geigy, D. R.-P. 139287 of 1902).



(ii.) β-**Naphthol** occurs in very small amount in the coal tar fractions of high boiling-point (Schulze, Annalen, 1885, 227, 150). On the large scale it is formed by mixing sodium naphthalene-β-sulphonate with 40 p.c. caustic soda solution (2–2·5 mols.), heating the paste with constant stirring until quite thick, and afterwards fusing it at 300° for about 12 hours. The product, dissolved in water, is decomposed by hydrochloric or 50 p.c. sulphuric acid, and the separated β-naphthol purified by distillation in a vacuum (*cf.* Wallach and Wichelhaus, Ber. 1870, 3, 846 (footnote); Levinstein, Eng. Pat. 2300 of 1883).

Properties.—β-Naphthol crystallises in odourless scales or rhombic tables (*cf.* Groth, Annalen, 1869, 152, 285), m.p. 122° (Schaeffer, *ibid.*), b.p. 285°–286° (Ebert and Merz, Ber. 1876, 9, 611), sp.gr. 1·217 at 4° (Schroeder, *ibid.* 1879, 12, 1613), and is readily soluble in alcohol, organic solvents, or caustic alkali solutions, but only sparingly in hot water. It is only slightly volatile with steam at 100°, but can be distilled with superheated steam. It has marked antiseptic properties. The *sodium* compound $C_{10}H_7{\cdot}ONa$ can be obtained crystalline (*v.* p. 615, footnote).

Reactions.—(1) It is converted by prolonged boiling in the air, more readily by distillation with phosphoric oxide or by heating with litharge, into *ββ'-dinaphthylene oxide* (Dianin, Ber. 1875, 8, 166; Graebe, Knecht, and Unzeitig, Annalen, 1881, 209, 138).

(2) Nitrous acid reacts with it, forming 1-*nitroso-β-naphthol* (Fuchs, Ber. 1875, 8, 1026; *v.* Naphthaquinoneoximes); or, in ethereal solution, 1 : 6-*dinitro-β-naphthol* (Schmidt, Ber. 1900, 33, 3246).

(3) On oxidation in alkaline solution with potassium permanganate it yields either ortho-*carboxycinnamic acid* (Ehrlich and Benedikt, Monatsh. 1888, 9, 527), or *phthalonic acid* (Henriques, Ber. 1888, 21, 1618), but on fusion with caustic alkali and copper oxide or hydrated manganese peroxide, it is converted, like α-naphthol, into *phthalic acid* and *benzoic acid* (Bindschedler, D. R.-P. 138790 of 1900; 139956; Eng. Pat. 15527 of 1901).

(4) The action of ammonia, acetamide, and aniline on β-naphthol is described in connection with β-naphthylamine (*q.v.*).

(5) When heated with 40 p.c. ammonium sulphite solution and 20 p.c. ammonia at 100°–150°, it is converted almost quantitatively into *β-naphthylamine* (Bucherer, J. pr. Chem. 1904, [ii.] 69, 88; Badische, D. R.-P. 117471 of 1899; Eng. Pat. 1387 of 1900).

(6) On reduction with sodium in amyl alcohol solution it is converted into a mixture of ac.-*tetrahydro-β-naphthol* as chief product, with ar.-*tetrahydro-β-naphthol* (Bamberger and Lodter, Ber. 1890, 23, 197).

(7) With nitrosodimethylaniline hydrochloride it yields the hydrochloride of *β-naphthol-violet* (Meldola, Ber. 1879, 12, 2066).

(8) Iodine solution added to a solution of β-naphthol in aqueous caustic soda gives a yellowish-green precipitate of so-called *β-naphthol iodide* (Messinger and Vortmann, Ber. 1889, 22, 2322; Bayer, D. R.-P. 49739; Eng. Pat. 5079 of 1889).

Colour reactions.—Bleaching-powder solution gives to an aqueous solution of β-naphthol a pale yellow colouration which disappears on addition of an excess. Ferric chloride added to an aqueous solution (Dianin, Ber. 1873, 6, 1252; 7, 125; *cf.* Walder, *ibid.* 1882, 15, 2166) gives a pale green colouration and afterwards a white flocculent precipitate of *ββ'-dinaphthol.* When warmed with strong caustic potash solution and chloroform at 50°, it gives (like α-naphthol) a Prussian-blue colouration which gradually changes through green into brown (Lustgarten, Monatsh. 1883, 3, 720; *cf.* Rousseau, Ann. Chim. Phys. 1883, [v.] 28, 148).

Tests.—Commercial β-naphthol should be almost colourless, have approximately the right melting-point, and dissolve completely in caustic alkali forming an almost colourless solution. According to Jorissen (Ann. chim. anal. 1902, 7, 217), a solution of iodine in potassium iodide with excess of caustic soda solution gives with β-naphthol a clear colourless solution, but, if α-naphthol be present, a turbid coloured liquid, the reaction being one which can be used colorimetrically to determine the proportion.

Estimation.—A 1 p.c. solution of the sample in aqueous caustic soda (4 mols.) is titrated at 60° with excess of N/10 iodine (the equation is

$$C_{10}H_8O+3I_2+3NaOH=C_{10}H_5I_3O+3NaI+3H_2O),$$

cooled, acidified with dilute sulphuric acid and the filtrate titrated back with N/10 sodium thiosulphate (Messinger and Vortmann, *l.c.*; *cf.* Küster, Ber. 1894, 27, 1907).

β-Naphthyl methyl ether, prepared by heating β-naphthol (5 pts.), with absolute methyl alcohol (5 pts.) and sulphuric acid (2 pts.) in a reflux apparatus under slight pressure at 125° (Gattermann, Annalen, 1888, 244, 72), forms scales, m.p. 72°, b.p. 274° (Marchetti, Jahresb. Chem. 1879, 543), dissolves sparingly in alcohol and has the odour of orange flowers (neroli).

β-Naphthyl ethyl ether, prepared like the methyl ether (Gattermann, *l.c.*; *cf.* Davis, Chem. Soc. Trans. 1900, 77, 33), m.p. 37°, b.p. 282°, dissolves readily in alcohol, and has the odour of pineapple. On nitration it yields 1-*nitro-β-ethoxynaphthalene*, m.p. 104° (Wittkampf, Ber. 1884, 17, 394; Cassella, D. P. Anm. C. 2883 of 1889); and, as minor product, 6-*nitro-β-ethoxynaphthalene*, m.p. 114° (Gaess, J. pr. Chem. 1891, [ii.] 43, 22).

ββ'-Dinaphthyl ether $(C_{10}H_7)_2O$, obtained by boiling β-naphthol for some hours with 50 p.c. sulphuric acid (Graebe, Ber. 1880, 13, 1850); *or* by heating sodium 'β-naphthylsulphate' with β-naphthol at 180°–200° (Nietzki, *ibid.* 1882, 15, 305); *or* β-naphthol with phosphoric chloride (1 mol.) at 100° for two hours (Berger, Compt. rend. 1905, 141, 1027), forms scales, m.p. 105°, b.p. above 360°, and yields *β-naphtholmono-, di-,* and *tri-sulphonic acids* when heated with sulphonating agents (Brönner, D. R.-P. 26938; Eng. Pat. 3606 of 1883).

β-Naphthylsulphuric acid (*v.* β-naphthol-1-sulphonic acid).

β-Naphthyl carbonate $CO(O{\cdot}C_{10}H_7)_2$, obtained by the interaction of phosgene and β-naphthol (Schering, D. P. Anm. C. 4197 of 1892), forms needles, m.p. 176°–177°, sparingly soluble in alcohol, and on sulphonation yields a mixture of the *β-naphthol*-6-, 7-, and 8-*sulphonic acids* (Reverdin and Kauffmann, Ber. 1895, 28, 3057).

β-Naphthyl acetate, obtained by heating β-naphthol with acetyl chloride (Schaeffer, *l.c.*), or with acetic acid at 240° (Graebe, Annalen, 1881, 209, 150), forms needles, m.p. 70° (Miller, Ber. 1881, 14, 1602, footnote), dissolves sparingly in water, and is hydrolysed by distillation with steam.

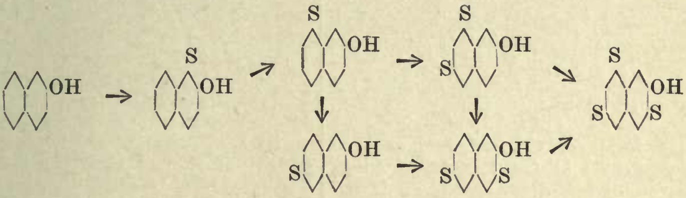
β-NAPHTHOLSULPHONIC ACIDS.

Introductory.—The greater number of the β-naphtholsulphonic acids are obtained by the sulphonation of β-naphthol, whereas in the α-series, for the production of α-naphtholsulphonic acids, direct sulphonation finds only a limited use. But this is only one of many differences between the two series. Another arises from the operation of the laws of (*a*) preferential sulphonation in α- rather than in β- positions, (*b*) preferential replacement of α- rather than of β-sulphonic groups by other radicles, which renders the methods most widely used in the α-series (*v.* p. 615) comparatively valueless for the production of β-naphtholsulphonic acids. For example:—

(1) Fusion of naphthalenesulphonic acids with caustic alkali can be applied in the β-series only to naphthalene-2 : 6- and 2 : 7 disulphonic acids, as these are the only two naphthalenepolysulphonic acids containing SO_3H radicles exclusively in β- positions;

(2) Exchange of the amino- group for hydroxyl in naphthylaminesulphonic acids, either by the diazo- reaction or by the bisulphite method, is limited in the β-series by the fact that the most convenient source of β-naphthylaminesulphonic acids is found in the β-naphtholsulphonic acids themselves.

The first product of the action of sulphuric acid on β-naphthol is β-naphthol-1-sulphonic acid, regarded by its discoverers as β-naphthylsulphuric acid. Without alteration in the concentration of the sulphuric acid, but with rise of temperature, there are obtained successively at 50°–60° β-naphthol-8-sulphonic acid, and at 90°–100° the 6-sulphonic acid. When the weight of sulphuric acid is doubled there are obtained, similarly, at 60° β-naphthol-6 : 8-disulphonic acid, and at 120°–130° the 3 : 6-disulphonic acid. With anhydro- acid, sulphonation of β-naphthol reaches its limit in the formation of the 3 : 6 : 8-trisulphonic acid. The relationship between these products is shown in the scheme[1]—



Another source of β-naphtholpolysulphonic acids is the 7-sulphonic acid, which, although known to occur in the sulphonation product of β-naphthol at 100°–130°, does not seem to have been isolated from this source, but is obtained from naphthalene-2 : 7-disulphonic acid by fusion with caustic alkali. The acids formed from it by sulphonation are shown on the next page, the agent used in the production of each being indicated under the symbol showing its constitution.

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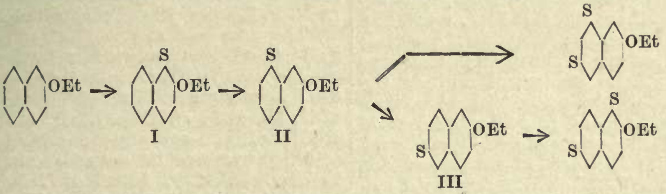
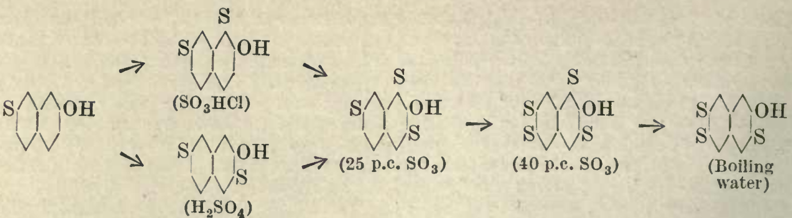
[1] This scheme is not to be regarded as complete. It leaves out of account the formation of β-naphthol-7-sulphonic acid (*q.v.*) recorded by Green, and should be compared with another, compiled from data furnished by Lapworth (Chem. Soc. Proc. 1895, 11, 49), in which the products formed in the sulphonation of β-ethoxynaphthalene by chlorosulphonic acid, under conditions excluding the presence of water, are displayed.



The change of acid I into acid II was found to take place at the ordinary temperature, and of acid II into acid III at the temperature of a water bath; moreover, acid III on sulphonation gave, not the 3 : 6-disulphonic acid as might be expected from the behaviour of β-naphthol-6-sulphonic acid, but the 1 : 6-disulphonic acid, not yet recognised among the sulphonation products of β-naphthol.



Bearing in mind the rule of preferential substitution in α- positions, it is noteworthy that the SO_3H radicle is not found in either the 4- or the 5- position in any of the products of the sulphonation of β-naphthol under the most varied conditions. And with reference to the 1-position, it is evident that, of the five acids obtained from β-naphthol-7-sulphonic acid by sulphonation, the three containing a SO_3H radicle in this position are formed under conditions which exclude the presence of water; whereas the two from which it is absent are obtained respectively by the use of ordinary sulphuric acid, and by desulphonation with boiling water.

The β-naphtholsulphonates are better defined, and more easily separated from mixtures than are the α-naphtholsulphonates. They can therefore be used for the production of pure β-naphthylaminesulphonic acids. Their chief use is in connection with the manufacture of *ortho*-azo- dyes, but they are not equally valuable for this purpose. For example: Of the numerous isomeric acids, those are most valuable which contain a sulphonic group in the 8- position, the shades obtained with them being orange rather than red: these acids are characterised by coupling only slowly with diazotised bases.

β-Naphtholmonosulphonic Acids.[1]

(i) **β-Naphthol-1-sulphonic acid** (β-naphthylsulphuric acid). When a solution of β-naphthol in 2–2·5 times its weight of 90–92 p.c. sulphuric acid at 35°–45° is kept for a short time until it solidifies to a crystalline mass (Tobias, D. R.-P. 74688; Eng. Pat. 15404 of 1893; *cf.* Armstrong, Ber. 1882, 15, 202; Nietzki, *ibid.* 305), *or* when chlorosulphonic acid (1 mol.) is added to β-naphthol dissolved in carbon disulphide (Armstrong, *l.c.*), a product is obtained which—at first considered to be β-naphthylsulphuric acid—was identified by Tobias as β-naphthol-1-sulphonic acid. It is separated from the 8- acid, which is also present in small quantity, by precipitation as the very sparingly soluble basic barium salt (Tobias, *l.c.*).

Identification.—Both normal and basic salts are known, which with the exception of the *basic barium* salt are easily soluble in water. The normal *barium* salt $BaA_2+2C_2H_6O$, *potassium* salt KA, and sodium salt NaA, crystallise from alcohol in scales; the *disodium* salt $Na_2A+2C_2H_6O$, in scales, shows no fluorescence in aqueous solution. In neutral solution the salts give an indigo-blue colouration with ferric chloride (Tobias, *l.c.*), and in acid solution yield β-naphthol and sulphuric acid on evaporation.

Reactions.—(1) Dissolved in sulphuric acid it is converted at 50°–60° into *β-naphthol-8-sulphonic*, *6-sulphonic*, and *6 : 8-disulphonic acids* (Höchst, D. R.-P. 36491; Eng. Pat. 816 of 1884; *cf.* Armstrong, *l.c.*).

(2) When heated with 20 p.c. ammonia under pressure at 220°-230° (Tobias, *l.c.*) or with ammonium sulphite solution and ammonia at 100°–150° (Bucherer, J. pr. Chem. 1904, [ii.] 70, 357; *cf.* Badische, D. R.-P. 117471 of 1899; Eng. Pat. 1387 of 1900) it yields *β-naphthylamine-1-sulphonic acid.*

(3) With diazotised bases coupling takes place in alkaline solution, but the *azo*-dyes are derivatives of β-naphthol, not of the acid, owing to elimination of the SO_3H radicle (Tobias, *l.c.*). In neutral or acid solution, *salts* formed by combination with diazo- or tetrazo-compounds are produced (Bayer, D. R.-P. 93305; Eng. Pat. 11757 of 1895).

(ii.) **β-Naphthol-4-sulphonic acid** is obtained from β-naphthylamine-4 : 8-disulphonic acid by digestion with water or 10 p.c. sulphuric acid under pressure at 170°–185° (Kalle, D. R.-P. 78603 of 1893). Its *sodium* salt is easily soluble.

Reactions.—(1) When heated with ammonia under pressure it is converted into *β-naphthylamine-4-sulphonic acid* (Kalle, *l.c.*).

(2) By digestion with 60 p.c. caustic soda solution at 230°–280° it yields *o-toluic acid* (Kalle, D. R.-P. 79028 of 1893).

(iii.) **β-Naphthol-5-sulphonic acid** has been prepared from β-naphthylamine-5-sulphonic acid by the diazo- reaction (Dahl, D. R.-P. 29084; Eng. Pat. 7712 of 1884; Claus, J. pr. Chem. 1889, [ii.] 39, 315). On fusion with caustic alkali, it gives 1 : 6-*dihydroxynaphthalene* (Claus, *l.c.*). The *azo*-dyes obtained from it are worthless (Dahl, *l.c.*).

(iv.) **β-Naphthol-6-sulphonic acid** ([α-]acid of Armstrong and of Schultz; Schaeffer acid) is formed as chief product, mixed with about 15–20 p.c. of the 8-acid, when β-naphthol is heated on a water-bath with twice its weight of sulphuric acid until completely sulphonated (Schaeffer, Annalen, 1869, 152, 296); *or*, mixed with some 7-acid, disulphonic acid and unattacked β-naphthol, when it is heated with monohydrate (1 mol.) at 100°–105° for 2–3 hours (Armstrong, Ber. 1882, 15, 201; *cf.* Green, Chem. Soc. Trans. 1889, 55, 37); *or*, as chief product, when ββ′-dinaphthyl ether is sulphonated with 2–3 parts of sulphuric acid at 90°–100° (Brönner, D. R.-P. 26938; Eng. Pat. 3606 of 1883).

The pure acid can be obtained from sodium 2 : 6-naphthalenedisulphonate by fusing it with caustic alkali (Ebert and Merz, Ber. 1876, 9, 610; Armstrong and Graham, Chem. Soc. Trans. 1881, 39, 136; *cf.* Cassella, D. R.-P. 45221 of 1887); *or* from 1-carboxy-β-naphthol-6-sulphonic acid by warming its aqueous solution at 60° (Seidler, D. R.-P. 53343 of 1889); *or* from β-naphthylamine-6-sulphonic acid, either by the diazo- reaction, or by boiling it with 40 p.c. sodium bisulphite solution, and then acidifying the product (Badische, D. R.-P. 134401 of 1899).

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[1] In every case where the constitution of a β-naphtholsulphonic acid is given the OH radicle is supposed to be in the position '2.'

On the laboratory scale, when prepared from β-naphthol, the acid is purified by conversion into its moderately soluble barium or calcium salt (*v.* 8-acid), which, when suspended in boiling water, becomes anhydrous and almost insoluble.

Identification.—The *acid* forms easily soluble non-deliquescent scales, m.p. 125°; the *lead* salt PbA_2+6H_2O, scales; the *barium* salt BaA_2+6H_2O, long prisms; the *calcium* salt CaA_2+5H_2O, scales, readily soluble in alcohol or in 30 parts of water at 18°; the *potassium* salt KA, prisms, soluble in about 50 parts of water at 15°; the *sodium* salt $NaA+2H_2O$, scales, soluble in about 3·3 parts of water at 80°, in 57·8 parts at 14°, and in 69 parts at 11·5° (Schaeffer, *l.c.*; Armstrong and Graham, *l.c.*); the *ammonium* salt NH_4A, long flat prisms soluble in about 34 parts of water at 24° (Meldola, Chem. Soc. Trans. 1881, 39, 41). In aqueous solution the salts show a pale blue fluorescence and give a pale green colouration with ferric chloride. With nitric acid, solutions of these salts become carmine-red when warmed (Schaeffer, *l.c.*; Armstrong and Graham, *l.c.*), the colouration being due to the formation of an *indophenol* derivative of [β-]naphthaquinone, which can be isolated in red crystals (Nietzki and Knapp, Ber. 1897, 30, 187).

Reactions.—(1) By sulphonation with anhydro- acid at 150°–160° it is converted into *β-naphthol*-3 : 6-*disulphonic acid* (Baum, D. P. Anm. B. 4199; Eng. Pat. 3523 (prov. spec.) of 1883).

(2) With nitrous acid it forms 1-*nitroso-β-naphthol*-6-*sulphonic acid* (Meldola, *l.c.*), convertible into *naphthol green-β* by interaction with iron salts (Gans & Co. D. R.-P. 28065; Eng. Pat. 2269 of 1884).

(3) When heated with ammonia under pressure at 180° (Brönner, D. R.-P. 22547; Eng. Pat. 3724 of 1882), or with 40 p.c. ammonium sulphite solution and ammonia at 100°–150° (Bucherer, J. pr. Chem. 1904, [ii.] 70, 357; *cf.* Badische, D. R.-P. 117471 of 1899; Eng. Pat. 1387 of 1900), it yields *β-naphthylamine*-6-*sulphonic acid.*

(4) With 10 p.c. methylamine sulphite solution and methylamine under pressure at 125°, it gives *methyl-β-naphthylamine*-6-*sulphonic acid* (Badische, D. R.-P. 121683; Eng. Pat. 18726 of 1900); with 40 p.c. sodium bisulphite solution and aniline at the boiling point, it forms *phenyl-β-naphthylamine*-6-*sulphonic acid* (Badische, D. R.-P. 122570; Eng. Pat. 18726 of 1900); and with 40 p.c. sodium bisulphite solution and fuchsin at 90°–100°, it gives the corresponding *fuchsin*-derivative (Badische, D. R.-P. 125589; Eng. Pat. 18726 of 1900).

(5) When fused with caustic alkali, it yields 2 : 6-*dihydroxynaphthalene* (Emmert, Annalen, 1887, 241, 369).

(6) With sulphur and caustic alkali solution under pressure at 200° it forms two 'thio-β-naphtholsulphonic acids' (Aktienges., D. R.-P. 50077 of 1889).

(7) It couples with diazotised bases forming *azo*-dyes (*cf.* Bayer, D. R.-P. 26231; Eng. Pat. 2411 of 1883; Höchst, D. R.-P. 86937 of 1894).

(v.) **β-Naphthol-7-sulphonic acid** ([δ-] acid; F-acid) is obtained technically from sodium naphthalene-2 : 7-disulphonate by digestion with concentrated (50–90 p.c.) caustic soda solution at 250°, until an acidified test gives traces of dihydroxynaphthalene when extracted by ether, or until a test freed from sulphur dioxide gives with diazoxylene an amount of azo-dye equivalent to the quantity of sodium salt employed (Weinberg, Ber. 1887, 20. 2907; Cassella D. R.-P. 42112; Eng. Pat. 12908 of 1886; *cf.* D. R.-P. 45221 of 1887).

Mixed with the 6-acid it is formed when β-naphthol is heated with monohydrate (1 mol.) at 100°–130° for 2–3 hours, but does not seem to have been isolated from the product (Green, Eng. Pat. 15849 of 1888; Chem. Soc. Trans. 1889, 55, 37). From β-naphthylamine-7-sulphonic acid it can be obtained either by the diazo- reaction (Bayer and Duisberg, Ber. 1887, 20, 431; *cf.* Schultz, *ibid.* 3158) or by the bisulphite method (Bucherer, J. pr. Chem 1904, [2] 69, 73).

Identification.—The *acid* forms hydrated needles, m.p. 89°, readily soluble in water or alcohol; the *barium* salt sparingly soluble prisms; the *magnesium* salt $MgA_2+5\frac{1}{2}H_2O$, scales; the *potassium* salt $KA+H_2O$, readily soluble rhombs; the *sodium* salt $NaA+2\frac{1}{2}H_2O$, large scales soluble in 12·5 parts of water at 15° (Weinberg, *l.c.*). In alkaline solution the salts show a pure blue fluorescence, and in neutral solution give a dark-blue colouration with ferric chloride (Cassella, *l.c.*). When heated with phosphorus pentachloride the sodium salt yields 2 : 7-*dichloronaphthalene* (Weinberg, *l.c.*; Bayer and Duisberg, *l.c.*).

Reactions.—(1) By sulphonation with chlorosulphonic acid it is converted into *β-naphthol*-1 : 7-*disulphonic acid* (Bayer, D. R.-P. 77596 of 1893; Eng. Pat. 1063 of 1894); with sulphuric acid at 120° into the 3 : 7-*disulphonic acid* (Cassella, D. R.-P. 44079; Eng. Pat. 8265 of 1887; Weinberg, *l.c.*), and with 30 p.c. anhydro-acid at 100° into the 1 : 3 : 7-*trisulphonic acid* (Bayer, D. R.-P. 78569; Eng. Pat. 17141 of 1893; Dressel and Kothe, Ber. 1894, 27, 1207).

(2) With nitrous acid it forms 1-*nitroso-β-naphthol*-7-*sulphonic acid*, convertible into a *naphthol green* by iron salts (Cassella, D. R.-P. 42112; Eng. Pat. 12908 of 1886).

(3) When heated with 20 p.c. ammonia solution under pressure at 250° (Cassella, D. R.-P. 43740 of 1886), or with 40 p.c. ammonium sulphite solution and ammonia at 100°–150° (Bucherer, J. pr. Chem. 1904, [ii.] 70, 357) it yields *β-naphthylamine*-7-*sulphonic acid.* With dimethylamine under pressure at 220°, it gives *dimethyl-β-naphthylamine*-7-*sulphonic acid* (Geigy, D. R.-P. 90310 of 1896).

(4) When fused with caustic alkali, it yields 2 : 7-*dihydroxynaphthalene* (Armstrong, Chem. Soc. Trans. 1881, 39, 139; Pfitzinger and Duisberg, Ber. 1889, 22, 398).

(5) It couples with diazotised bases forming *azo*-dyes (*cf.* Cassella, *l.c.*; Höchst, D. R.-P. 86937 of 1894).

(vi.) **β-Naphthol-8-sulphonic acid** ([α-] acid of Bayer & Co.'s patents, [β-]acid of Schultz, and *o*-acid of Claus and Volz [1]; croceïc acid; Bayer or Rumpff acid) is formed as chief product (80 p.c.) together with the 2 : 6-acid, when β-naphthol is rapidly sulphonated with twice its

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[1] Claus and Volz assign the constitution [2 : 3] to this acid, but the method employed by them has been shown to be untrustworthy (*cf.* Armstrong, Chem. Soc. Proc., 1889, 5, 9; Pfitzinger and Duisberg, Ber. 1889, 22, 397; Nietzki and Zübelen, *ibid.*, 454).

weight of sulphuric acid either at 50° or 60° (Bayer, D. R.-P. 18027; Eng. Pat. 1225 of 1881; D. R.-P. 20397 of 1882; D. R.-P. 26231[1]; Eng. Pat. 2411 of 1883) or during several days at a temperature not exceeding 20° (Leonhardt and Schulz, D. R.-P. 33857 of 1884; *cf.* Bang and Roussin, D. P. Anm. B. 13709 of 1892). It occurs (15–20 p.c.) in the product formed when β-naphthol is heated with twice its weight of sulphuric acid on a water-bath until dissolved (Schaeffer, Annalen, 1869, 152, 296), and in the so-called Armstrong acid produced when β-naphthol is heated with monohydrate (1 mol.) at 100° (Beyer and Kegel, D. R.-P. 32964; Eng. Pat. 7098 of 1884).

It is obtained pure from β-naphthylamine-8-sulphonic acid either by boiling it with 40 p.c. sodium bisulphite solution, adding alkali, and then acidifying (Badische, D. R.-P. 134401 of 1899), or by boiling its diazo- compound with 2 p.c. sulphuric acid (Dahl, D. R.-P. 29084; Eng. Pat. 7712 of 1884).

On the laboratory scale, when prepared from β-naphthol, the 8-acid is freed from the 6-acid by converting the sulphonation product into calcium salt, filtering the solution while hot, and concentrating the filtrate until the 6-salt separates out as a precipitate. About four-fifths of the 6-acid being removed as calcium salt, the remainder can be separated from the mother liquor by conversion into neutral (basic) sodium salt, which is either coupled with the requisite quantity of a diazotised base (as determined by a preliminary test) and the dye salted out, or dried and extracted with 90 p.c. alcohol in which the 6- sodium salt is practically insoluble. The filtrate in either case contains pure sodium β-naphthol-8-sulphonate (*cf.* Bayer, *l.c.*).

Identification.—The *acid* decomposes into β-naphthol and sulphuric acid when its solution is evaporated; it forms both normal (acid) and basic (neutral) salts, which are much more soluble in water than the salts of the 6-acid. The *barium* and *calcium* salts are insoluble in absolute alcohol; the *lead* salt $PbA_2+2\frac{1}{2}H_2O$, forms rhombohedra; the *zinc* salt $ZnA+2H_2O$, needles; the *sodium* salt NaA, six-sided scales; the basic *disodium* salt $Na_2A+2C_2H_6O$, deliquescent needles from 95 p.c. alcohol in which it dissolves very easily at the boiling-point, but only sparingly (1 in 100) at 15° (Badische, D. R.-P. 20760 of 1881; Claus and Volz, Ber. 1885, 18, 3155). Unlike its isomerides, it does not give a nitroso- compound (Gans & Co., D. R.-P. 28065; Eng. Pat. 2269 of 1884).

Reactions.—(1) By sulphonation with sulphuric acid below 50° it is converted into *β-naphthol-*6 : 8-*disulphonic acid* (Gans and Hoffmann, Eng. Pat. 816 of 1884).

(2) When warmed with dilute nitric acid it yields 1 : 6-*dinitro-β-naphthol-*8-*sulphonic acid* (croceïn yellow; Bayer, D. R.-P. 18027; Eng. Pat. 1225 of 1881; Nietzki and Zübelen, Ber. 1889, 22, 454).

(3) When heated with ammonia under pressure (Bayer, D. R.-P. 42273 of 1887 Pfitzinger and Duisberg, Ber. 1889, 22, 397), or with ammonium bisulphite solution and ammonia (Bucherer, J. pr. Chem. 1904, [ii.] 70, 358), it forms *β-naphthylamine-*8-*sulphonic acid.*

(4) When fused with caustic alkali it gives 1 : 7-*dihydroxynaphthalene* (Emmert, Annalen, 1887, 241, 371; Bayer, D. R.-P. 53915; Eng. Pat. 14230 of 1889).

(5) It couples only slowly with diazotised bases, forming many valuable *azo-*dyes (Schultz, Ber. 1884, 17, 461; *cf.* Bayer, D. R.-P. 26231; Eng. Pat. 2411 of 1883; Aktienges., D. R.-P. 62659 of 1891).

β-Naphtholdisulphonic Acids.

(i.) **β-Naphthol-1 : 6-disulphonic acid** is mentioned by Bucherer (J. pr. Chem. 1904, [ii.] 69, 73; *cf.* Badische, D. R.-P. 117471 of 1899; Eng. Pat. 1387 of 1900) as furnishing the corresponding naphthylamine derivative by the bisulphite method, but no description of it seems to have been published.

(ii.) **β-Naphthol-1 : 7-disulphonic acid** is obtained either from sodium β-naphthol-7-sulphonate by sulphonation in the cold with chlorosulphonic acid (Bayer, D. R.-P. 77596 of 1893; Eng. Pat. 1063 of 1894; Dressel and Kothe, Ber. 1894, 27, 1206), or from β-naphthylamine-1 : 7-disulphonic acid by the diazo- reaction (Dressel and Kothe, *ibid.* 1207).

Identification.—The *barium* salt forms sparingly soluble needles; the *potassium* salt $K_2A+1\frac{1}{2}H_2O$, moderately soluble prisms; the *sodium* salt, very soluble needles. In alkaline solution the salts give a pale blue fluorescence. It does not couple with diazotised bases.

Reactions.—(1) When heated either with 25 p.c. ammonia solution under pressure at 180°–200° (Bayer, *l.c.*; D. P. Anm. F. 7274 of 1893), or with ammonium sulphite solution and ammonia at 100°–150° (Badische, D. R.-P. 117471 of 1899; Eng. Pat. 1387 of 1900), it yields *β-naphthylamine-*1 : 7-*disulphonic acid.*

(2) When boiled with 10 p.c. hydrochloric acid, it reverts to *β-naphthol-*7-*sulphonic acid* (Dressel and Kothe, *l.c.*).

(iii.) **β-Naphthol-3 : 6-disulphonic acid** ([α-] disulphonic acid; R-acid) is formed as chief product, mixed with some 6 : 8-acid, when β-naphthol is heated with 3–4 times its weight of sulphuric acid at 100°–110° for 12 hours (Höchst, D. R.-P. 3239; Eng. Pat. 1715 of 1878; Griess, Ber. 1880, 13, 1956), or at 125°–150° for 5–6 hours (Beyer and Kegel, D. R.-P. 33916; Eng. Pat. 7097 of 1884). It is said to be the only product when equal weights of potassium β-naphthol-6-sulphonate, potassium pyrosulphate, and sulphuric acid are heated for 5–6 hours at 160° (Baum, D. P. Anm. B. 4199; Eng. Pat. 3523 (prov. spec.) of 1883).

On the laboratory scale, the product from any of these sources is freed from 6 : 8- salt and any other impurities by conversion through the calcium salt into the sodium salt, which when dry is extracted with 80–90 p.c. alcohol, the impurities passing into solution, leaving pure R-salt (*cf.* Höchst, *l.c.*). Or the greater part of the R-acid in the product can be separated as the crystalline sodium salt by pouring the sulphonation melt into brine, the mother

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[1] In this Patent reference is made to the presence of a third acid in the sulphonation product, and it is suggested that this acid may have been derived from impurity (doubtless α-naphthol) in the β-naphthol used (*cf.* however, Bayer, D. R.-P. 30077; Eng. Pat. 8495 of 1884). There is no reason to suppose that more than two β-naphtholsulphonic acids are formed under these conditions.

liquor containing 6 : 8-salt with the remainder of the R-salt (*cf.* Beyer and Kegel, *l.c.*).

Identification.—The *acid* forms silky, deliquescent needles very soluble in water or alcohol, the *barium* salt $BaA+6H_2O$, needles soluble in 12 parts of boiling water, but insoluble in alcohol, the *sodium* salt aggregates of minute needles readily soluble in cold water, but only sparingly soluble in alcohol or in brine. In aqueous solution the salts show a bluish-green fluorescence (Griess, *l.c.*).

The readily soluble *aluminium* salt has been introduced as an antiseptic and astringent under the name 'Alumnol' (Höchst, D. R.-P. 74209; Eng. Pat. 10668 of 1892). By warming a solution of the sodium salt with mercuric chloride a *compound* is obtained in which the mercury present (32 p.c.) cannot be detected by the ordinary reagents (Aktienges., D. R.-P. 143448 of 1901).

Reactions.—(1) By sulphonation with 20 p.c. anhydro- acid, it is converted into *β-naphthol*-3 : 6 : 8-*trisulphonic acid* (*cf.* Höchst, D. R.-P. 22038; Eng. Pat. 2544 of 1882).

(2) When heated either with ammonia under pressure (Pfitzinger and Duisberg, Ber. 1889, 22, 398; *cf.* Landshoff, D. R.-P. 27378 of 1883), or with ammonium sulphite solution and ammonia (Badische, D. R.-P. 117471 of 1899; Eng. Pat. 1387 of 1900) it yields *β-naphthylamine*-3 : 6-*disulphonic acid.*

(3) When fused with caustic soda at 220°–240° it gives 2 : 3-*dihydroxynaphthalene*-6-*sulphonic acid* (Höchst, D. P. Anm. F. 4153; Eng. Pat. 9642 of 1889; Badische, D. R.-P. 57525; Eng. Pat. 15803 of 1890: Friedlaender and Zakrzewski, Ber. 1894, 27, 762).

(4) It is not hydrolysed by dilute (20 p.c.) mineral acids at the boiling-point (*cf.* Bayer, D. R.-P. 77596 of 1893), but at higher temperatures, or by means of sodium amalgam, it reverts to *β-naphthol*-6-*sulphonic acid* (Friedlaender and Lucht, Ber. 1893, 26, 3029, 3032).

(5) It couples readily with diazotised bases and is an important source of *azo*- dyes (*cf.* Höchst, D. R.-P. 3229, 7217; Eng. Pats. 1715, 4914 of 1878; Aktienges., D. R.-P. 94082; Eng. Pat. 16569 of 1892; Badische, D. R.-P. 160788; Eng. Pat. 19165 of 1904).

(iv.) **β-Naphthol-3 : 7-disulphonic acid** ([δ-] disulphonic acid; disulphonic acid F) is the product formed when sodium β-naphthol-7-sulphonate is heated with twice its weight of sulphuric acid at 120° for about 12 hours (Cassella, D. R.-P. 44079; Eng. Pat. 8265 of 1887), or with 3–4 times its weight of the acid on a water-bath (Dressel and Kothe, Ber. 1894, 27, 1206). It can be obtained by partial hydrolysis of β-naphthol-1 : 3 : 7-trisulphonic acid with 10 p.c. hydrochloric acid (Bayer, D. R.-P. 78569; Eng. Pat. 17141 of 1893; Dressel and Kothe, *l.c.*).

Identification.—The *barium* salt $BaA+2\frac{1}{2}H_2O$, forms small prisms soluble in 185 parts of boiling water; the *sodium* salt Na_2A is soluble in 100 parts of 80 p.c. alcohol and very soluble in water, the solution showing green fluorescence (Cassella, *l.c.*; Weinberg, Ber. 1887, 20, 2911).

Reactions.—(1) By sulphonation with 25 p.c. anhydro- acid at 80°–90° it is converted into *β-naphthol*-1 : 3 : 7-*trisulphonic acid* (Bayer, *l.c.*; Dressel and Kothe, *l.c.*).

(2) When heated either with 25 p.c. ammonia solution under pressure at 200° (Cassella, D. R.-P. 46711 of 1888), or with ammonium sulphite solution and ammonia (Badische D. R.-P. 117471 of 1899; Eng. Pat. 1387 of 1900), it yields *β-naphthylamine*-3 : 7-*disulphonic acid.*

(3) Fusion with caustic alkali converts it into 2 : 7-*dihydroxynaphthalene*-3-*sulphonic acid* (*cf.* Bayer, D. R.-P. 57166; Eng. Pat. 13665 of 1889: D. R.-P. 85241; Eng. Pat. 3580 of 1895).

(4) Boiling it with dilute (20 p.c.) mineral acids does not effect hydrolysis (*cf.* Bayer, D. R.-P. 77596 of 1893), but at higher temperatures it yields *β-naphthol*-7-*sulphonic acid* (*cf.* Friedlaender and Lucht, Ber. 1893, 26, 3029).

(v.) **β-Naphthol-4 : 7-disulphonic acid** has been prepared from β-naphthylamine-4 : 7-disulphonic acid by the diazo- reaction (Bayer, D. R.-P. 77866: Eng. Pat. 16780 of 1893), but its salts have not been described. When heated with aniline and aniline hydrochloride at 150°–170° it is converted into *diphenyl*-1 : 3-*diaminonaphthalene*-6-*sulphonic acid* (Bayer, *l.c.*).

(vi.) **β-Naphthol-4 : 8-disulphonic acid** (C-acid) is obtained from β-naphthylamine-4 : 8-disulphonic acid by the diazo- reaction (Cassella, D. R.-P. 65997 of 1890). The *calcium* salt forms prisms; the solution of the *sodium* salt shows blue fluorescence.

Reactions.—(1) When heated with aniline and aniline hydrochloride at 150°–170° it yields *diphenyl* - 1 : 3-*diaminonaphthalene* - 5 - *sulphonic acid* (Bayer, D. R.-P. 77866; Eng. Pat. 16780 of 1893).

(2) In concentrated solution it couples with diazotised bases forming *azo*-dyes (Cassella, *l.c.*).

(vii.) **β-Naphthol-5 : 7-disulphonic acid** has been prepared from β-naphthylamine-5 : 7-disulphonic acid by heating its acid sodium salt with 30 p.c. sodium bisulphite solution, decomposing the sulphite with alkali, and afterwards acidifying to remove sulphurous acid (Badische, D. R.-P. 134401 of 1899; Bucherer, J. pr. Chem. 1904, [ii.] 70, 347). No description of the acid has been published.

(viii.) **β-Naphthol-6 : 8-disulphonic acid** ([γ-] disulphonic acid; G-acid (Y-acid of some English Patents); also known as [β-]disulphonic acid when mixed with some R-acid (*cf.* Griess, Ber. 1880, 13, 1956), is formed as chief product when a mixture of β-naphthol either with 5 parts of sulphuric acid at 0° is gradually heated to 60° in the course of 36 hours, or with 4 parts of acid is maintained at 60° during 48 hours or at 20° during 8–10 days (Höchst, D. R.-P. 36491; Gans and Hoffmann, Eng. Pat. 816 of 1884); *or* when β-naphthol-8-sulphonic acid, mixed with 3 times its weight of sulphuric acid, is either heated at 40°–50° during 5–6 hours or left at 25° for 8–10 days (Gans and Hoffmann, *l.c.*). It has been prepared from β-naphthylamine-6 : 8-disulphonic acid by the diazo- reaction (Gans & Co. D. R.-P. 35019; Eng. Pat. 816 of 1884).

To purify the sulphonation product advantage is taken of the fact that G-acid, like the 8- or Bayer acid, couples less readily with diazo-compounds than the accompanying Schaeffer and R-acids. The process consists in adding to an alkaline solution of the sodium salt the quantity of diazo- compound calculated from a test, and salting out the azo-dye; the filtrate contains the sodium salt of technically pure G-acid (Hochst, *l.c.*).

Identification.—With the exception of the *potassium* salt which dissolves in 2·5 parts of boiling water, the salts of pure G-acid have not been described. They are much more soluble in water than the corresponding R- or Schaeffer salts and the first (incomplete) separation of G- from R-acid was achieved by means of the different solubilities of the respective barium salts (Griess, *l.c.*). The *barium* salt $BaA+8H_2O$, and *sodium* salt Na_2A of the so-called [β-] acid form prisms, and in solution give a bluish-green fluorescence (Griess, *l.c.*).

Reactions.—(1) By sulphonation with 20 p.c. anhydro- acid it is converted into *β-naphthol*-3 : 6 : 8-*trisulphonic acid* (*cf.* Höchst, D. R.-P. 22038; Eng. Pat. 2544 of 1882).

(2) When heated with ammonia under pressure (*cf.* Landshoff, D. R.-P. 27378 of 1883) or with ammonium sulphite and ammonia at 100°–150° (Badische, D. R.-P. 117471 of 1899; Eng. Pat. 1387 of 1900; Bucherer, J. pr. Chem. 1904, [ii.] 70, 358) it yields *β-naphthylamine*-6 : 8-*disulphonic acid.*

(3) When fused with caustic soda at 220°–230° it gives 2 : 8-*dihydroxynaphthalene*-6-*sulphonic acid* (Höchst, D. P. Anm. F. 4153; Eng. Pat. 9642 of 1889), but at 260°–320° *hydroxytoluic acid* (Höchst, D. R.-P. 81333 of 1893).

(4) It is not hydrolysed when boiled with dilute (20 p.c.) acids (*cf.* Bayer, D. R.-P. 77596 of 1893), but at higher temperatures, or by means of sodium amalgam, it is converted into *β-naphthol*-6-*sulphonic acid* (Friedlaender and Lucht, Ber. 1893, 26, 3032).

(5) It couples only slowly and in concentrated solutions with diazotised bases, but is an important source of *azo*- dyes (*cf.* Cassella, D. R.-P. 54084; Eng. Pat. 12560 of 1889; Bayer, D. P. Anm. F. 6114; Eng. Pat. 14927 of 1892.

β-NAPHTHOLTRISULPHONIC ACIDS.

(i.) **β-Naphthol-1 : 3 : 7-trisulphonic acid** is prepared by sulphonating either β-naphthol-7-sulphonic acid or β-naphthol-3 : 7-disulphonic acid with 25 p.c. anhydro- acid at 80°–90° (Bayer, D. R.-P. 78569; Eng. Pat. 17141 of 1893; Dressel and Kothe, Ber. 1894, 27, 1207).

Identification.—The *barium* salt is easily soluble; the *sodium* salt Na_3A is very soluble in water, but only sparingly in alcohol, and gives with ferric chloride a violet colouration. In alkaline solution it shows a bluish-green fluorescence and does not couple with diazotised bases (Dressel and Kothe, *l.c.*).

Reactions.—(1) By sulphonation with 40 p.c. anhydro-acid at 120°–130° it is converted into *β-naphthol*-1 : 3 : 6 : 7-*tetrasulphonic acid* (Bayer, D. P. Anm. F. 6991; Eng. Pat. 17141 of 1893; Dressel and Kothe, *l.c.*).

(2) When heated with 25 p.c. ammonia solution under pressure at 190°, it yields *β-naphthylamine*-1 : 3 : 7-*trisulphonic acid* (Bayer, D. P. Anm. F. 7003; Eng. Pat. 17141 of 1893; Dressel and Kothe, *l.c.*).

(3) When boiled with dilute mineral acids it reverts to *β-naphthol*-3 : 7-*disulphonic acid* (Bayer, *l.c.*; Dressel and Kothe, *l.c.*).

(ii.) **β-Naphthol-3 : 5 : 7-trisulphonic acid**, obtained from β-naphthylamine-3 : 5 : 7-trisulphonic acid by the diazo-reaction, couples with diazotised bases forming *azo*-dyes (Dressel and Kothe, Ber. 1894, 27, 1203).

(iii.) **β-Naphthol-3 : 6 : 7-trisulphonic acid** is formed either from β-naphthol-1 : 3 : 6 : 7-tetrasulphonic acid by boiling it with water or dilute acids (Bayer, D. R.-P. 78569; Eng. Pat. 17141 of 1893; Dressel and Kothe, Ber. 1894, 27, 1209), or from β-naphthylamine-3 : 6 : 7-trisulphonic acid by the diazo- reaction (Dressel and Kothe, *l.c.*).

Identification.—The *barium* salt is gelatinous; the *sodium* salt Na_3A, in needles, is less soluble than its isomerides in water, brine, or alcohol, gives a violet colouration with ferric chloride, and shows in alkaline solution a bluish-green fluorescence. It is not hydrolysed by dilute acids.

Reactions.—(1) When heated with 25 p.c. ammonia solution under pressure it yields *β-naphthylamine*-3 : 6 : 7-*trisulphonic acid* (Bayer, D. P. Anm. F. 7019; Eng. Pat. 17141 of 1893; Dressel and Kothe, *l.c.*).

(2) By digestion with 65 p.c. caustic soda at 220°–300° it gives 2 : 7-*dihydroxynaphthalene*-3 : 6-*disulphonic acid* (Bayer, D. P. Anm. F. 7243; Eng. Pat. 25074A of 1893).

(3) It couples with diazotised bases forming sparingly soluble *azo*-dyes (Dressel and Kothe, *l.c.*).

(iv.) **β-Naphthol-3 : 6 : 8-trisulphonic acid** has been prepared by sulphonating β-naphthol either with 4–5 p.c. times its weight of 20 p.c. anhydro-acid at 140°–160° (Höchst, D. R.-P. 22038; Eng. Pat. 2544 of 1882), or with 40 p.c. anhydro- acid at 90°–120° (Nietzki, Chem. Zeit. 1891, 15, 296). Instead of β-naphthol, β-naphthol-6- or 8-sulphonic acid, *or* β-naphthol-3 : 6- or 6 : 8-disulphonic acid may be used (*cf.* Levinstein, Eng. Pat. 706 of 1883; Ber. 1883, 16, 462; Limpach, *ibid.* 726).

By Nietzki's process a crystalline powder is obtained when the melt is mixed with 3 times its weight of ice. This is considered to be a 2 : 3-anhydride or sultone. In solution it is non-fluorescent, and does not give a colouration with ferric chloride. Alkalis convert it into salts of the trisulphonic acid, which with ferric chloride give a violet colouration, and in alkaline solution show a yellowish-green fluorescence (Nietzki, *l.c.*).

Reactions.—(1) When heated with ammonia under pressure it yields *β-naphthylamine*-3 : 6 : 8-*trisulphonic acid* (Landshoff, D. R.-P. 27378 of 1883; *cf.* Dressel and Kothe, Ber. 1894, 27, 2154).

(2) By fusion with caustic alkali at 220°–280° it gives a mixture of 1 : 7-*dihydroxy*-3 : 6-*disulphonic* and 2 : 3-*dihydroxy*-6 : 8-*disulphonic acids* (Höchst, D. P. Anm. F. 4154; Eng. Pat. 9642 of 1889; D. R.-P. 67563 of 1890; *cf.* Friedlaender and Silberstern, Monatsh. 1902, 23, 527).

(3) It couples with diazotised bases, forming *azo*-dyes (*cf.* Bayer, D. P. Anm. F. 17644 of 1903; F. 18438 of 1904).

β-NAPHTHOLTETRASULPHONIC ACID.

β-Naphthol-1 : 3 : 6 : 7-tetrasulphonic acid is obtained by the sulphonation of β-naphthol-7-sulphonic, or 3 : 7-disulphonic, or 1 : 3 : 7-trisulphonic acid with 40 p.c. anhydro- acid at 120°–130°, provided care be taken to prevent the solution of the product, so long as it is acid, becoming warm (Bayer, D. P. Anm. F. 6991; Eng. Pat. 17141 of 1893; Dressel and Kothe, Ber. 1894, 27, 1208).

Identification.—The *barium* salt is a very sparingly soluble sandy powder; the sodium salt Na_4A is easily soluble in water but insoluble in alcohol, and in alkaline solution shows a bluish-green fluorescence. It does not couple with diazotised bases.

Reactions.—(1) When heated with 25 p.c. ammonia solution under pressure at 190° it gives *β-naphthylamine*-1 : 3 : 6 : 7-*tetrasulphonic acid* (Bayer, D. P. Anm. F. 7003; Eng. Pat. 17141 of 1893; Dressel and Kothe, *l.c.*).

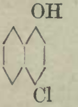
(2) When boiled with dilute mineral acids it yields *β-naphthol*-3 : 6 : 8-*trisulphonic acid* (Bayer, D. R.-P. 78569; Eng. Pat. 17141 of 1893; Dressel and Kothe, *l.c.*).

CHLORONAPHTHOLS.

Introductory.—By chlorination both α- and β-naphthol give rise only to homonucleal derivatives. When the operation is carried out by passing chlorine into a cooled acetic acid solution of the naphthol, the substitution product is:

From α-naphthol, 2 : 4-*dichloro-α-naphthol*; then the additive compounds trichloro-α-keto- and pentachloro-α-keto-naphthalene are formed (Zincke and Kegel, Ber. 1888, 21, 1030).

From β-naphthol, 1-*chloro-β-naphthol*; then dichloro-β-keto- and tetrachloro-β-keto-naphthalene (Zincke and Kegel, *ibid.* 3378).



4-Chloro-α-naphthol (m.p. 117°–118°) can be obtained by chlorinating either α-naphthyl carbonate (Reverdin and Kauffmann, Ber. 1895, 28, 3051), or α-naphthyl toluene-*p*-sulphonate in carbon tetrachloride solution (Aktienges., D. R.-P. 240038 of 1910). It is also formed from α-naphthol by employing sulphuryl chloride as the chlorinating agent (Kast, Ber. 1911, 44, 1337); but when the naphthol dissolved in alkali is chlorinated by hypochlorous acid (Kalle, D. R.-P. 167458 of 1904), a pure product is not formed (*cf.* King, Proc. Chem. Soc. 1911, 27, 266), although pure 1-*chloro-β-naphthol* (m.p. 70°) is the product from β-naphthol under similar conditions (Kalle, D. R.-P. 168824 of 1904).

Four chloro-α-naphtholsulphonic acids have been used for coupling with diazotised dehydrothiotoluidine in the production of *o*-azo- dyes. They are respectively the 6- and 7-*chloro-α-naphthol*-3-*sulphonic acids*, the 6-*chloro-α-naphthol*-3 : 5- and the 8-*chloro-α-naphthol*-3 : 6-*disulphonic acids*, formed from the corresponding aminonaphtholmono- and di-sulphonic acids by the Sandmeyer reaction (Bayer, D. R.-P. 96768; Eng. Pat. 9441 of 1894).

8-Chloro-α-naphthol-3 : 6-disulphonic acid, a crystalline, deliquescent substance, forms an *acid barium* salt, BaA_2+6H_2O, in needles; *acid potassium* salt, in scales, and *acid sodium* salt in needles. The normal salts dissolve easily, yielding non-fluorescent solutions, which with ferric chloride give a dark green colouration (Cassella, D. R.-P. 79055 of 1893; Eng. Pat. 1920 of 1894). Compared with the azo- dyes from α-naphthol-3 : 6-disulphonic acid, those from this *peri*-chloro- acid are much bluer in shade and of enhanced fastness (Cassella, *l.c.*; D. R.-P. 82285 of 1893; 99227 of 1894).

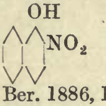
NITROSONAPHTHOLS.

(*v. Naphthaquinoneoximes*).

NITRONAPHTHOLS.

Introductory.—Nitronaphthols are obtained usually from naphtholsulphonic acids, nitrosonaphthols, or nitrosonaphtholsulphonic acids, containing the nitroso- group or at least one sulphonic group in the same nucleus as the hydroxyl radicle, as when produced by direct nitration of the naphthols, the yields are unsatisfactory owing to the formation of tars. Only in one instance has the preparation from a chloronitronaphthalene been achieved, the 1 : 4-derivative yielding 4-nitro-α-naphthol when digested with sodium carbonate solution.

The nitro-α-naphthols containing a nitro-group in the *ortho-* position relatively to the hydroxyl radicle dye wool and silk in various shades of yellow.



(i.) **2-Nitro-α-naphthol** is obtained by boiling 2-nitroacet-α-naphthalide (Liebermann and Dittler, Annalen, 1876, 183, 246; Lellmann and Remy, Ber. 1886, 19, 802) with aqueous caustic soda; by hydrolysing 2-nitro-α-ethoxynaphthalene-4-sulphonic acid (Witt and Schneider, *ibid.* 1901, 34, 3189); *or*, together with 2 : 4-dinitro-α-naphthol, by boiling α-diazonaphthalene sulphate with nitric acid in mol. prop. (Noelting and Wild, *ibid.* 1885, 18, 1339); *or*, better, by suspending 2-nitroso-α-naphthol (5 grms.) in water (60 c.c.), adding nitric acid of sp.gr. 1·3 (45 c.c.) in the cold, and, after 15 hours, distilling the product with steam (Grandmougin and Michel, *ibid.* 1892, 25, 973).

Properties.—It crystallises in greenish-yellow scales, m.p. 128°, dissolves sparingly in dilute alcohol, but less readily in water, and resembles *o*-nitrophenol in being volatile with steam and in forming dark red salts. Its *acetate* forms bright-yellow needles, m.p. 118° (Grandmougin and Michel, *l.c.*), and *ethyl ether*, bright yellow needles, m.p. 84° (Heermann, J. pr. Chem. 1891, [ii.] 44, 240).

(ii.) **4-Nitro-α-naphthol** (*French yellow*; *Campobello yellow*; *Chryseïc acid*) can be prepared by boiling 4-nitroacet-α-naphthalide with aqueous caustic soda (Andreoni and Biedermann, Ber. 1873, 6, 343; *cf.* Lellmann and Remy, *ibid.* 1886, 19, 796); and is formed when bis-4-nitro-α-naphthyl carbonate, m.p. 212°, is heated with alcoholic potash (Reverdin and Kauffmann, *ibid.* 1895, 28, 3050); *or* when 4-nitro-α-chloronaphthalene is heated with aqueous sodium carbonate under pressure at 150°–155° (Griesheim, D. R.-P. 117731; Eng. Pat. 7692 of 1900).

Properties.—It crystallises from hot water in golden-yellow needles, m.p. 164°, is readily soluble in alcohol or acetic acid, and, like *p*-nitrophenol, does not volatilise with steam. The salts (Biedermann, Ber. 1873, 6, 1118) are orange-red to dark red in colour, and dissolve readily in water; the *sodium* salt, $NaA + 2H_2O$, carmine-red needles, was formerly used as a yellow dye for silk or wool. The *methyl ether*, m.p. 85°–86 (Griesheim, *l.c.*), and *ethyl ether*, needles, m.p. 116°–117° (Heermann, *l.c.*; Witt and Schneider, *l.c.*) have been described.

Reactions.—(1) On nitration, it is converted into 2 : 4-*dinitro-α-naphthol* (Liebermann and Dittler, Annalen, 1876, 183, 249).

(2) When heated with 20 p.c. caustic soda solution under pressure at 170°–250°, it yields a mixture of *phthalic* and *benzoic acids* (Bindschedler, D. R.-P. 136410; Eng. Pat. 15527 of 1901).

(iii.) 5-**Nitro-α-naphthol**, obtained from 5-nitro-α-naphthylamine sulphate by the diazo-reaction, separates from hot water in dark yellow crystals, m.p. 165°; gives an *acetate*, needles, m.p. 114°; and *benzoate*, needles, m.p. 109°; couples with diazotised bases; and with nitrous acid yields 5-*nitro*-4-*nitroso-α-naphthol* (Kaufler and Bräuer, Ber. 1907, 40, 3271).

(iv.) 1-**Nitro-β-naphthol** is produced when 1-nitroso-β-naphthol is oxidised by dilute nitric acid (Stenhouse and Groves, Chem. Soc. Trans. 1877, 32, 51; *cf.* Hewitt and Mitchell, *ibid.* 1906, 89, 1172); *or* when 1-nitroacet-β-naphthalide is boiled with 6 p.c. caustic soda solution (Liebermann and Jacobson, Annalen, 1882, 211, 46); *or* when α-nitronaphthalene is heated at 50°–60° with 20 times its weight of pulverised caustic soda (Wohl, D. R.-P. 116790 of 1899; *cf.* Wohl and Aue, Ber. 1901, 34, 2444). It forms yellow needles, m.p. 103°; its *sodium* salt, red needles; *ethyl ether*, yellow needles, m.p. 103°–104° (Wittkampf, Ber. 1884, 17, 394), and *acetate*, colourless needles, m.p. 61° (Böttcher, *ibid.* 1883, 16, 1938).

(v.) 5-**Nitro-β-naphthol**, prepared from 5-nitro-β-naphthylamine by the diazo- reaction, crystallises from water in yellow needles, m.p. 147°. The salts are reddish-yellow and easily soluble; the *ethyl ether* forms yellow needles, m.p. 115° (Friedlaender and Szymanski, Ber. 1892, 25, 2079).

(vi.) 8-**Nitro-β-naphthol**, obtained from the ethyl ether by hydrolysis with hydrochloric acid at 160° (Gaess, J. pr. Chem. 1891, [ii.] 44, 614), *or* from 8-nitro-β-naphthylamine by the diazo-reaction (Friedlaender and Szymanski, Ber. 1892, 25, 2028), forms deep yellow needles, m.p. 144°–145°. The *ethyl ether*, prepared by nitration of β-ethoxynaphthalene, forms long golden-yellow needles, m.p. 72°–73° (Gaess, J. pr. Chem. 1891, [ii.] 43, 25), and the *acetate*, needles, m.p. 101°–102° (Gaess, *ibid.* 45, 615).

DINITRONAPTHOLS.

(i.) 2 : 4-**Dinitro-α-naphthol** (*Martius yellow, Manchester yellow, Naphthalene yellow, Naphthol yellow*) is obtained by the action of nitric acid on α-naphthol (Dale, Caro and Martius, Eng. Pat. 2785 of 1864; Martius, J. pr. Chem. 1867, 102, 442), 2-nitroso- or 4-nitroso-α-naphthol (Fuchs, Ber. 1875, 8, 629), 4-nitro-α-naphthol, 1-nitro-β-naphthol (Liebermann and Dittler, Annalen, 1876, 183, 249), α-naphthol-2-sulphonic acid (Darmstaedter and Wichelhaus, Eng. Pat. 89 of 1869; Annalen, 1869, 152, 299), α-naphthol-4-sulphonic acid (Cleve, Förhandl. 1876, 7, 40), α-naphthol-2 : 4-disulphonic acid (Bender, Ber. 1889, 22, 996), or (mixed with 2-nitro- and 4-nitro-α-naphthol) on α-ethoxynaphthalene-4-sulphonic acid (Witt and Schneider, Ber. 1901, 34, 3186). It is also formed when α-naphthylamine is heated with concentrated nitric acid (Balló, Ber. 1870, 3, 288); *or* when 2 : 4-dinitroacet-α-naphthalide is boiled with aqueous caustic soda (Liebermann and Hammerschlag, Annalen, 1876, 183, 273); *or* when nitrous fumes are led into an ethereal solution of α-naphthol at 0° (Schmidt, Ber. 1900, 33, 3245).

Preparation.—Direct nitration of α-naphthol, or of any of its derivatives except α-naphthol-2 : 4-disulphonic acid, results in the production of much resinous matter. In practice, either α-naphthol-2 : 4-disulphonic acid, made by dissolving α-naphthol in its own weight of sulphuric acid, is heated with dilute nitric acid at 100°, or the two α-naphtholsulphonic acids, formed when α-naphthol is sulphonated under Schaeffer's conditions (*v.* α-naphthol-2-sulphonic acid), are converted into their nitroso- derivatives by interaction with sodium nitrite and sulphuric acid in the cold, and the mixed product is then warmed with nitric acid (*cf.* Bender, *l.c.* footnote).

Properties.—It crystallises from alcohol in citron-yellow needles, m.p. 138°, does not volatilise with steam, is almost insoluble in water, and dissolves only sparingly in alcohol, ether, or benzene. It is sufficiently acidic to expel carbon dioxide from carbonates, and it forms soluble, orange-coloured salts (Martius, *l.c.*; for salts with organic bases *cf.* Norton and Lowenstein, J. Amer. Chem. Soc. 1897, 19, 923; Korczyński, Ber. 1909, 42, 174). The *sodium* salt $NaA+H_2O$, *ammonium* salt NH_4A+H_2O, and *calcium* salt CaA_2+6H_2O, crystallise in needles (Martius, *l.c.*), and were used formerly as golden-yellow dyes for silk and wool. Dinitro-α-naphthol, however, has little affinity for the fibre, being removed from it either by volatilisation or by washing.

Reactions.—(1) Nitration in the presence of much sulphuric acid at temperatures below 50° converts it into a mixture of 2 : 4 : 5-*trinitro-* (Ekstrand, Ber. 1878, 11, 162; Diehl and Merz, *ibid.* 1661) with 2 : 4 : 7-*trinitro-α-naphthol* (Kehrmann and Haberkant, *ibid.* 1898, 31, 2420). Prolonged boiling with concentrated nitric acid oxidises it to *phthalic* and *oxalic acids* (Martius, *l.c.*).

(2) When heated with alcoholic ammonia at 190°–200° it yields 2 : 4-*dinitro-α-naphthylamine* (Witt, Ber. 1886, 19, 2033).

(3) With potassium cyanide in hot alcoholic solution it yields *naphthylpurpuric acid*, or, in hot aqueous solution of its ammonium salt, a mixture of this substance with *indophan* (Sommaruga, Annalen, 1871, 157, 328).

(ii.) 4 : 5-**Dinitro-α-naphthol**, formed when 5-nitro-4-nitroso-α-naphthol is oxidised by alkaline potassium ferricyanide solution, crystallises in yellow needles, m.p. 230°, dissolves only sparingly in water, and has only feeble dyeing properties (Friedlaender, Ber. 1899, 32, 3529). The *methyl* ether, m.p. 216°, and *ethyl* ether, scales, m.p. 182°, have been described (Ullmann and Consonno, Ber. 1902, 35, 2808).

(iii.) 4 : 8-**Dinitro-α-naphthol**, obtained similarly from 8-nitro-4-nitroso-α-naphthol, has m.p. 235°, but otherwise resembles the 4 : 5- derivative in properties (Graebe and Oeser, Annalen, 1904, 335, 154).

(iv.) 1 : 6-**Dinitro-β-naphthol** is formed from β-naphthol by nitration in alcoholic solution (Wallach and Wichelhaus, Ber. 1870, 3, 846), or by means of nitrous fumes in cold ethereal solution (Schmidt, *ibid.* 1900, 33, 3246); *or* by boiling diazotised β-naphthylamine with dilute nitric acid (Graebe and Drews, *ibid.* 1884, 17, 1170).

Properties.—It crystallises in yellow needles, m.p. 195°; the *potassium* salt $KA+2H_2O$, in sparingly soluble needles; and the *ethyl ether* in yellow needles, m.p. 144° (Gaess, J. pr. Chem. 1891, [ii.] 43, 29). It dyes wool and silk yellow. When heated with alcoholic ammonia at 150°–160°, it yields 1 : 6-*dinitro-β-naphthylamine* (Kehrmann and Matis, Ber. 1898, 31, 2419).

1:8-Dinitro- and 5:8-dinitro-β-naphthol have not been isolated, but their *ethyl ethers* are known (*cf.* Gaess, *l.c.* and Onufrowicz, Ber. 1890, 23, 3360, respectively).

TRINITRONAPHTHOLS.

(i.) 2:4:5-**Trinitro-α-naphthol** (*Naphthopicric acid*) is formed when 5-nitro-4-nitroso-α-naphthol is warmed with dilute nitric acid (Graebe, Ber. 1899, 32, 2878; Graebe and Oeser, Annalen, 1904, 335, 147; Friedlaender and Scherzer, *cf.* J. Soc. Chem. Ind. 1900, 19, 339); *or*, mixed with the 2 : 4 : 7-trinitro- derivative, when 2 : 4-dinitro-α-naphthol is nitrated in the cold with nitrosulphuric acid (Kehrmann and Haberkant, Ber. 1898, 31, 2421; *cf.* Diehl and Merz, *ibid.* 1878, 11, 1662).

Properties.—It forms needles, m.p. 190°, and its *potassium* salt $KA+H_2O$, needles, easily soluble in hot, but only sparingly soluble in cold water (Kehrmann and Steiner, *ibid.* 1900, 33, 3281), It is a strong acid, dyes wool yellow, and on oxidation yields 3-*nitrophthalic acid*.

(ii.) 2 : 4 : 7-**Trinitro-α-naphthol** is the more soluble product obtained when 2 : 4-dinitro-α-naphthol is nitrated in the cold with nitrosulphuric acid (Kehrmann and Haberkant, Ber. 1898, 31, 2421), and is freed from the 2 : 4 : 5- compound by conversion into the sparingly soluble sodium salt (Kehrmann and Steiner, Ber. 1900, 33, 3286).

Properties.—It forms yellow needles, m.p. 145°, but, from benzene or acetic acid, prisms containing solvent which effloresce in the air. On oxidation it yields 4-*nitrophthalic acid* (Kehrmann and Haberkant, *l.c.*). The *potassium* salt is easily, but the *sodium* salt, yellow needles, only sparingly soluble in water.

(iii.) 2 : 4 : 8-**Trinitro-α-naphthol,** obtained by mixing 8-nitro-4-nitroso-α-naphthol with 50 p.c. nitric acid in the cold (Graebe and Oeser, Annalen, 1904, 335, 156; Friedlaender and Scherzer, *cf.* J. Soc. Chem. Ind. 1900, 19, 339), forms yellow prisms, m.p. 175°, and dyes wool yellow. The *potassium* salt KA, crystallises well (Friedlaender, Ber. 1899, 32, 3530).

(iv.) 4 : 5 : 7- (or 4 : 6 : 8-) Trinitro-α-naphthol has not been isolated, but its *methyl ether* is formed by the interaction of 1 : 3 : 5 : 8-tetranitronaphthalene and sodium methoxide. This ether crystallises in yellow needles, m.p. 186°, and on oxidation yields 3 : 5-*dinitrophthalic acid* (Will, Ber. 1895, 28, 372).

TETRANITRONAPHTHOL.

2 : 4 : 5 : 7-**Tetranitro - α - naphthol** (*Heliochrysin*) is obtained by digesting tetranitro-α-bromonaphthalene (m.p. 170·5°) with warm, concentrated sodium carbonate solution (Höchst, D. R.-P. 14954; Eng. Pat. 5327 of 1880; Merz and Weith. Ber. 1882, 15. 2714). It crystallises in yellow scales, m.p. 180°, and forms reddish-yellow salts, which dissolve only sparingly in water. The *potassium* salt $KA+1\frac{1}{2}H_2O$, prisms, is soluble in 340 parts, and the *sodium* salt $NaA+2H_2O$, scales, in about 94 parts of water at 19°. It dyes silk and wool golden-yellow, but has no technical value.

NITRONAPHTHOLSULPHONIC ACIDS.

(i.) 2-**Nitro-α-naphthol-4-sulphonic acid** can be obtained from the corresponding ethyl ether by hydrolysis with caustic potash solution. The *basic barium* salt $BaA+H_2O$ is very sparingly soluble; the yellow *potassium* and orange *basic potassium* salts form needles easily soluble in water. When its salts are heated with hydrochloric acid under pressure at 150°–160° 2-*nitro-α-naphthol* is obtained (Witt and Schneider, Ber. 1901, 34, 3189).

(ii.) 2 - **Nitro-α - naphthol - 7 - sulphonic acid,** formed from diazotised 2-nitro-4-amino-α-naphthol-7-sulphonic acid (*v.* 2 : 4-dinitro- acid) by means of copper powder, crystallises with 1 mol. H_2O in yellow needles, and its *copper* salt CuA_2+5H_2O in greenish-yellow needles. On reduction it yields 2-*amino-α-naphthol*-7-*sulphonic acid* (Finger, J. pr. Chem. 1909, [ii.] 79, 441).

(iii.) 6 - **Nitro - β - naphthol - 8 - sulphonic acid,** obtained from 6-nitro-β-naphthylamine-8-sulphonic acid by the diazo- reaction, forms long yellow prisms, with 4 mols. H_2O; the *barium* salt $BaA_2+6\frac{1}{2}H_2O$, dark-yellow prisms; *potassium* salt KA, orange prisms; *sodium* salt $NaA+5H_2O$ (?), orange-red needles (Jacchia, Annalen, 1902, 323, 122).

(iv.) 2 : 4-**Dinitro - α -naphthol - 7 - sulphonic acid** (*Naphthol yellow S; acid yellow S*) is formed by nitration of α-naphthol-7-sulphonic acid (Liebmann and Studer, Eng. Pat. 7812 of 1887; *cf.* Bender, Ber. 1889, 22, 996), *or* of α-naphthol-4 : 7-disulphonic acid (Dahl, D. R.-P. 41957 of 1886), *or* of a mixture of α-naphthol-2 : 7- and 4 : 7-disulphonic acids (Seltzer, D. R.-P. 20716 of 1882; Levinstein, Eng. Pat. 5692 of 1882; L. Vignon & Co., Eng. Pat. 9808 (prov.) of 1884; Leonhardt, Eng. Pat. 11318 of 1887), *or* of α-naphthol-2 : 4 : 7-trisulphonic acid (Badische, D. R.-P. 10785; Eng. Pat. 5305 of 1879; *cf.* Lauterbach, Ber. 1881, 14, 2028; Höchst, D. R.-P. 22545; Eng. Pat. 2178 of 1882), *or* of α-methoxynaphthalenedisulphonic acid (Dahl, Eng. Pat. 1964 of 1883).

Preparation.—(1) The melt obtained by the trisulphonation of α-naphthol (10 kilos.), after being diluted with water, is mixed gradually with nitric acid of sp.gr. 1·38 (25 kilos.) below 50°, and the reaction completed either at 50° or by allowing the mixture to remain in the cold for 12 hours. From the solution dinitro-α-naphtholsulphonic acid separates in needles, the mother liquors containing other nitration products, of which nothing definite is known (Badische, *l.c.*).

(2) The mixed α-naphtholdisulphonic acids of Leonhardt & Co.'s Eng. Pat. 11318, after conversion into nitroso- compounds by means of sodium nitrite, are nitrated at 50° with nitric acid, also in the proportion of 25 kilos. to every 10 kilos. of α-naphthol sulphonated (Leonhardt, *l.c.*).

Salts.—The *acid* crystallises from hydrochloric acid in yellow needles. The *barium* and *basic potassium* K_2A salts are very sparingly soluble; the *acid potassium* KA, *basic sodium* Na_2A, and *ammonium* salts are readily soluble in water and are orange-yellow (Lauterbach, *l.c.*).

It is a strong acid, has considerable tinctorial power, is used as a yellow dye for wool, and, unlike 2:4-dinitro-α-naphthol, does not volatilise from the fibre, and is not poisonous.

Reactions.—(1) On oxidation with nitric acid of sp.gr. 1·33 it is converted into *β-sulphophthalic acid* (Graebe, Ber. 1885, 18, 510; Rée, Chem. Soc. Trans. 1886, 49, 511).

(2) On reduction with stannous chloride and hydrochloric acid it yields 2-*nitro*-4-*amino-α-naphthol*-7-*sulphonic acid* (Lauterbach, *l.c.*; Finger, J. pr. Chem. 1909, [2] 79, 441); but in ammoniacal solution with sodium sulphide, the isomeric 4-*nitro*-2-*amino-α-naphthol*-7-*sulphonic acid* is the product (Gesellsch., D. R.-P. 189513 of 1905; Eng. Pat. 7535 of 1906).

(v.) **2:4-Dinitro-α-naphthol-8-sulphonic acid** (*brilliant yellow*) is formed when sodium nitroso-α-naphthol-8-sulphonate in dilute sulphuric acid solution, is mixed with nitre in the cold, the reaction being completed on a water-bath (Schöllkopf, D. R.-P. 42304 of 1886); *or* when sodium α-naphthol-4:8-disulphonate in aqueous solution is heated with dilute nitric acid at 60°–70° (Schöllkopf, D. R.-P. 40571; Eng. Pat. 15775 of 1885); or its nitroso- derivative is boiled with nitric acid (Karpeles, *cf.* J. Soc. Chem. Ind. 1898, 17, 837); *or* when sodium α-naphthol-2:4:8-trisulphonate dissolved in sulphuric acid is mixed with nitrosulphuric acid at 20° (Dressel and Kothe, Ber. 1894, 27, 2145).

Properties.—The *potassium* salt $KA+H_2O$ (Karpeles, *l.c.*), and the *sodium* salt NaA (Dressel and Kothe, *l.c.*) form sparingly soluble yellow needles, and in an acid bath dye silk and wool a more orange shade than that produced with naphthol yellow S. As a dyestuff it has no technical value.

(vi.) **1:6-Dinitro-β-naphthol-8-sulphonic acid** (*croceïn yellow*) is produced by warming sodium β-naphthol-8-sulphonate with dilute nitric acid at 30°–40° until nitration is complete (Bayer, D. R.-P. 18027; Eng. Pat. 1225 of 1881; Nietzki and Zübelen, Ber. 1889, 22, 454). The *potassium* salt, KA, forms yellow needles, but the *basic potassium* salt K_2A, sparingly soluble, yellow scales. It dyes wool yellow, but has little tinctorial power.

VII.—AMINOHYDROXY-DERIVATIVES.

Introductory.—All the fourteen isomeric aminonaphthols theoretically possible have been prepared, and are obtained by methods which usually afford evidence of their structure. Summarised, these methods are—

(1) Reduction of the corresponding nitronaphthols;

(2) Reduction of nitroso- or azo- derivatives of α- or β-naphthol;

(3) Fusion of α- or β-naphthylaminemonosulphonic acids with caustic alkali, α-naphthylamine-4-sulphonic acid being an exception, as it furnishes α-naphthol-4-sulphonic acid under these conditions (*cf.* Aktienges., D. R.-P. 46307 of 1888);

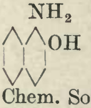
(4) Fusion of naphtholmonosulphonic acids with sodamide;

(5) Interaction of dihydroxynaphthalenes with ammonia, or with ammonium bisulphite and ammonia.

The only instances of change in structure observed in any of these reactions occur with the β-naphthol-6-, 7-, and 8-sulphonic acids, all of which yield 5-amino-β-naphthol on fusion with sodamide.

The aminonaphthols are basic compounds forming salts with acids; but, nevertheless, dissolve readily in alkalis. In solution, or in the moist state, they are readily oxidised in the air, and those which contain the radicles relatively in 1:2- or 1:4- positions form naphthaquinones on oxidation with ferric chloride, chromic acid, or nitrous acid in acid solution.

AMINONAPHTHOLS.[1]



(i.) **1-Amino-2-naphthol** (1-*amino-β-naphthol*) is formed when 1-nitroso-β-naphthol is reduced by ammonium sulphide (Stenhouse and Groves, Chem. Soc. Trans. 1877, 32, 52), or by stannous chloride (Groves, *ibid.* 1884, 45, 296; Paul, *cf.* J. Soc. Chem. Ind. 1897, 16, 733); *or* when 1-nitro-β-naphthol is reduced by tin and hydrochloric acid (Jacobson, Ber. 1881, 14, 806; Zincke, Annalen, 1892, 268, 273).

Preferably, it is obtained when benzeneazo-β-naphthol (Liebermann, Ber. 1883, 16, 286; Groves, *l.c.*), orange II (Liebermann, Ber. 1881, 14, 1311; Witt, *ibid.* 1888, 21, 3472; Grandmougin and Michel, *ibid.* 1892, 25, 981; Russig, J. pr. Chem. 1900, [ii.] 62, 55; Paul, *l.c.*), or other azo- derivatives of β-naphthol are reduced either by stannous chloride and hydrochloric acid or (Grandmougin, Ber. 1906, 39, 2495) by sodium hyposulphite. Its production electrolytically from orange II has been described (Boehringer, D. R.-P. 121835; Eng. Pat. 13542 of 1900), and it can be obtained from the 4-sulphonic acid by means of sodium amalgam (Friedlaender and Reinhardt, Ber. 1894, 27, 241).

Properties.—It forms scales, sparingly soluble in boiling water, and in alkaline or ammoniacal solution rapidly becomes brown on exposure to air. Ferric chloride and acid oxidising agents convert it into [β-]*naphthaquinone* (for references *cf.* Grandmougin and Michel, *l.c.*). The *hydrochloride* B·HCl forms needles (Jacobson, *l.c.*); N-*acetyl* derivative, scales, m.p. 235° (Michel and Grandmougin, Ber. 1892, 25, 3433); *diacetyl* derivative, m.p. 116° (Grandmougin, *l.c.*); *dibenzoyl* derivative, silky needles, m.p. 235·5° (Sachs, Ber. 1906, 39, 3024); and *ethyl ether*, prisms, m.p. 51°, b.p. 300°–302° (Cassella, D. P. Anm. C. 2883 of 1889; Gaess, J. pr. Chem. 1891, [ii.] 43, 27). It has been used in the production of *oxazine* dyes (Bayer, D. R.-P. 77120; Eng. Pat. 8093 of 1893).

Reactions.—It couples in acetic acid solution with diazotised bases forming *azo-* dyes (Aktienges., D. R.-P. 77256, 79103; Eng. Pat. 13833 of 1893), but with nitrous acid in the presence

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[1] In this section, which includes the aminonaphthols, aminonaphtholsulphonic acids and diaminonaphthols, a departure is made from the rule that the numbering indicates the position occupied by the substituted group (NH_2) relatively to the characteristic radicle (OH) of the substance (naphthol) in which substitution is supposed by the name (aminonaphthol) to have occurred. This departure has been made to avoid confusion when German Patents, in which the numbering is given with reference to the amino-group, are consulted. The alternative numbering, based on the rule, is given in brackets.

of mineral acids diazotisation does not occur, although in neutral solution with copper salts present, *naphthalene*-1-*diazo*-2-*oxide* is obtained (Geigy, D. R.-P. 172446; Eng. Pat. 10235 of 1904).

(ii.) **1-Amino-3-naphthol**[1] (4-*amino-β-naphthol*) is formed when α-naphthylamine-3-sulphonic acid is fused with caustic potash at 250°–260° (Friedlaender, Ber. 1895, 28, 1952). It crystallises in needles, decomp. at 185°, is sparingly soluble in water, gives a violet-brown colouration with ferric chloride, forms easily soluble salts, couples readily, and yields an unstable *diazo*- compound. The N-*acetyl* derivative forms needles, m.p. 179° (Friedlaender, *l.c.*), and has been used in the production of *oxazine* dyes (Bayer, D. R.-P. 77802; Eng. Pat. 15045 of 1893); the *dibenzoyl* derivative, scales, m.p. 309°–310° (Sachs, Ber. 1906, 39, 3024).

Reactions.—(1) By prolonged boiling with acidified water, its amino- group is eliminated as ammonia, and 1 : 3-*dihydroxynaphthalene* is formed (Friedlaender, *l.c.*; Friedlaender and Rüdt, Ber. 1896, 29, 1609).

(2) When heated with aqueous ammonia under pressure, it is converted into 1 : 3-*diaminonaphthalene* (Friedlaender, *l.c.*).

(3) On sulphonation with monohydrate at the ordinary temperature, it yields 1-*amino*-3-*naphthol*-4-*sulphonic acid* (Friedlaender and Rüdt, *l.c.*).

(iii.) **1-Amino-4-naphthol** (4-*amino-α-naphthol*) can be prepared from 4-nitroso-α-naphthol (Grandmougin and Michel, Ber. 1892, 25, 976); *or* from 4-nitro-α-naphthol (Liebermann and Dittler, Annalen, 1876, 183, 247); *or* from α-naphthol-orange (Liebermann and Jacobson, *ibid.* 1882, 211, 61; Seidel, Ber. 1892, 25, 423; Russig, J. pr. Chem. 1900, [ii.] 62, 30) or other *p*-azo- derivatives of α-naphthol, by reduction with stannous chloride and hydrochloric acid. It is also formed when 4-amino-α-naphthol-2-carboxylic acid is heated at 230°, carbon dioxide being eliminated (Nietzki and Guitermann, Ber. 1887, 20, 1276).

Properties.—It crystallises in very soluble needles, which, when moist, rapidly become blue on exposure to the air, forms easily soluble salts, does not couple, and has not been diazotised. The N-*formyl* derivative forms rosettes, m.p. 168° (Gaess, D. R.-P. 149022 of 1902); the *diacetyl* derivative, prisms, m.p. 158° (Grandmougin and Michel, *l.c.*); the *dibenzoyl* derivative, rhombic crystals, m.p. 215° (Sachs, Ber. 1906, 39, 3026); the N-*dimethyl* derivative, prisms, m.p. 113° (Friedlaender and Lagodzinski (*cf.* J. Soc. Chem. Ind. 1897, 16, 793); and the *ethyl ether*, needles, m.p. 96° (Heermann, J. pr. Chem. 1892, [ii.] 45, 545; *cf.* Cassella, D. P. Anm. C. 2883 of 1889).

Reactions.—(1) It is converted into [α-]*naphthaquinone* by oxidising agents (*cf.* Liebermann, Ber. 1881, 14, 1796), including nitrous acid (*cf.* Badische, D. R.-P. 55404 of 1889).

(2) When its hydrochloride is heated with methyl or ethyl alcohol under pressure at 170°–180°, the corresponding *monoalkyl ether* of 1 : 4-*dihydroxynaphthalene* is obtained (Höchst, D. R.-P. 234411 of 1910).

(3) On sulphonation with 10 p.c. anhydro-acid at 30°–40°, it gives 1-*amino*-4-*naphthol*-3-*sulphonic acid* (Seidel, *l.c.*; *cf.* Conrad and Fischer, Annalen, 1893, 273, 114).

1-Acetylamino-4-naphthol (*naphthacetol*), obtained by acetylating the hydrochloride in presence of sodium acetate (Witt, D. R.-P. 90596; Eng. Pat. 20676 of 1896; Witt and Dedichen, Ber. 1896, 29, 2948), forms needles, m.p. 187°, moderately soluble in warm water, and couples in alkaline solution with diazotised bases, giving ortho-*azo*- dyes (Witt, *l.c.*; D. R.-P. 93312; Eng. Pat. 20676 of 1896). The *ethyl ether* (naphthacetin) forms needles, m.p. 189°, soluble in 7·4 parts of boiling alcohol (Henriques, Ber. 1892, 25, 3060; Heermann, *l.c.*).

(iv.) **1-Amino-5-naphthol** (5-*amino-α-naphthol*) can be obtained from α-naphthylamine-5-sulphonic acid by digestion with 60 p.c. caustic soda solution at 240°–250° (Aktienges., D. R.-P. 49448 of 1889; *cf.* Friedlaender and Lagodzinski, J. Soc. Chem. Ind. 1897, 16, 793); *or* from 1 : 5-diaminonaphthalene either by digestion with dilute mineral acids under pressure (*cf.* Aktienges., D. P. Anm. A. 4029 of 1894), or, in 80 p.c. yield, by the bisulphite method (Bucherer, J. pr. Chem. 1904, [ii.] 69, 84). It is also formed from α-naphthol, *or* from α-naphthol-5-sulphonic acid by fusion with sodamide and naphthalene at 190° or 230° respectively (Sachs, D. R.-P. 173522 of 1904; 181333; Eng. Pat. 22412 of 1905; Ber. 1906, 39, 3018).

Properties.—In alkaline solution it undergoes little change on exposure to the air. The *hydrochloride* is crystalline, and the *dibenzoyl* derivative forms rhombic scales, m.p. 276°. The *azo*-dye obtained by coupling it with diazotised naphthionic acid is not red as is the case with its isomerides, but cornflower-blue in colour (Sachs, *l.c.*).

Reactions.—(1) It yields 1 : 5-*dihydroxynaphthalene* by prolonged heating with dilute hydrochloric acid at 180° (*cf.* Aktienges., D. P. Anm. A. 4029 of 1894), or by the bisulphite reaction (*cf.* Bucherer, J. pr. Chem. 1904, [ii.] 69, 84).

(2) When heated with ammonium sulphite solution and ammonia at 125°, it is converted into 1 : 5-*diaminonaphthalene* (Badische, D. R.-P. 117471 of 1899; Eng. Pat. 1387 of 1900).

(3) With sulphuric acid in the cold it gives 1-*amino*-5-*naphthol*-6-*sulphonic acid* (Aktienges., D. R.-P. 68564 of 1891); but with 23 p.c. anhydro- acid at 100° a *disulphonic acid* is formed (*ibid.*, D. P. Anm. A. 3767 of 1894).

(4) It can be diazotised (*cf.* Bayer, D. R.-P. 79166 of 1891), and it couples in acid or alkaline solution with diazotised bases forming *monoazo*-dyes (*cf.* Bayer, D. R.-P. 66688; Eng. Pat. 5984 of 1891; Cassella, D. R.-P. 78875; Eng. Pat. 24715 of 1893; D. R.-P. 95190; Eng. Pat. 24134 of 1896; Bayer, D. R.-P. 174557 of 1902; 180481; Eng. Pat. 26132 of 1903).

(v.) **1-Amino-6-naphthol** (5-*amino-β-naphthol*) is formed when 5-nitro-β-naphthol is reduced by stannous chloride and hydrochloric acid (Friedlaender and Szymanski, Ber. 1892, 25, 2079); *or* when α-naphthylamine-6-sulphonic acid is fused with caustic alkalis (Bayer, D. R.-P. 74060; Eng. Pat. 11533 of 1892); *or* when 1-amino-6-naphthol-4-sulphonic acid interacts with sodium amalgam (Friedlaender and Kielbasinski, Ber. 1896, 29, 1979). It is also formed

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[1] The substance described as αγ-aminonaphthol (Gesellsch., D. R.-P. 55059 of 1889), is probably a mixture of 1-amino-6- and 1-amino-7-naphthol (Friedlaender and Szymanski, Ber. 1892, 25, 2076).

when β-naphthol, or β-naphthol-6-, or 7-, or 8-sulphonic acid is heated with sodamide and naphthalene at 230° (Sachs, D. R.-P. 173522 of 1904; 181333; Eng. Pat. 22412 of 1905; Ber. 1906, 39, 3016).

Properties.—It crystallises in scales, m.p. 186°, shows blue fluorescence in ammoniacal solution, rapidly darkens when moist on exposure to the air, and with ferric chloride gives a dark violet colouration. The following derivatives have been described: N-*acetyl*, needles, m.p. 215°–216° (Kehrmann and Deuk, Ber. 1900, 33, 3296; Sachs, Ber. 1906, 39, 3025); *diacetyl*, m.p. 187°; N-*benzoyl*, needles, m.p. 152°; *dibenzoyl*, needles, m.p. 223°; *picrate*, yellow needles, m.p. 183° (Sachs, *l.c.*).

Reactions.—It can be diazotised (Sachs, *l.c.*), and it couples in alkaline solution with diazotised bases (1 or 2 mols). forming *azo-* dyes (*cf.* Cassella, D. R.-P. 78875; Eng. Pat. 24715 of 1893; D. R.-P. 86848 of 1894).

(vi.) **1-Amino-7-naphthol** (8-*amino-β-naphthol*) is obtained from 8-nitro-β-naphthol by reduction with stannous chloride and hydrochloric acid (Friedlaender and Syzmanski, Ber. 1892, 25, 2082); *or* from α-naphthylamine-7-sulphonic acid by digestion with 60 p.c. caustic soda solution at 250° (Cassella, D. R.-P. 69458 of 1891; Friedlaender and Zinberg, Ber. 1896, 29, 41).

Properties.—It crystallises from water in needles, decomp. 212°–218° (m.p. 206°, Cassella, *l.c.*), gives with ferric chloride a greenish-blue colouration, and in acid or alkaline solution shows blue fluorescence. The N-*acetyl* derivative forms tablets, m.p. 165° (Friedlaender and Zinberg, *l.c.*); the *dibenzoyl* derivative, needles, m.p. 208° (Sachs, Ber. 1906, 39, 3026); and the *ethyl ether*, prisms, m.p. 67°, b.p. 315° (Gaess, J. pr. Chem. 1891, [ii.] 43, 28).

Reactions.—(1) With sulphuric acid at 20°–30°, it yields 1-*amino*-7-*naphthol*-(4)-*sulphonic acid* (Cassella, D. R.-P. 75066 of 1891), and at 100°, or with anhydro- acid, a *disulphonic acid* (Cassella, D. R.-P. 69458 of 1891).

(2) It can be diazotised, and it couples in acid or in alkaline solution with diazotised bases (1 or 2 mols.) forming *azo-* dyes (*cf.* Cassella, D. R.-P. 78875; Eng. Pat. 24715 of 1893; D. R.-P. 84610, 86848; Eng. Pat. 22273 of 1894; Bayer, D. R.-P. 164319; Eng. Pat. 18569 of 1902; D. R.-P. 197034, 198137; Eng. Pat. 18698 of 1907; Friedlaender and Zinberg, *l.c.*).

(vii.) **1-Amino-8-naphthol** (8-*amino-α-naphthol*) can be prepared by fusing α-naphthylamine-8-sulphonic acid with caustic alkali at 230°–240° (Badische, D. R.-P. 55404; 62289 of 1889; Eng. Pat. 9676 of 1890; Fichter and Gaguer, Ber. 1906, 39, 3331); *or* by heating 1:8-diaminonaphthalene either with dilute mineral acids under pressure (*cf.* Aktienges., D. P. Anm. A. 4029 of 1894), or with sodium bisulphite solution (Bucherer, J. pr. Chem. 1904 [ii.] 69, 58); *or* by digesting 1:8-diaminonaphthalene-4-sulphonic acid with 25 p.c. sulphuric acid, or 1-amino-8-naphthol-5-sulphonic acid with 20 p.c. sulphuric acid under pressure at 135°–140° (Cassella, D. R.-P. 73381 of 1893). It is also formed by heating α-naphthol-8-sulphonic acid with sodamide and naphthalene at 230° (Sachs, D. R.-P. 173522 of 1904; Eng. Pat. 22412 of 1905; Ber. 1906, 39, 3018).

Properties.—It crystallises in needles, m.p. 95°–97°, is sparingly soluble in cold, and its *sulphate* in hot, water (Badische, *l.c.*; *cf.* Friedlaender and Silberstern, Monatsh. 1902, 23, 516). The N-*acetyl* derivative, forms needles, m.p. 168°–169°; the *diacetyl* derivative, needles, m.p. 118·5°; the *nitroso-* derivative, brown needles, decomp. 175°–180° (Fichter and Gaguer, *l.c.*); and the N-*dimethyl* derivative, hexagonal tablets, m.p. 112° (Gesellsch., D. R.-P. 50142 of 1889).

Reactions.—(1) With 75 p.c. sulphuric acid at 130°–160°, it gives 1-*amino*-8-*naphthol*-7-*sulphonic acid* (Badische, D. R.-P. 82900 of 1894), but with sulphuric acid at 15°–20° it yields a mixture of this acid with the 5-*sulphonic acid* as chief product (Badische, D. R.-P. 62289 of 1889; 77937, 82900, 84951 of 1894), and at 100° the 5 : 7-*disulphonic acid* (Badische, D. R.-P. 62289, 82900).

(2) It can be diazotised (Badische, D. R.-P. 62289; *cf.* Fichter and Gaguer, *l.c.*) and it couples in alkaline solution with diazotised bases forming *azo-* dyes (*cf.* Cassella, D. R.-P. 78875; Eng. Pat. 24715 of 1893; Friedlaender and Silberstern, *l.c.*).

Its sulphite, when diazotised, has been used for the production of *azo*-dyes (Bayer, D. R.-P. 211381; Eng. Pat. 11878 of 1908).

(viii.) **2-Amino-1-naphthol** (2-*amino-α-naphthol*) is obtained by reducing 2-nitroso-α-naphthol with stannous chloride (Liebermann and Jacobson, Annalen, 1882, 211, 55; Grandmougin and Michel, Ber. 1892, 25, 974); *or* 2-nitro-α-naphthol with tin and hydrochloric acid (Liebermann and Dittler, Annalen, 1876, 183, 248); *or* [β-]naphthaquinonephenylhydrazone with sodium hyposulphite (Grandmougin, Ber. 1906, 39, 2496; *cf.* Zincke and Rathgen, *ibid.* 1886, 19, 2483). It is also formed from 2-amino-1-naphtholsulphonic acids by interaction with sodium amalgam (Gattermann and Schulze, Ber. 1897, 30, 51).

Properties.—It crystallises in needles, and is only sparingly soluble in cold water. When dissolved in ammonia and shaken with air it gives a green solution, on the surface of which a characteristic violet skin forms (Liebermann and Jacobson, *l.c.*). The N-*acetyl* derivative, needles, m.p. 128°–129°, which couples with diazotised bases; *diacetyl* derivative, needles, m.p. 116° (Grandmougin, *l.c.*); and N-*dialkyl* derivatives, which can be diazotised (Grandmougin and Michel, Ber. 1892, 25, 975), have been described. It has been used in the production of *oxazine* dyes (Bayer, D. R.-P. 77120; Eng. Pat. 8093 of 1893).

Reactions.—(1) Nitrous acid oxidises it to [β-]*naphthaquinone* (Michel and Grandmougin, Ber. 1892, 25, 3430), but in presence of copper salts converts it in neutral solution into *naphthalene-2-diazo-1-oxide* (Geigy, D. R.-P. 172446; Eng. Pat. 10235 of 1904).

(2) When boiled with sodium bisulphite solution it gives 1-*amino*-8-*naphthyl sulphite* with only a very small proportion of the *ester* of 1 : 8-*dihydroxynaphthalene* (Bucherer, J. pr. Chem. 1904, [ii.] 69, 61).

(3) On sulphonation with 10 p.c. anhydro-acid at 40°–50° it furnishes a *monosulphonic acid* (Sandoz, D. R.-P. 69228 of 1892; Reverdin and de la Harpe, Ber. 1893, 26, 1281).

(ix.) **2-Amino-3-naphthol** (3-*amino-β-naphthol*) is formed when 2 : 3-dihydroxynaphthalene is heated with 30 p.c. ammonia solution at 140°–150° (Höchst, D. R.-P. 73076 of 1893; Friedlaender and Zakrzewski, Ber. 1894, 27, 763), or with ammonium sulphite solution and ammonia at 80°, the product afterwards being acidified (Badische, D. R.-P. 117471 of 1899; Eng. Pat. 1387 of 1900). It crystallises in needles, m.p. 234°, sparingly soluble in cold water, and its N-*benzoyl* derivative in hexagonal scales, m.p. 233·5° (Sachs, Ber. 1906, 39, 3024). By coupling it in alkaline solution with diazotised bases, *disazo-* dyes have been obtained (*cf.* Bayer, D. R.-P. 99468; Eng. Pat. 28090 of 1897).

(x.) **2-Amino-4-naphthol** (3-*amino-α-naphthol*) has been prepared by heating 1 : 3-dihydroxynaphthalene with ammonia at 130°–140°. Its *hydrochloride* is sparingly soluble; its N-*phenyl* derivative forms needles, and is rapidly oxidised in alkaline solution to [*α*-]*naphthaquinoneanil*. The *azo-* dyes derived from it resemble closely those from 1-amino-3-naphthol (Friedlaender and Rüdt, Ber. 1896, 29, 1612).

(xi.) **2-Amino-5-naphthol** (6-*amino-α-naphthol*) can be obtained from *β*-naphthylamine-5-sulphonic acid by fusion with caustic potash at 260°–270° (Bayer, D. P. Anm. F. 7372; Eng. Pat. 5267 of 1894); *or* from 2-amino-5-naphthol-8-sulphonic acid by means of sodium amalgam (Friedlaender and Lucht, Ber. 1893, 26, 3034), but no description of it has been published. On sulphonation it yields a mixture of two *monosulphonic acids*, of which the less soluble constitutes 30 p.c. of the product (Bayer, *l.c.*).

(xii.) **2-Amino-6-naphthol** (6-*amino-β-naphthol*), obtained from 2-amino-6-naphthol-4-sulphonic acid by means of sodium amalgam, crystallises in scales, m.p. 190°–195° (Jacchia, Annalen, 1902, 323, 127); its *dibenzoyl* derivative, in needles, m.p. 233·5° (Sachs, Ber. 1906, 39, 3025); and its *ethyl ether* in pyramids, m.p. 90°–91°, b.p. 330° (Gaess, J. pr. Chem. 1891, [ii.] 43, 28). It couples in alkaline solution with diazotised *o*-aminophenolsulphonic acids forming *monoazo-* dyes (Bayer, D. R.-P. 164516; Eng. Pat. 18569 of 1902).

(xiii.) **2-Amino-7-naphthol** (7-*amino-β-naphthol*) is formed when *β*-naphthylamine-7-sulphonic acid is digested with 50 p.c. caustic soda solution at 260°–300° (Gesellsch., D. R.-P. 47816 of 1888); *or* when 2 : 7-diaminonaphthalene is boiled with sodium bisulphite solution, and the product made alkaline with caustic soda (Badische, D. R.-P. 134401 of 1899); *or* when 2 : 7-dihydroxynaphthalene is heated either with ammonia under pressure (Gesellsch., D. R.-P. 55059 of 1889), or with ammonium sulphite solution and ammonia in a reflux apparatus (Franzen and Deibel, J. pr. Chem. 1908, [ii.] 78, 155). It is also obtained, mixed with 1-amino-6-naphthol (Sachs, Ber. 1906, 39, 3017), when *β*-naphthol-7-sulphonic acid is heated with sodamide and naphthalene at 230° (Sachs, D. R.-P. 173522 of 1904; Eng. Pat. 22412 of 1905).

Properties.—It crystallises in needles, m.p. 201° (Franzen and Deibel, *l.c.*; *cf.* Gesellsch., *l.c.*), and is sparingly soluble in water. The N-*acetyl* derivative forms scales, m.p. 220° (Kehrmann and Wolff, Ber. 1900, 33, 1538); the *dibenzoyl* derivative, needles, m.p. 187·5° (Sachs, *l.c.*); and N-*phenyl* derivative, needles, m.p. 160° (Kalle, D. R.-P. 60103 of 1891; Fischer and Schütte, Ber. 1893, 26, 3087).

Reactions.—(1) When heated with 40 p.c. ammonium sulphite solution and 20 p.c. ammonia at 130°–140°, it yields 2 : 7-*diaminonaphthalene* (Bucherer, J. pr. Chem. 1904, [ii.] 69, 89).

(2) It can be diazotised (*cf.* Bayer, D. R.-P. 79166 of 1891), and it couples in acid or in alkaline solution with diazotised bases forming *azo-* dyes (*cf.* Cassella, D. R.-P. 71329 of 1891; 78875; Eng. Pat. 24715 of 1893; D. R.-P. 117298; Eng. Pat. 16149 of 1899).

The trimethylammonium chloride, obtained by heating the aminonaphthol in alkaline alcoholic solution with methyl chloride under pressure at 110° (Geigy, D. R.-P. 90310 of 1896), couples with diazotised bases forming *azo-* dyes (Geigy, *l.c.*; Höchst, D. R.-P. 97244; Eng. Pat. 27896 of 1896).

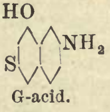
(xiv.) **2-Amino-8-naphthol** (7-*amino-α-naphthol*), obtained either by fusing *β*-naphthylamine-8-sulphonic acid with caustic alkali at 260°–270° (Bayer, D. P. Anm. F. 7335; Eng. Pat. 5148 of 1894), *or* by heating 1 : 7-dihydroxy-*β*-naphthoic acid with ammonia at 170°–180° (Friedlaender and Zinberg, Ber. 1896, 29, 40), crystallises in scales, m.p. 158° (Bayer, *l.c.*), and its N-*acetyl* derivative in needles, m.p. 210°–211° (Friedlaender and Zinberg, *l.c.*).

Reactions.—(1) With sulphuric acid at 20°–30°, it yields a mixture of the 'V' and 'Sch.' 2-*amino*-8-*naphtholmonosulphonic acids* in about equal amount (Bayer, *l.c.*).

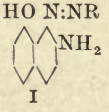
(2) It couples in acetic acid or in alkaline solution with diazotised bases forming *azo-* dyes (Bayer, D. P. Anm. F. 25069 of 1908; Friedlaender and Zinberg, *l.c.* 42).

AMINONAPHTHOLSULPHONIC ACIDS.

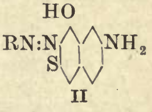
Introductory.—Aminonaphtholsulphonic acids came into use as components of azo- dyes about the year 1889 (*cf.* Cassella, D. R.-P. 55024, 55648; Eng. Pat. 16699 of 1889), when the discovery was made that certain of them have the property of forming two series of these dyes, tinctorially as well as chemically different in character. Provided the NH$_2$ and OH radicles be contained in different nuclei, and the position of the sulphonic group or groups be such[1] as to determine the entry of the diazo-complex only into *ortho-* positions relatively to these radicles, coupling in weak acid solution will lead to the production of an azo-dye of type I, and in alkaline solution to one of type II:—



G-acid.



I



II

The compounds of type I do not couple further in *acid* solution and cannot be diazotised; those of type II, on the other hand, are diazotisable. In many cases monoazo- dyes of either type will couple in *alkaline* solution, to form disazo- dyes, containing the aminonaphtholsulphonic acid as the middle component, but there are exceptions. For example, of the

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[1] Compare pp. 570, 589, 601, 616.

two monoazo- dyes obtained from G-acid (I and II, p. 635), only that numbered I can be coupled further under any conditions. This capacity for further coupling cannot be foreseen, and the reasons which promote or inhibit it are unknown.

The importance of the aminonaphtholsulphonic acids for the production of azo- dyes, and the extent to which this group of naphthalene derivatives has been explored, can be gauged from the tables which follow (see also p. 567).

The chief methods employed for the preparation of acids of this series are—

(1) Reduction of nitroso- or azo- derivatives of naphtholsulphonic acids with tin or stannous chloride and hydrochloric acid, or with sodium hyposulphite. By these methods the 1 : 2-, 1 : 4-, and 2 : 1-aminonaphtholsulphonic acids are produced;

(2) Digestion of naphthylaminedi- or trisulphonic acids with concentrated caustic alkali solution at 180°–200°. With sulphonic acids from *α-naphthylamine*, the SO_3H group in position 8 is the most easily displaced, then that in 5, the group in 2 or 4 resisting displacement; with acids from *β-naphthylamine*, the SO_3H group in position 4, 5, or 8 is easily displaced, but that in 1 or 6 resists displacement.

If the temperature be too high, the amino-group also may be eliminated, and a dihydroxynaphthalenesulphonic acid result from the fusion.

(3) Heating diaminonaphthalenesulphonic acids with dilute mineral acids or water under pressure, or with sodium bisulphite solution at the boiling-point, the ester formed in the latter case being afterwards decomposed with alkali.

(4) Heating dihydroxynaphthalenesulphonic acids with aqueous ammonia under pressure, the replacement by NH_2 being effected more easily when the OH radicle is in a *β*- position.

(5) Sulphonation of certain aminonaphthols with sulphuric acid or anhydro-acid.

Reference to the tables will show that the constitution of most of the acids is known. This has been determined chiefly by a knowledge of the structure of the naphthylaminesulphonic acid employed in the second method, or of the naphtholsulphonic acid, the nitroso- or azo-derivative of which is reduced when the first method is used. Confirmatory evidence can be obtained in many cases by a study of the interaction of the acid with sodium amalgam, as SO_3H groups in *α*- positions are more readily eliminated than those in *β*- positions (Friedlaender and Lucht, Ber. 1893, 26, 3028); or of the hydrolytic action of 20 p.c. hydrochloric acid at the boiling point, which occurs only when the OH and SO_3H radicles occupy relatively the 1 : 4- position (Bucherer and Uhlmann, J. pr. Chem. 1909, [ii.] 80, 204).

Only scanty information is given in the Patent literature about the properties of the aminonaphtholsulphonic acids and their salts. Apart from their behaviour towards nitrous acid, and towards diazotised bases (*cf.* Cassella, D. R.-P. 82676 of 1894), these compounds are usually distinguished by the fluorescence or non-fluorescence of solutions of their alkali salts and by the colourations given with ferric chloride or bleaching powder solutions (*cf.* Aktienges., D. R.-P. 68564 of 1891; Bayer, D. R.-P. 75317 of 1891). They reduce ammoniacal silver nitrate solution in the cold, and in some cases separate silver from an acid solution of the salt (*cf.* Bayer, D. R.-P. 81621 of 1893). In the tables which follow, references to fluorescence and to the colourations with bleaching powder solution are usually omitted for want of room.

Allusion has been made to the fact that many of the aminonaphtholsulphonic acids furnish two series of monoazo- dyes, according as coupling takes place in an acid or in an alkaline bath. Among acids of this type are included all that are most valuable for the production of disazo- dyes, as, for example, the G-, J-, and S-monosulphonic, and the B-, H-, and K-disulphonic acids.

The acids derived from 1-amino-8-naphthol, of which all the possible monosulphonic, and many disulphonic acids have been prepared, divide themselves into two groups: (*a*) those which furnish *ortho*-azo- dyes by coupling with diazotised bases, viz. the 4- and 5- (or S-) monosulphonic, and the 3 : 5- (or B-), 3 : 6- (or H-) and 4 : 6- (or K-) disulphonic acids, and are of much importance; (*b*) those, comprising the remainder, which form *para*-azo- dyes and have no industrial value.

Among the aminonaphtholsulphonic acids derived from *β*-naphthylamine, two, *viz.* the G- and J-acids, are largely used. They, too, give *ortho*-azo- dyes when coupled with diazotised bases, and J-acid is remarkable as it endows azo- derivatives, of which it is a component, with the property of dyeing unmordanted cotton (*v.* p. 567).

Of the other aminonaphtholsulphonic acids, mention may be made of the 2 : 1- and 1 : 2-derivatives, which are oxidised by nitrous acid, but when diazotised in the absence of free acid (*v.* p. 571), furnish valuable *ortho*-hydroxyazo-dyes.

By substitution of alkyl, acyl, or aryl radicles in the NH_2 group, a series of derivatives, chiefly from 1-amino-8-naphthol-, 2-amino-5-naphthol-, and 2-amino-8-naphthol-sulphonic acids, has been obtained. For an account of some of these, reference may be made to the following Patents:—

Alkyl (Cassella, D. R.-P. 73128 of 1892; Eng. Pat. 5407 of 1893; Geigy, D. R.-P. 91506 of 1895; Eng. Pat. 2771 of 1896);

Acetyl (Höchst, D. R.-P. 129000 of 1899; Eng. Pat. 17366 of 1898; Bayer, D. R.-P. 206455 of 1907).

Aryl monosulphonic acids (Cassella, D. R.-P. 79014; Eng. Pat. 11157 of 1894; D. R.-P. 80417 of 1894; Leonhardt, D. R.-P. 114248 of 1896; Badische, D. R.-P. 122570; Eng. Pat. 18726 of 1900); disulphonic acids (Bayer, D. R.-P. 181929, 179829 of 1905; Eng. Pat. 5749 of 1906);

Nitroacyl, *nitroaryl*, etc. (Gesellsch., D. R.-P. 101286 of 1897; 170045 of 1902).

These substituted acids, or their nitroso-derivatives, by coupling with diazotised bases, furnish monoazo- dyes which differ in shade and degree of fastness from those obtained with the respective aminonaphtholsulphonic acids, and belong exclusively to the type numbered II on the preceding page.

Aminonaphtholmonosulphonic Acids.

Constitution.	Preparation.	Acids, Salts and Reactions.
N:O:S		
1:2:4	(1) Reduction of nitroso-β-naphthol with sulphurous acid (Böniger, Ber. 1894, 27, 23). (2) Action of sodium bisulphite on [β]-naphthaquinone-α-chlorimide (Friedlaender and Reinhardt, Ber. 1894, 27, 241).	*Acid*, $HA+\frac{1}{2}H_2O$, very sparingly soluble needles; *sodium* salt, NaA, needles. Diazotised, in absence of mineral acids, giving *diazo-oxide* (*cf.* Geigy, D. R.-P. 171024; Eng. Pat. 10235 of 1904; *v.* p. 571).
1:2:5	Reduction of azo-derivatives of β-naphthol-5-sulphonic acid (Witt, Ber. 1888, 21, 3478).	*Acid*, very sparingly soluble. Gives brown colouration with ferric chloride.
1:2:6	(1) Reduction of nitroso-β-naphthol-6-sulphonic acid (Meldola, Chem. Soc. Trans. 1881, 39, 47). (2) Reduction of azo-derivatives of β-naphthol-6-sulphonic acid (Witt, Ber. 1888, 21, 3475).	*Acid*, HA, sparingly soluble needles; *sodium* salt (*Eikonogen*), $NaA+2\frac{1}{2}H_2O$. Solutions, especially if alkaline, are very sensitive to air. Gives brown colouration with ferric chloride. For *diazo-oxide*, *cf.* Geigy, *l.c.*; *v.* p. 571. Couples with diazotised bases (*cf.* Aktienges., D. R.-P. 79103; Eng. Pat. 13833 of 1893).
1:2:7	Reduction of azo-derivatives of β-naphthol-7-sulphonic acid (Witt, Ber. 1888, 21, 3477).	*Acid*, very sparingly soluble needles. Gives brown colouration with ferric chloride. For *diazo-oxide*, *cf.* Geigy, *l.c.*; *v.* p. 571. Couples with diazotised bases (*cf.* Aktienges., *l.c.*).
1:2:8	Reduction of azo-derivatives of β-naphthol-8-sulphonic acid (Witt, Ber. 1888, 21, 3474).	*Acid*, very sparingly soluble leaflets. Gives brown colouration with ferric chloride. For *diazo-oxide*, *cf.* Geigy, *l.c.*; *v.* p. 571.
1:3:4 [4:2:1]	1-Amino-3-naphthol sulphonated with monohydrate (Friedlaender and Rüdt, Ber. 1896, 29, 1609).	*Acid*, very sparingly soluble needles. Hydrolysed by water at 120° to 1:3-*dihydroxynaphthalene*.
1:3:6 [4:2:7]	Mixed with 1:6:3-acid, by boiling α-naphthylamine-3:6-disulphonic acid with 75 p.c. caustic potash solution (Cassella, D. R.-P. 82676 of 1894).	*Acid*, very sparingly soluble; *sodium salt* salted out to separate from 1:6:3-acid. Forms a readily soluble *diazo*-compound.
1:3:7 [4:2:6]	Mixed with 1:7:3-acid, by heating α-naphthylamine-3:7-disulphonic acid with 40 p.c. caustic soda solution under pressure at 200° (Cassella, D. R.-P. 57007, 58352 of 1890).	*Acid*, readily soluble.
1:4:2 [4:1:3]	Reduction of nitroso- or azo-derivatives of α-naphthol-3-sulphonic acid (Reverdin and de la Harpe, Ber. 1893, 26, 1281).	No description published.
1:4:3 [4:1:2]	(1) 1-Amino-4-naphthol sulphonated with 10 p.c. anhydro- acid at 30°-40° (Seidel, Ber. 1892, 25, 424; *cf.* Friedlaender and Reinhardt, Ber. 1894, 27, 239). (2) Reduction of nitroso- (Conrad and Fischer, Annalen, 1893, 273, 114), or of azo-derivatives (Reverdin and de la Harpe, Ber. 1892, 25, 1403), of α-naphthol-2-sulphonic acid.	*Acid*, very sparingly soluble needles, which give a grass-green solution in caustic soda. Oxidised by nitric acid to [α-]*naphthaquinone*-3-*sulphonic acid*.
1:4:5 [4:1:8]	(1) Reduction of azo-derivatives of α-naphthol-8-sulphonic acid (Reverdin and de la Harpe, Ber. 1892, 25, 1404). (2) Electrolytic reduction of α-nitronaphthalene-5-sulphonic acid in sulphuric acid solution (Gattermann, Ber. 1893, 26, 1852; Bayer, D. R.-P. 81621 of 1893).	*Acid*, leaflets soluble in water but insoluble in cold alcohol, solution in ammonia yellow; *lead* and *barium* salts, sparingly soluble in water (Bayer, *l.c.*).
1:4:6 [4:1:7]	Electrolytic reduction of α-nitronaphthalene-6-sulphonic acid in sulphuric acid solution (Bayer, D. R.-P. 81621 of 1893).	*Acid*, needles soluble in water or cold alcohol, solution in ammonia yellow; *lead* and *barium* salts soluble in water (Bayer, *l.c.*).
1:4:7 [4:1:6]	Electrolytic reduction of α-nitronaphthalene-7-sulphonic acid in sulphuric acid solution (Bayer, D. R.-P. 81621 of 1893).	*Acid*, needles soluble in water or cold alcohol, solution in ammonia yellow; *lead* and *barium* salts soluble in water (Bayer, *l.c.*).
1:5:2 [5:1:6]	(1) α-Naphthylamine-2:5-disulphonic acid heated with 50 p.c. caustic soda solution at 250° (Landshoff, Eng. Pat. 6195 of 1890; D. P. Anm. C. 4479 of 1892). (2) 1:5-Diaminonaphthalene-2-sulphonic acid boiled with sodium bisulphite solution and product decomposed by alkali (Bucherer and Uhlmann, J. pr. Chem. 1909, [ii.] 80, 213).	*Acid*, sparingly soluble needles. Gives green colouration with ferric chloride (*cf.* Bayer, D. R.-P. 75317 of 1891). Forms sparingly soluble *diazo*-compound. Couples with diazotised bases (*cf.* Cassella, D. R.-P. 82676 of 1894).

Constitution.	Preparation.	Acids, Salts and Reactions.
N : O : S		
1 : 5 : 4 [5 : 1 : 8]	(1) 1-Acetylamino-5-aminonaphthalene-4-sulphonic acid boiled with sodium bisulphite solution and product decomposed by alkali (Bucherer and Uhlmann, J. pr. Chem. 1909, [ii.] 80, 229). (2) 1 : 5-Dihydroxynaphthalene-4-sulphonic acid heated with sodium bisulphite solution and ammonia (*ibid.* 223).	*Acid*, HA, crystallises in needles. Couples with diazotised bases forming *azo*-dyes.
1 : 5 : 6 [5 : 1 : 2]	1-Amino-5-naphthol sulphonated with sulphuric acid below 100° (Aktiengcs., D. R.-P. 68564 of 1891).	*Acid*, very sparingly soluble needles. Gives blue colouration with ferric chloride. Forms greenish-yellow solution with nitrous acid. Couples with diazotised bases.
1 : 5 : 7 [5 : 1 : 3] **M-acid.**	(1) α-Naphthylamine-5 : 7-disulphonic acid heated with 75 p.c. caustic soda solution at 170° (Badische, D. R.-P. 73276, Eng. Pat. 2370 of 1893). (2) 1 : 5-Diaminonaphthalene-7-sulphonic acid heated with water under pressure at 160° (Cassella, D.R.-P. 85058 of 1894). (3) 1 : 5-Dihydroxynaphthalene-7-sulphonic acid heated with ammonium sulphite and ammonia (Badische, D. R.-P. 117471 of 1899 ; Eng. Pat. 1387 of 1900) (4) 1-Amino-5-naphthol-2 : 7-disulphonic acid heated with 10 p.c. sulphuric acid under pressure at 135° (Cassella, D. R.-P. 188505 of 1905).	*Acid* and *sodium* salt, sparingly soluble leaflets. Gives black colouration with ferric chloride. Forms a deep orange-yellow sparingly soluble *diazo*-compound (*cf.* Cassella, D. R.-P. 82676 of 1894). Couples in alkaline solution with diazotised bases forming *azo*-dyes (*cf.* Badische, D. R.-P. 75327, 82572 ; Eng. Pat. 2370 of 1893).
1 : 5 : 8 [5 : 1 : 4]	1 : 5-Diaminonaphthalene-4-sulphonic acid boiled with sodium bisulphite solution and product decomposed by alkali (Bucherer and Uhlmann, J. pr. Chem. 1909, [ii.] 80, 226).	*Acid*, $HA + 3\frac{1}{2}H_2O$. Couples with diazotised bases forming *azo*-dyes.
1 : 6 : 3 [5 : 2 : 7]	(1) Mixed with 1 : 3 : 6-acid, by boiling α-naphthylamine-3 : 6-disulphonic acid with 75 p.c. caustic potash solution (Cassella, D. R.-P. 82676 of 1894). (2) 1-Amino-6-naphthol-3 : 5-disulphonic acid boiled with dilute acids (Cassella, D. P. Anm. C. 5163 of 1894).	*Acid*, sparingly soluble ; *sodium* salt readily soluble. Forms a yellow sparingly soluble *diazo*-compound. Couples with diazotised bases (Cassella, D. R.-P. 82676 of 1894).
1 : 6 : 4 [5 : 2 : 8]	α-Naphthylamine-4:6-disulphonic acid fused with caustic soda at 180°–200° (Dahl, D. R.-P. 68232 of 1891 ; Friedlaender and Kielbasinski, Ber. 1896, 29, 1979).	*Acid*, sp. sol. needles ; *sodium* salt, NaA, needles, *barium* salt, prisms, readily soluble. Gives brownish colouration with ferric chloride. Forms sp. sol. *diazo*-compound. Couples with diazotised bases (*cf.* Cassella, D. R.-P. 82676 of 1894).
1 : 7 : 3 [8 : 2 : 6] **B-acid.**	Mixed with 1 : 3 : 7-acid by heating α-naphthylamine-3 : 7-disulphonic acid with 40 p.c. caustic soda under pressure at 200° (Cassella, D. R.-P. 57007, 58352 of 1890).	*Acid*, very sparingly soluble needles ; *sodium* salt readily soluble leaflets. Forms a very sparingly soluble *diazo*-compound. Couples with diazotised bases, giving two series of *monoazo*-dyes (Cassella, *l.c.*).
1 : 7 : (4) [8 : 2 : (5)]	1-Amino-7-naphthol sulphonated with sulphuric acid below 30° (Cassella, D. R.-P. 75066 of 1891).	*Acid*, sp. sol. ; *alkali* salts readily soluble. Forms a sp. sol. *diazo*-compound. Couples in alkaline solution with diazotised bases (Cassella, *l.c.* ; Bayer, D. R.-P. 198138 of 1907).
1 : 8 : 2 [8 : 1 : 7]	(1) α-Naphthylamine-2 : 8-disulphonic acid fused with caustic soda at 170°–220° (Cassella, D. R.-P. 75710 of 1893). (2) 1-Amino-8-naphthol-2 : 4-disulphonic acid boiled with 50 p.c. sulphuric acid (*ibid.*).	*Acid*, sparingly soluble radiate prisms. Forms a dark brown sparingly soluble *diazo*-compound. Couples with diazotised bases (*cf.* Cassella, D. R.-P. 82676 of 1894).
1 : 8 : 3 [8 : 1 : 6]	(1) α-Naphthylamine-3 : 8-disulphonic acid fused with caustic alkali below 210° (Bayer, D.P.Anm.F.4723 ; Eng.Pat.13443 of 1890). (2) 1-Amino-8-naphthol-3 : 5-disulphonic acid boiled with dilute sulphuric acid at 140° (Leonhardt, D. P. Anm. F. 8626 ; Eng. Pat. 19253 of 1895).	*Acid*, sparingly soluble prisms or needles ; *sodium* salt readily soluble. Forms an orange-yellow sparingly soluble *diazo*-compound. Couples with diazotised bases (*cf.* Cassella, D. R.-P. 82676 of 1894).
1 : 8 : 4 [8 : 1 : 5] **S-acid.**	(1) α-Naphthylamine-4 : 8-disulphonic acid fused with caustic alkali at 210° (Badische, D. R.-P. 63074 ; Eng. Pat. 20275 of 1891 ; Bayer, D. R.-P. 75317 of 1891). (2) 1 : 8-Diaminonaphthalene-4-sulphonic acid, heated with 40 p.c. sodium bisulphite solution at 95° in presence of acetone, and product decomposed by alkali (Badische, D. R.-P. 120016 ; Eng. Pat. 16921 of 1900 ; Bucherer, J. pr. Chem. 1904, [ii.] 70, 349).	*Acid*, sparingly soluble needles ; *alkali* salts readily soluble, showing bluish-green fluorescence in solution (Bayer, *l.c.*). Gives emerald-green colouration with ferric chloride (*ibid.*). Forms an orange sp. sol. *diazo*-compound (*cf.* Cassella, D. R.-P. 82676 of 1894). Couples in acid or in alkaline solution with diazotised bases, being used as middle component for *disazo*-dyes (*cf.* Badische, D. R.-P. 91855 of 1891 ; Eng. Pat. 9894 of 1893 ; D. R.-P. 114976 of 1899). For *acetyl*, *aryl*, and *nitroaryl* derivatives, see p. 636.

Constitution.	Preparation.	Acids, Salts and Reactions.
N:O:S		
1:8:5 [8:1:4]	(1) 1:8-Diaminonaphthalene-5-sulphonic acid boiled with 20 p.c. sulphuric acid (Cassella, D.R.-P. 73607 of 1892; Eng. Pat. 4613 of 1893); or heated with 40 p.c. sodium bisulphite solution, and product decomposed with alkali (Bayer, D. R.-P. 109102, Eng. Pat. 16807 of 1899). (2) α-Naphthylamine-5:8-disulphonic acid heated with 75 p.c. caustic potash solution at 150° (Bayer, D. R.-P. 75055, Eng. Pat. 15269 of 1893). (3) 8-Chloro-α-naphthylamine-5-sulphonic acid heated with 50 p.c. caustic soda solution under pressure at 190° (Badische, D. R.-P. 112778 of 1899). (4) Mixed with 1:8:7 acid, when 1-amino-8-naphthol is sulphonated with sulphuric acid at 15°–20° (Badische, D. R.-P. 62289 of 1889; Eng. Pat. 9676 of 1890; D. R.-P. 77937, 84951 of 1894).	*Acid*, very sparingly soluble needles; *sodium* and *potassium* salts readily soluble, showing violet fluorescence in solution (Cassella, *l.c.*). The *calcium* salt is easily soluble (Badische, D. R.-P. 77937 of 1894). Gives dirty green colouration with ferric chloride (Bayer, D. R.-P. 75055 of 1893). Forms a readily soluble yellow *diazo*-compound (Cassella, *l.c.*). Couples in acid or in alkaline solution with diazotised bases, being used as a middle component for *disazo*-dyes (*cf.* Badische, D. R.-P. 81241 of 1891; 114906 of 1896). For *benzoyl* derivative and *azo*-dyes therefrom, *cf.* Badische, D. R.-P. 54662; Eng. Pat. 9676 of 1890.
1:8:6 [8:1:3] H-acid.	(1) 1:8-Diaminonaphthalene-3-sulphonic acid heated with 15 p.c. sulphuric acid at 120° (Cassella, D. R.-P. 70780; E. P. 6972 of 1891; *cf.* Cassella, D. R.-P. 73607 of 1892). (2) α-Naphthylamine-6:8-disulphonic acid heated with 50 p.c. caustic potash solution under pressure at 200° (Bayer, D. R.-P. 80853; Eng. Pat. 15269 of 1893).	*Acid*, sp. sol. needles; *sodium* and *potassium* salts readily soluble; *barium* salt, needles (Bayer, *l.c.*). Gives green colouration with ferric chloride (Bayer, *l.c.*). Forms a yellow sparingly soluble *diazo*-compound (Bayer, *l.c.*). Couples in alkaline solution with diazotised bases (*cf.* Bayer, D. R.-P. 82074, 85389; Eng. Pat. 15269 of 1893).
1:8:7 [8:1:2]	1-Amino-8-naphthol sulphonated with 75 p.c. sulphuric acid at 130°–160° (Badische, D. R.-P. 82900 of 1894), *or* (mixed with 1:8:5 acid) with sulphuric acid at 15°–20° (*ibid.* D. R.-P. 62289 of 1889; 84951 of 1894.	*Acid*, sparingly soluble; *acid calcium* salt almost insoluble. Forms a readily soluble *diazo*-compound. Couples with diazotised bases.
2:1:3	Reduction of azo-derivatives of α-naphthol-3-sulphonic acid (Gattermann and Schulze, Ber. 1897, 30, 54).	*Acid*, HA, broad needles.
2:1:4[1]	(1) Reduction of azo- (König, Ber. 1890, 23, 808) *or* nitroso-derivatives of α-naphthol-4-sulphonic acid (Witt and Kaufmann, Ber. 1891, 24, 3162). (2) 2-Nitroso-α-naphthol boiled with 35 p.c. sodium bisulphite solution (Schmidt, J. pr. Chem. 1891, [ii.] 44, 531; *cf.* Böniger, Ber. 1894, 27, 29).	*Acid*, HA (Friedlaender and Reinhardt, Ber. 1894, 27, 242), sparingly soluble needles. Forms a violet-black dyestuff by oxidation (Reverdin and de la Harpe, D. R.-P. 63043; Eng. Pat. 16377 of 1891). Not diazotisable in acid solution (*cf.* Cassella, D. R.-P. 82676 of 1894), but if not acid, gives *diazo-oxide* (*cf.* Geigy, D. R.-P. 171024; *v.* p. 571).
2:1:5[1]	Reduction of azo-derivatives of α-naphthol-5-sulphonic acid (Gattermann and Schulze, Ber. 1897, 30, 51; *cf.* Reverdin and de la Harpe, Ber. 1893, 26, 1280).	*Acid*, HA, sparingly soluble scales or needles. Diazotised in absence of free mineral acid giving *diazo-oxide* (*cf.* Geigy, D. R.-P. 171024; Eng. Pat. 10235 of 1904; *v.* p. 571).
2:1:7	Reduction of 2-nitro-α-naphthol-7-sulphonic acid (Finger, J. pr. Chem. 1909, [ii.] 79, 444).	*Acid*, $HA + 2H_2O$, needles; alkaline solution becomes dark green on exposure to the air.
2:3:6 [3:2:7] R-acid.	β-Naphthylamine-3:6-disulphonic acid heated with 75 p.c. caustic soda at 230°–250° (Höchst, D. R.-P. 53076; Eng. Pat. 15176 of 1889; Friedlaender and Zakrzewski, Ber. 1894, 27, 763).	*Acid*, very sp. sol. needles; *sodium* salt, leaflets; *barium* salt BaA_2, sparingly soluble. Gives dark blue col. with ferric chloride (Höchst, *l.c.*). Forms an orange *diazo*-compound (*cf.* Höchst, *l.c.*; Cassella, D. R.-P. 109932; Eng. Pat. 28107 of 1897). Couples in alkaline solution with diazotised bases (*cf.* Aktienges., D. R.-P. 84145 of 1894).
2:4:6 [3:1:7]	α-Naphthol-3:7-disulphonic acid heated with ammonia under pressure at 180° (Kalle, D. R.-P. 94079 of 1896).	*Acid*, sp. sol. leaflets; *alkali* salts readily soluble. Forms a yellow *diazo*-compound. Couples with diazotised bases.
2:4:7 [3:1:6]	(1) β-Naphthylamine-4:7-disulphonic acid fused with caustic alkali at 215° (Bayer, D.P.Anm.F.7978; Eng.Pat.25214 of 1894). (2) α-Naphthol-3:6-disulphonic acid heated with ammonia under pressure at 180° (Kalle, D. R.-P. 94079 of 1896).	*Acid*, moderately soluble leaflets; *alkali* salts readily soluble. Forms a yellow *diazo*-compound. Couples in alkaline solution with diazotised bases (*cf.* Bayer, *l.c.*).
2:4:8 [3:1:5]	β-Naphthylamine-4:8-disulphonic acid fused with caustic alkali at 215° (Bayer, D. R.-P. 85241; D. P. Anm. F. 8070; Eng. Pat. 3580 of 1895).	*Acid*, sp. sol. needles; *alkali* salts easily soluble. Gives no colouration with ferric chloride. Forms a yellow sp. sol. *diazo*-compound. Couples in alkaline solution with diazotised bases.
2:5:(6) [6:1:(2)] and 2:5:(8) [3:1:(4)]	2-Amino-5-naphthol sulphonated with sulphuric acid at 20°–30° (Bayer, D. P. Anm. F. 7372; Eng. Pat. 5267 of 1894) forms two acids, about which little is known, the yield of the less soluble being 30 p.c.	One of the acids gives a dirty precipitate, the other a bluish-grey precipitate with ferric chloride. Each acid forms a yellow *diazo*-compound and couples with diazotised bases.

[1] An acid containing the sulphonic group in either the 4- or the 5- position is produced when 2-amino-1-naphthol is sulphonated with 10 p.c. anhydro-acid at 40°. It is sparingly soluble and gives a brown colouration with ferric chloride (Reverdin and de la Harpe, Ber. 1893, 26, 1280; Kern and Sandoz, D. R.-P. 69228 of 1891).

Constitution.	Preparation.	Acids, Salts and Reactions.
N:O:S		
2:5:1 [6:1:5]	β-Naphthylamine-1:5-disulphonic acid fused with caustic alkali (Kalle, D. R.-P. 242052 of 1909).	Forms a *diazo*-compound. Couples in alkaline solution with diazotised bases, but in acid solution loses SO_3H in coupling.
2:5:7 [6:1:3] **J-acid.**	(1) β-Naphthylamine-5 : 7-disulphonic acid fused with caustic alkali at 180°, or under pressure with 50 p.c. caustic soda solution at 190° (Badische, D. P. Anm. B. 14154; D. R.-P. 75469; Eng. Pat. 2614 of 1893. (2) 1 : 6-Dihydroxynaphthalene-3-sulphonic acid heated with ammonium sulphite solution and ammonia at 150° (Badische, D. R.-P. 117471 of 1899; Eng. Pat. 1387 of 1900).	*Acid*, sparingly soluble; *alkali* salts readily sol. Gives no colouration with cold, but brownish-black precipitate with hot ferric chloride (*cf.* Badische, D. R.-P. 73276) of 1893. Forms a yellow *diazo*-compound giving violet product with sodium carbonate solution. Couples in acid or in alkaline solution with diazotised bases, forming two series of *monoazo*-dyes (*cf.* Gesellsch., D. R.-P. 126802 of 1901). Extensively used as a source of direct cotton dyes. For *alkyl*, *aryl*, and other derivatives, *v.* p. 568.
2:5:8 [6:1:4]	1:6-Dihydroxynaphthalene-4-sulphonic acid heated with 28 p.c. ammonia under pressure at 140°–180° (Dahl, D. R.-P., 70285 of 1891; Eng. Pat. 4110 of 1892).	*Acid*, sparingly soluble; *alkali* salts readily soluble. Gives brown colouration with ferric chloride. Forms a yellow sp. sol. *diazo*-compound. Couples in acid or in alkaline solution with diazotised bases (Dahl, *l.c.*; D. R.-P. 67258 of 1891).
2:6:4 [6:2:8]	Reduction of 6-nitro-β-naphthol-8-sulphonic acid (Jacchia, Annalen, 1902, 323, 124).	*Acid*, $HA + H_2O$, sparingly soluble needles. Forms a yellow sp. sol. *diazo*-compound.
2:7:(3) [7:2:(6)] **F-acid.**	2 : 7-Dihydroxynaphthalenesulphonic acid heated with 30 p.c. ammonia under pressure at 120°–150° (Aktienges., D. R.-P. 63956 of 1891).	*Acid*, very sp. sol.; *alkali* salts easily soluble. Gives greenish-black col. with ferric chloride. Forms a yellow sp. sol. *diazo*-compound. Couples in acid or in alkaline solution with diazotised bases.
2:7:? [7:2:?]	Partial hydrolysis of the disulphonic acid formed from 2-amino-7-naphthol by sulphonation with sulphuric acid at 30° (Cassella, D. R.-P. 131526 of 1901).	*Acid*, needles; *sodium* salt, $NaA + H_2O$, sp. soluble. Gives violet precipitate with ferric chloride. Forms a yellow sp. sol. *diazo*-compound. Couples in acid or in alkaline solution with diazotised bases, giving two series of *azo*-dyes.
2:8:(5) [7:1:(4)] 2:8:(7) [7:1:(2)]	2-Amino-8-naphthol sulphonated with sulphuric acid at 30° forms two acids in about equal proportion (Bayer, D. P. Anm. F. 7335; Eng. Pat. 5148 of 1894).	"*Sch.*" *acid*, readily, "*V*" *acid*, sp. sol.; separated by adding acid to soln. of mixed calcium salts. Each acid forms a yellow soluble *diazo*-compound and couples with diazotised bases.
2:8:6 [7:1:3] **G-acid.**	(1) β-Naphthylamine-6 : 8-disulphonic acid heated with 75 p.c. caustic soda solution at 230°–250° (Höchst, D. R.-P. 53076; Eng. Pat. 15176 of 1889; *cf.* Cassella, D. P. Anm. C. 3063; Eng. Pat. 16699 of 1889). (2) 2 : 8-Dihydroxynaphthalene-6-sulphonic acid heated with 30 p.c. ammonia under pressure at 120°–150° (Aktienges., D. R.-P. 62964 of 1890). (3) 2 : 8-Dihydroxynaphthalene-6-sulphonic acid heated with ammonium sulphite solution and ammonia at 150° (Bucherer, J. pr. Chem. 1904, [ii.] 69, 89).	*Acid*, very sparingly soluble needles; *alkali* and *alkaline earth* salts, readily soluble; *lead* salt sparingly soluble needles (Täuber and Walder, Ber. 1896, 29, 2268). Gives dirty claret colouration with ferric chloride. Forms a yellow sparingly soluble *diazo*-compound which gives a blue dye with sodium carbonate solution (Täuber and Walder, *l.c.*). Couples in acid or in alkaline solution forming two series of *monoazo*-dyes (*cf.* Cassella, D. R.-P. 55024, 55648; Eng. Pat. 16669 of 1889; *v.* p. 635). Is largely used for production of *polyazo*-dyes. For *alkyl*, *acetyl*, *aryl*, etc., derivatives, see p. 636.

Aminonaphtholdisulphonic Acids.

Constitution.	Preparation.	Acids, Salts and Reactions.
N:O:S:S		
1:2:3:6	Reduction of azo-derivatives of β-naphthol-3 : 6-disulphonic acid (Witt, D. R.-P. 49857 of 1889; Ber. 1888, 21, 3479).	*Acid sodium* salt, NaHA, readily soluble needles. Gives dark brown colouration with ferric chloride. In absence of mineral acid gives *diazo-oxide* (*cf.* Geigy, D. R.-P. 171024 of 1904; *v.* p. 571). Does not couple with diazotised bases.
1:2:3:7	Reduction of nitroso-β-naphthol-3 : 7-disulphonic acid (Geigy, D. R.-P. 171024; Eng. Pat. 10235 of 1904).	*Acid*, sp. sol.; *alkaline* solutions greenish yellow. Diazotised in absence of mineral acid giving *diazo-oxide* (*cf.* Geigy, *l.c.*; *v.* p. 571).
1:2:4:6	Interaction of nitroso-β-naphthol-6-sulphonic acid and sulphurous acid (Böniger, Ber. 1894, 27, 3052).	*Acid sodium* salt, NaHA, readily soluble needles. Diazotised in absence of mineral acid giving *diazo-oxide* (*cf.* Geigy, *l.c.*; *v.* p. 571).
1:2:4:?	Sulphonation of 1-amino-2-naphthol-4-sulphonic acid with monohydrate below 100° (Griesheim, D. P. Anm. C. 15414 of 1907; Eng. Pat. 3655 of 1908; D. P. Anm. C. 15820 of 1907).	*Acid sodium* salt, NaHA, very soluble, shows in solution bluish-green fluorescence like the acid sodium salt of the 4 : 6-disulphonic acid, with which it may be identical.
1:2:4:7	Interaction of nitroso-β-naphthol-7-sulphonic acid and sulphurous acid (Böniger, Ber. 1894, 27, 3052).	*Acid sodium* salt, NaHA, sp. sol. needles. Diazotised in absence of mineral acid giving *diazo-oxide* (*cf.* Geigy. *l.c.*; *v.* p. 571).

Constitution.	Preparation.	Acids, Salts and Reactions.
N:O:S:S		
1:2:6:8	Reduction of azo-derivatives of β-naphthol-6:8-disulphonic acid (Witt, D. R.-P. 49857 of 1889; Ber. 1888, 21, 3981).	*Acid sodium* salt, NaHA, easily soluble prisms. Gives dark brown colouration with ferric chloride. For *diazo-oxide, cf.* Geigy, *l.c.*; *v.* p. 571.
1:4:3:6 [4:1:2:7]	(1) Reduction of azo-derivatives of α-naphthol-2:7-disulphonic acid (Reverdin and de la Harpe, Ber. 1892, 25, 1405. (2) Electrolytic reduction of α-nitronaphthalene-3:6-disulphonic acid (Bayer, D. R.-P. 81621 of 1893).	*Acid* sp. soluble needles; *sodium* salt readily soluble. Gives a dark red colouration with ferric chloride (Bayer, *l.c.*). Is not diazotisable (*cf.* Reverdin and de la Harpe, Ber. 1893, 26, 1284).
1:4:3:7 [4:1:2:6]	Electrolytic reduction of α-nitronaphthalene-3:7-disulphonic acid (Bayer, D. R.-P. 81621 of 1893).	*Barium* salt sparingly soluble. Gives a rose-red colouration with ferric chloride.
1:4:3:8 [4:1:2:5]	Reduction of 4-nitroso-α-naphthol-3:8-disulphonic acid (Friedlaender, Ber. 1895, 28, 1536).	*Acid*, readily soluble needles. Is not diazotisable, and does not couple with diazotised bases.
1:5:2:7 [5:1:3:6]	α-Naphthylamine-2:5:7-trisulphonic acid heated with 50 p.c. caustic potash at 180°–200° (Bayer, D. P. Anm. F. 7001; Eng. Pat. 17141B of 1893; Cassella, D. R.-P. 188505 of 1905).	*Acid sodium* salt, moderately soluble needles. Gives wine-red colouration with ferric chloride. Forms an orange-red soluble *diazo*-compound, which with sodium carbonate solution becomes sky-blue and then orange.
1:5:3:7 [5:1:3:7]	Fusion of α-naphthylamine-3:5:7-trisulphonic acid with caustic soda at 160°–170° (Cassella, D. R.-P. 75432 of 1891).	*Acid* and *acid sodium* salt readily soluble (Cassella, D. R.-P. 84952 of 1894). Gives dark-green col. with ferric chloride (*ibid.*). Forms an orange *diazo*-compound. Couples in alkaline solution with diazotised bases (*cf.* Cassella, *l.c.*; D. R.-P. 83011 of 1892).
1:5:(4):(6) 5:1:(2):(8)	1-Amino-5-naphthol sulphonated with 23 p.c. anhydro-acid at 100° (Aktienges., D.P. Anm. A. 3767 of 1894).	*Acid* and *sodium* salt readily soluble. Forms a yellow *diazo*-compound. Couples with diazotised bases.
1:6:3:5 [5:2:1:7]	1-Amino-6-naphthol-3-sulphonic acid sulphonated with 12 p.c. anhydro-acid below 20° (Cassella, D. P. Anm. C. 5163 of 1894; *cf.* Cassella, D. R.-P. 84952 of 1894).	*Acid sodium* salt readily, *calcium* salt sparingly sol. Gives violet-black col. with ferric chloride. Forms a yellow soluble *diazo*-compound. Couples in acid or alkaline solution with diazotised bases, but gives only one series of *monoazo*-dyes.
1:6:3:7 [5:2:3:7]	1-Amino-6-naphthol-3-sulphonic acid heated with sulphuric acid at 140°–150°, *or* the 3:5-disulphonic acid heated with sulphuric acid at 150° (Cassella, D. R.-P. 84952 of 1894).	*Acid sodium* salt, sparingly soluble needles. Gives greenish-black col. with ferric chloride. Forms a soluble *diazo*-compound. Couples in alkaline solution with diazotised bases (*cf.* Cassella, *l.c.*; D. R.-P. 95988 of 1894).
1:7:(4):? [8:2:(5):?]	1-Amino-7-naphthol sulphonated with sulphuric acid above 100° (Cassella, D. R.-P. 69458; *cf. ibid.*, D. R.-P. 75066 of 1891).	*Acid* readily soluble.
1:8:2:4 [8:1:5:7] **S-acid**	(1) Fusion of α-naphthylamine-2:4:8-trisulphonic acid with caustic alkali (Cassella, D. R.-P. 75710 of 1893; Aktienges., D.P.Anm.A.3346; Eng.Pat.2984 of 1893). (2) Fusion of naphthasultam-2:4-disulphonic acid S with 90 p.c. caustic soda at 170° (Bayer, D. R.-P. 79566, 80668; Eng. Pat. 4979 of 1893; Dressel and Kothe, Ber. 1894, 27, 2141).	*Acid* readily sol.; *acid sodium* salt, NaHA + H_2O, easily sol. needles; *calcium* salt moderately sol. Gives greenish-black col. with ferric chloride. Forms a reddish-yellow soluble *diazo*-compound. Couples in acetic acid or in alkaline solution with diazotised bases giving only one series of *monoazo*-dyes; but in HCl solution, *disazo*-dyes of the 4-monosulphonic acid may be formed (*cf.* Bayer D. R.-P. 77703; Eng. Pat. 4979 of 1893).
1:8:(2):(5) 8:1:(4):(7) **L-acid**	1:8-Diaminonaphthalene-(2):5-disulphonic acid boiled with 20 p.c. sulphuric acid (Cassella, D. R.-P. 73048 of 1893).	*Acid* moderately, *acid sodium* salt readily soluble. Gives brown colouration with ferric chloride. Forms yellow *diazo*-compound. Couples with diazotised bases (*cf.* Cassella, D. R.-P. 84952 of 1894).
1:8:2:? [8:1:?:7]	1:8-Diaminonaphthalenetrisulphonic acid boiled with water or 10 p.c. sulphuric acid (Fischesser & Co., D. P. Anm. F. 7595; Eng. Pat. 13203 of 1894).	*Acid sodium* salt, NaHA, moderately soluble. Gives green colouration with ferric chloride. Forms a yellow soluble *diazo*-compound. Couples in acid solution with diazotised bases.
1:8:3:5 [8:1:4:6] **B-acid**	1-Amino-8-naphthol-3-sulphonic acid sulphonated with monohydrate at the ordinary temperature (Leonhardt, D. P. Anm. F. 8626; Eng. Pat. 19253 of 1895; Cassella, D. R.-P. 108848 of 1895).	*Acid* and *acid sodium* salt sparingly soluble. Forms a yellow sparingly soluble *diazo*-compound. Couples in acid or alkaline solution with diazotised bases, forming two series of *monoazo*-dyes (*cf.* Cassella, *l.c.*). For *aryl* derivatives, see p. 636.
1:8:3:6 [8:1:3:6] **H-acid**	(1) 1:8-Diaminonaphthalene-3:6-disulphonic acid heated with 10 p.c. sulphuric acid at 100°–120°, or with 40 p.c. caustic soda at 200° (Cassella, D. R.-P. 67062 of 1890; Eng. Pat. 1742 of 1891), *or* its azimido- derivative heated with 80 p.c. sulphuric acid at 170° (*ibid.* D. R.-P. 69963 of 1891).	*Acid* sparingly soluble in cold water; *acid sodium* salt, NaHA + $1\frac{1}{2}H_2O$, and *acid barium* salt, $BaH_2A_2 + 4\frac{1}{2}H_2O$, sparingly soluble needles (Dressel and Kothe, Ber. 1894, 27, 2150). Gives brownish-red colouration with ferric chloride. Forms a yellow soluble *diazo*-compound. Couples in acid or alkaline solution with diazotised bases, forming two series of *monoazo*-dyes

Constitution.	Preparation.	Acids, Salts and Reactions.
N:O:S:S 1:8:3:6 (*contd.*)	(2) Naphthasultam-3 : 6-disulphonic acid fused with 90 p.c. caustic soda at 170° (Bayer, D. R.-P. 80668 ; Eng. Pat. 4979 of 1893 ; Dressel and Kothe, Ber. 1894, 27, 2150), *or* α-naphthylamine-3 : 6 : 8-trisulphonic acid with caustic soda at 180°–190° (Bayer, D. R.-P. 69722 ; Eng. Pat. 13443 of 1890), *or* 8-chloro-α-naphthylamine-3 : 6-disulphonic acid with caustic alkali (Badische, D. R.-P. 147852 of 1903). (3) 1 : 8-Dinitronaphthalene-3:6-disulphonic acid heated with sodium bisulphite solution at 90°–100° (Bayer, D. R.-P. 113944 ; Eng. Pat. 21138 of 1899).	(*cf.* Bayer, D. R.-P. 62368 ; Eng. Pat. 13443 of 1890 ; Cassella, D. R.-P. 65651 ; Eng. Pat. 1742, 6972 of 1891). Largely used in the production of *azo*-dyes. For *alkyl, acetyl, aryl, nitrobenzoyl* derivatives, see p. 636.
1:8:3:? [8:1:6:?]	Fusion of naphthasultamdisulphonic acid ε with caustic alkali (Bayer, D. R.-P. 79566 ; Eng. Pat. 4979 of 1893).	No description published.
1:8:4:6 [8:1:3:5] K-acid	Fusion of α-naphthylamine-4 : 6 : 8-trisulphonic acid with 70 p.c. caustic soda under pressure at 175° (Bayer, D. R.-P. 80741 ; Eng. Pat. 17141c of 1893 ; Kalle, D. R.-P. 99164 of 1893 ; Eng. Pat. 515 of 1894).	*Acid sodium* salt readily soluble needles (Bayer, *l.c.*). Gives yellowish-green col. with ferric chloride. Forms a yellow readily soluble *diazo*-compound. Couples in acid or alkaline solution with diazotised bases forming two series of *monoazo*-dyes (*cf.* Kalle, *l.c.* ; D. R.-P. 108266 of 1896).[1] For *acetyl, aryl, nitroaryl* derivatives, see p. 636.
1 : 8 : 4 : (7) [8 : 1 : (2) : 5]	1 - Amino - 8 - naphthol - 4 - sulphonic acid sulphonated with 23 p.c. anhydro-acid at the ordinary temperature (Aktienges., D. P. Anm. A. 3918 of 1894 ; Badische, D. R.-P. 125696 ; Eng. Pat. 18366 of 1900).	*Acid sodium* salt sparingly soluble needles. Gives brownish-black col. with ferric chloride. Forms a yellowish-brown *diazo*-compound. Couples with diazotised bases (*cf.* Aktienges., *l.c.*).
1:8:5:7 [8:1:2:4]	1-Amino-8-naphthol-5-sulphonic or 7-sulphonic acid sulphonated with monohydrate at 100° (Badische, D. R.-P. 62289 of 1889 ; Eng. Pat. 9676 of 1890 ; *cf.* Badische, D. R.-P. 82900 of 1894).	*Acid* readily soluble leaflets ; *acid sodium* salt readily soluble. Gives blue colouration with ferric chloride. Forms a yellow sparingly soluble *diazo*-compound and couples with diazotised bases (*cf.* Cassella, D. R.-P. 84952 of 1894).
1:8:(5):? [8:1:(4):?] D-acid	Fusion of naphthasultamdisulphonic acid D with 90 p.c. caustic soda at 170° (Bayer, D. R.-P. 80668 ; Eng. Pat. 4979 of 1893).	*Acid sodium* salt moderately soluble needles. Gives green colouration with ferric chloride. Couples with diazotised bases.
2:1:3:6	Reduction of 2-nitroso-α-naphthol-3 : 6-disulphonic acid (Geigy, D. R.-P. 171024 ; Eng. Pat. 10235 of 1904).	*Acid sodium* salt easily soluble needles. Forms a *diazo-oxide* in absence of mineral acid (*cf.* Geigy, *l.c.* ; *v.* p. 571).
2:1:3:8	Reduction of azo-derivatives of α-naphthol-3 : 8-disulphonic acid (Bernthsen, Ber. 1890, 23, 3093).	Forms a *diazo-oxide* in absence of mineral acid (*cf.* Geigy, D. R.-P. 171024 ; Eng. Pat. 10235 of 1904 ; *v.* p. 571).
2:1:4:6	Reduction of azo-derivatives of α-naphthol-4 : 6-disulphonic acid (Reverdin and de la Harpe, Ber. 1893, 26, 1282 ; *cf.* Böniger, Ber. 1894, 27, 3052).	*Acid* readily soluble ; *acid sodium* salt sparingly soluble needles.
2:1:4:7	Reduction of azo- or nitroso-derivatives of α-naphthol-4 : 7-disulphonic acid (Reverdin and de la Harpe, Ber. 1893, 26, 1282 ; *cf.* Böniger, Ber. 1894, 27, 3054).	*Acid* moderately soluble needles ; *sodium* salt readily soluble. Forms a *diazo-oxide* in absence of mineral acid (*cf.* Geigy, *l.c.*).
2:1:4:8	Reduction of azo-derivatives of α-naphthol-4 : 8-disulphonic acid (Reverdin and de la Harpe, Ber. 1893, 26, 1283).	*Acid* and *acid sodium* salt moderately soluble. Forms a *diazo-oxide* in absence of mineral acid (*cf.* Geigy, D. R.-P. 171024 ; Eng. Pat. 10235 of 1904 ; *v.* p. 571).
2:3:6:8 [3:2:5:7]	Sulphonation of 2-amino-3-naphthol-6-sulphonic acid (Aktienges., D. R.-P. 86448 ; Eng. Pat. 8645 of 1895).	No description published.
2:4:6:8 [3:1:5:7]	Fusion of β-naphthylamine-4 : 6 : 8 -trisulphonic acid with 60 p.c. caustic soda at 170°–180° (Bayer, D. P. Anm. F. 8154 ; D. R.-P. 89242 of 1895.	*Acid sodium* salt, moderately soluble. Gives bluish-green colouration with ferric chloride. Forms a pale yellow *diazo*-compound. Couples with diazotised bases.
2:5:1:7 [6:1:3:5]	Fusion of β-naphthylamine-1 : 5 : 7-trisulphonic acid with 66 p.c. caustic soda at 160°–220° (Bayer, D. R.-P. 80878 ; Eng. Pat. 20580 of 1893).	*Acid sodium* salt readily soluble needles. Gives green colouration with ferric chloride. Forms an orange-yellow soluble *diazo*-compound. Couples in alkaline solution with diazotised bases (*cf.* Bayer, D. R.-P. 92708 ; Eng. Pat. 1062 of 1894).
2:5:3:7 [6:1:3:7]	β-Naphthylamine-3 : 5 : 7-trisulphonic acid heated with 30 p.c. caustic soda at 190° (Oehler, D. R.-P. 158147 of 1903 ; Eng. Pat. 1581 of 1904).	*Acid sodium* salt easily soluble. Gives yellowish-brown col. with ferric chloride. Forms an easily soluble orange *diazo*-compound. Couples in alkaline solution with diazotised bases.

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[1] The colouration produced by the interaction of this acid with sulphanilic acid in the presence of nitrous acid forms a delicate test for minute quantities of nitrites in water (Erdmann, Ber. 1900, 33, 213).

Constitution.	Preparation.	Acids, Salts and Reactions.
N:O:S:S 2:7:3:6 [7:2:3:6]	(1) β-Naphthylamine-3 : 6 : 7-trisulphonic acid heated with 55 p.c. caustic soda at 180°–240° (Bayer, D. P. Anm. F. 7019; Eng. Pat. 17141 of 1893; *cf. ibid.*, D. R.-P. 80878 of 1893). (2) 2 : 7-Dihydroxynaphthalene-3 : 6-disulphonic acid heated with 23 p.c. ammonia at 180°–220° (Aktienges., D. R.-P. 75142; Eng. Pat. 16199 of 1893). (3) 2-Amino-7-naphthol sulphonated with sulphuric acid at 30° (Cassella, D. R.-P. 131526 of 1901).	*Acid* sparingly soluble; *acid sodium* salt sparingly soluble needles. Gives deep violet colouration with ferric chloride (Bayer, *l.c.*; Aktienges., *l.c.*). Forms a sparingly soluble yellow *diazo*-compound (Cassella, *l.c.*). Couples only slowly or not at all with diazotised bases (Cassella, *l.c.*).
2:8:3:6 [7:1:3:6] 2 R-acid	Fusion of β-naphthylamine-3 : 6 : 8-trisulphonic acid with 80 p.c. caustic soda at 200°–260° (Höchst, D. R.-P. 53023; Eng. Pat. 15175 of 1889).	*Acid* and *salts* readily soluble. Gives dark green colouration with ferric chloride. Forms a yellow sparingly soluble *diazo*-compound. Couples in alkaline solution with diazotised bases (*cf.* Aktienges., D. R.-P. 108215; Eng. Pat. 14895 of 1893).

Aminonaphtholtrisulphonic Acids.

1-Amino-2-naphthol- and 2-amino-1-naphthol-3:6:8-trisulphonic acids are obtained by reduction of azo-derivatives of the corresponding β-naphthol- and α-naphthol-3 : 6 : 8-trisulphonic acids. They give *diazo-oxides* on diazotisation in absence of mineral acid (Geigy, D. R.-P. 171024; Eng. Pat. 10235 of 1904).

1-Amino-8-naphthol-2:4:6-trisulphonic acid, obtained by fusing naphthasultam-2 : 4 : 6-trisulphonic acid with 85 p.c. caustic potash at 150°–160°, forms a sparingly soluble *acid potassium* salt, gives a green colouration with ferric chloride, also a readily soluble orange *diazo*-compound, and couples with diazotised bases (Bayer, D. R.-P. 84597 of 1894).

NITROAMINONAPHTHOLSULPHONIC ACIDS.

Nitroamino-1-naphthol, obtained from 2 : 4-dinitro-α-naphthol by reduction with ammonium sulphide, forms yellow needles, m.p. 130° (Ebell, Ber. 1875, 8, 564).

(i.) **3-Nitro-1-amino-4-naphthol-6-sulphonic acid**, obtained from naphthol yellow S by reduction with stannous chloride and hydrochloric acid (Lauterbach, Ber. 1881, 14, 2029; Finger, J. pr. Chem. 1909, [ii.] 79, 442) forms sparingly soluble golden-yellow scales. Its *diazo-* compound couples with β-naphthol, &c., but the *azo-* dyes are valueless (Gesellsch., D. R.-P. 189513 of 1905; Eng. Pat. 7535 of 1906); when boiled with alcohol and copper powder, it is converted into *copper 2-nitro-α-naphthol-7-sulphonate* (Finger, *l.c.*).

(ii.) **4-Nitro-2-amino-1-naphthol-7-sulphonic acid**, obtained when naphthol yellow S in ammoniacal solution is reduced by sodium sulphide at 90°–95°, forms yellow crystals, sparingly soluble in cold water. Its *diazo-* compound couples with β-naphthol, &c., giving *azo-* dyes (Gesellsch., D. R.-P. 189513 of 1905; Eng. Pat. 7535 of 1906).

(iii.) **(8)-Nitro-2-amino-3-naphthol-6-sulphonic acid** can be prepared by adding nitre to a solution of 2-amino-3-naphthol-6-sulphonic acid in sulphuric acid at 5°. It forms yellow needles, and its *potassium* and *sodium* salts are easily soluble (Cassella, D. R.-P. 110369 of 1899). The *diazo-* compound couples with phenols and amines giving *azo-* dyes (*ibid.* D. R.-P. 111933 of 1899).

Although the corresponding nitro-amino-2-naphthol-(or 2-amino-1-naphthol-)sulphonic acids have not been described, the diazo- compounds, to which they would give rise, can be obtained by nitrating *o*-diazonaphtholsulphonic acids. Nitro-1-diazo-2-naphthol-4-sulphonic acid (Geigy, D. R.-P. 171024; Eng. Pat. 10235 of 1904; D. R.-P. 164655; Eng. Pat. 15418 of 1904) forms pale yellow crystals, and couples with phenols and amines forming *azo-* dyes (*ibid.* D. R.-P. 169683; Eng. Pat. 15982 of 1904). Nitro-1-diazo-2-naphthol-6-sulphonic and nitro-2-diazo-1-naphthol-5-sulphonic acids give *azo-* dyes, in which, with alkaline reducing agents, the NO_2 radicle can be converted into a diazotisable NH_2 group (Kalle, D. R.-P. 176619 of 1905).

DIAMINONAPHTHOLS.

Introductory.—The diaminonaphthols have been isolated only in three cases, being very rapidly oxidised on exposure of their solutions to the air. In the table a summary is given of the hydrochlorides, obtained chiefly by reduction processes; the acetyl derivatives, by which the diaminonaphthols have been characterised; and the sulphonic acids belonging to this group of compounds:

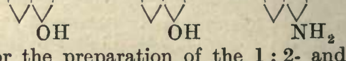
NH_2 : NH_2 : OH	
1 : 2 : 3 [3 : 4 : 2]	Unknown. 6-Sulphonic acid obtained by reduction of azo-dye from 2-amino-3-naphthol-6-sulphonic acid (Cassella, D. P. Anm. C. 19212 of 1910).
1 : 2 : 4 [3 : 4 : 1]	Unknown. *Diacetyl methyl ether*, m.p. 254° (Henriques, Ber. 1892, 25, 3067); *ethenyl* derivative, needles, m.p. 179° (Heermann, J. pr. Chem. 1892, [ii.] 45, 552).
1 : 2 : 7 [7 : 8 : 2]	Not described. Obtained by reduction of 7-hydroxy-[β-]naphthaquinonedioxime. *Hydrochloride*, B·2HCl; *triacetyl* derivative, m.p. 244°–245° (Nietzki and Knapp, Ber. 1897, 30, 1124).
1 : 2 : 8 [7 : 8 : 1]	Not isolated. Obtained by reduction of sulphonanilazo-2-amino-8-naphthol (Badische, D. R.-P. 90212; Eng. Pat. 15953 of 1896). The 4-, 5-, 6-mono-, and 3 : 6- and 5 : 7-disulphonic acids have been obtained from the corresponding 2-amino-8-naphtholsulphonic acids (*cf.* Badische, *l.c.*).

NH_2:NH_2:OH	
1 : 3 : 4 [2 : 4 : 1]	Not isolated. Obtained by reduction of 2 : 4-dinitro-α-naphthol. *Hydrochloride*, B·2HCl, scales, and *sulphate*, $B{\cdot}H_2SO_4+2H_2O$, needles, are both rapidly oxidised in air to diimino-α-naphthol (Graebe and Ludwig, Annalen, 1870, 154, 307); *triacetyl* derivative, needles, m.p. 280°, decomp. (Meerson, Ber. 1888, 21, 1196). The 7-sulphonic acid, obtained by reduction of naphthol yellow S, gives *hydrochloride* B·HCl, in needles (Gaess, Ber. 1899, 32, 232; *cf.* Lauterbach, Ber. 1881, 14, 2028), is not diazotisable, does not couple (*cf.* Aktienges., D. R.-P. 86448; Eng. Pat. 8645 of 1895), and is readily oxidised to the diimino- compound (Lauterbach, *l.c.*; Gaess, *l.c.*).
1 : 3 : 5 [5 : 7 : 1]	Unknown. The 7-sulphonic acid, obtained by digesting 1 : 3-diaminonaphthalene-5 : 7-disulphonic acid with 60 p.c. caustic soda solution at 210°, couples with diazotised bases (Kalle, D. R.-P. 92239 of 1896).
1 : 3 : 8 [5 : 8 : 1]	Unknown. The 6-sulphonic acid, obtained similarly from 1 : 3-diaminonaphthalene-6 : 8-disulphonic acid, couples with diazotised bases (Kalle, D. R.-P. 92239 of 1896).
1 : 4 : 2	Not isolated. Obtained by reduction of 4-nitrodiacetyl-1-amino-2-naphthol, *or* of azo- derivative of 1-amino-2-naphthol (Nietzki and Becker, Ber. 1907, 40, 3397; Kalle, D. R.-P. 195901 of 1906); rapidly oxidised to blue *oxazine* in the air (*ibid.*). *Hydrochloride*, B·2HCl, needles; N-*diacetyl* derivative, m.p. 250°–260°, decomp. (Kehrmann and Hertz, Ber. 1896, 29, 1417). The 6-sulphonic acid, obtained by reduction of azo- derivative of 1-amino-2-naphthol-6-sulphonic acid, forms *hydrochloride*, B·HCl, (Nietzki and Becker, *l.c.*; Kalle, *l.c.*). The 8-sulphonic acid, obtained by reduction of croceïn yellow, forms *hydrochloride*, B·HCl, needles, readily oxidised to the diimide, and is diazotisable (Nietzki and Zübelen, Ber. 1889, 22, 455).
1 : 4 : 8 [5 : 8 : 1]	Not described. Obtained by reduction of 4-nitroacet-1-amino-8-naphthol (Fichter and Gaguer, Ber. 1906, 39, 3336).
1 : 5 : 3 [4 : 8 : 2]	Unknown. The 7-sulphonic acid, obtained by fusing 1 : 5-diaminonaphthalene-3 : 7-disulphonic acid with 90 p.c. caustic soda solution at 200°–240°, forms needles sparingly soluble in hot water, and couples with diazotised bases (Cassella, D. R.-P. 91000 of 1896).
1 : 5 : 8 [4 : 8 : 1]	Not isolated. Obtained by reduction of 1-nitro-5-nitroso-8-naphthol (Friedlaender and Scherzer, *cf.* J. Soc. Chem. Ind. 1900, 19, 339; Graebe and Oeser, Annalen, 1904, 335, 155); *or* of azo- derivatives of 1-amino-8-naphthol (Fichter and Gaguer, Ber. 1906, 39, 3333). *Hydrochloride*, B·2HCl; N-*diacetyl* derivative, needles, m.p. 247°; *triacetyl* derivative, m.p. 258° (Fichter and Gaguer, *l.c.*).
1 : 6 : 2	M.p. 194° (*cf.* Cassella, D. R.-P. 117298; Eng. Pat. 16149 of 1899). Obtained by reduction of 1 : 6-dinitro-β-naphthol (Loewe, Ber. 1890, 23, 2543; Kehrmann and Matis, Ber. 1898, 31, 2413). *Hydrochloride*, B·2HCl, needles; N-*diacetyl* derivative, needles, m.p. 235°; *triacetyl* derivative, needles, m.p. 203° (Loewe, *l.c.*).
1 : 7 : 2	Scales, m.p. 220° (decomp.). Obtained by reduction of azo-derivative of 7-amino-2-naphthol (Cassella, D. R.-P. 117298; Eng. Pat. 16149 of 1899). *Sulphate*, sparingly soluble (*ibid.*); N-*diacetyl* derivative, needles, m.p. 226°; *triacetyl* derivative, needles (Kehrmann and Wolff, Ber. 1900, 33, 1540).
1 : 7 : 8 [2 : 8 : 1]	Not isolated. Obtained by reduction of 1-amino-7-nitroso-8-naphthol. *Hydrochloride*, B·2HCl, needles; *triacetyl* derivative, needles, m.p. 234° (Fichter and Gaguer, Ber. 1906, 39, 3338). The 3 : 6-disulphonic acid, obtained by reduction of azo- derivative of 1-amino-8-naphthol-3 : 6-disulphonic acid (H-acid), is not diazotisable in acid solution (Höchst, D. R.-P. 92012 of 1896). The 4-mono- and 4 : 6-disulphonic acids, obtained similarly from S-monosulpho- and K- acids, have been introduced, like the 3 : 6-acid, as photographic developers (Schultz, D. R.-P. 101953 of 1897).
1 : 8 : 4 [4 : 5 : 1]	Not isolated. Obtained by reduction of 8-nitro-1-nitroso-4-naphthol (Friedlaender and Scherzer, *cf.* J. Soc. Chem. Ind. 1900, 19, 339; Graebe and Oeser, Annalen, 1904, 335, 152). *Hydrochloride*, B·2HCl.
2 : 3 : 8 [6 : 7 : 1]	Unknown. The 6-sulphonic acid, obtained by fusing 2 : 3-diaminonaphthalene-6 : 8-disulphonic acid with 90 p.c. caustic potash solution at 190°–200°, forms an *azimide* with nitrous acid, and couples with diazotised bases (Aktienges., D. R.-P. 86448; Eng. Pat. 8645 of 1895).
2 : 6 : 1	Not isolated. Obtained by reduction of 6-nitronaphthalene-2-diazo-1-oxide. *Hydrochloride*, not described; *triacetyl* derivative, needles, m.p. 261°, decomp. (Gaess and Ammelburg, Ber. 1894, 27, 2213).
2 : 7 : 8 [2 : 7 : 1]	Unknown. The 6-sulphonic acid, obtained by reduction of azo- derivative of β-naphthylamine-6 : 8-disulphonic acid, is not diazotisable in acid solution (Höchst, D. R.-P. 92012 of 1896).

VIII. DIHYDROXY-DERIVATIVES.

Introductory.—The dihydroxynaphthalenes, like the naphthols, can be obtained from sulphonic acids by fusion with caustic alkali. For this purpose the four disulphonic acids producible from naphthalene by sulphonation, six of the naphtholsulphonic acids, β-naphthol-3 : 6-disulphonic acid, and α-naphthylamine-8-sulphonic acid have been employed. It has not been possible to prepare 1 : 2-, 1 : 3-, or 1 : 4-dihydroxynaphthalene by this method.

Another process, although less general, in which diaminonaphthalenes, aminonaphthols, aminonaphtholsulphonic acids, or dihydroxynaphthalenesulphonic acids are heated with dilute mineral acid under pressure, leads to the formation of dihydroxynaphthalenes from the amino- derivatives by exchange of NH_2 for OH, and—when a sulphonic acid is employed—elimination of the SO_3H group by hydrolysis.



For the preparation of the 1 : 2- and 1 : 4-dihydroxynaphthalenes (naphthaquinols), reduction of the respective naphthaquinones is the only practicable method.

The dihydroxynaphthalenes, of which the complete series of ten is known, are easily soluble in caustic alkali solutions, but only sparingly in cold water; the alkaline solutions rapidly become dark brown or black on exposure to the air.

When heated with ammonia under pressure, the four *αβ*-dihydroxynaphthalenes yield *β*-amino-*α*-naphthols as intermediate products, thus resembling *β*- rather than *α*-naphthol.

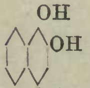
With nitrous acid the dihydroxynaphthalenes yield mononitroso-, and in some cases dinitroso-compounds, of which the *ortho*-mononitroso-compounds form lakes with chromium or iron salts. The nitroso- derivatives formed from the monoalkyl ethers of 1 : 8-, 2 : 6-, and 2 : 7-dihydroxynaphthalenes closely resemble 2-nitroso-*α*-naphthol and nitroso-*β*-naphthol, respectively, in properties, and like these can be employed in the production of thiazines (Bayer, D. R.-P. 91234; Eng. Pat. 6035A of 1893).

The azo- dyes obtained by coupling the following dihydroxynaphthalenes with diazotised bases:

1 : 2- (Witt, D. R.-P. 49979; Eng. Pat. 2499 of 1889);
2 : 3- (Badische, D. R.-P. 62947 of 1891);
1 : 8- (Badische, D. R.-P. 51559, 52958 of 1889);

form lakes, a property associated in dyestuffs of various types with the presence of hydroxyl groups in relatively *ortho*- positions. Those obtained by coupling 1 : 3 - dihydroxynaphthalene have a characteristic yellow shade.

DIHYDROXYNAPHTHALENES.



(i.) **1:2-Dihydroxynaphthalene** ([*β*-]naphthaquinol, [*β*-]naphthahydroquinone) is obtained by reducing [*β*-]naphthaquinone with sulphurous acid in the cold (Liebermann and Jacobson, Annalen, 1882, 211, 58; Paul, *cf.* J. Soc. Chem. Ind. 1897, 16, 733); *or* by heating 1-amino-2-naphthol-6 : 8-disulphonic acid with water under pressure above 200° (Bayer, D. R.-P. 89242 of 1895).

Identification.—It forms scales, m.p. 60°, dissolves in alkalis forming yellow solutions which become green on exposure to the air, and in aqueous solution exerts a severe caustic action on the skin (Liebermann and Jacobson, *l.c.*). The *diacetate* forms scales, m.p. 110° (Crépieux, Bull. Soc. chim. 1891, [3] 5, 158); the 1-*methyl ether*, monoclinic plates, m.p. 90·5°; the *dimethyl ether*, m.p. 31°, b.p. 278°–280° (Bezdzik and Friedlaender, Monatsh. 1909, 30, 280).

Reactions.—(1) In aqueous solution with ferric chloride, it yields [*β*-]*naphthaquinone* (Zincke, Annalen, 1892, 268, 275).

(2) By nitric acid of sp.gr. 1·48 it is converted into 3-*nitro*-[*β*-]*naphthaquinone* (Korn, Ber. 1884, 17, 3024; *cf.* Zincke, *l.c.*).

(3) With diazotised bases it couples, forming *azo*- dyes which give red to bluish-violet lakes with aluminium or chromium salts (Witt, D. R.-P. 49979; Eng. Pat. 2499 of 1889).

(4) It has been used for the production of *oxazines* (Bayer, D. R.-P. 77120; Eng. Pat. 8093 of 1893), and *thiazines* (Badische, D. R.-P. 96690; Eng. Pat. 19962 of 1893).

(ii.) **1 : 3-Dihydroxynaphthalene** is obtained when 1-amino-3-naphthol is boiled with dilute acid (Friedlaender, Ber. 1895, 28, 1952); *or* when 1-amino-3-naphthol-4-sulphonic acid is heated with water or dilute acid at 120° (Friedlaender and Rüdt, Ber. 1896, 29, 1609); *or* when 2-amino-4-naphthol-8-sulphonic acid (Bayer, D. R.-P. 87429; Eng. Pat. 3580 of 1895), or 1 : 3-dihydroxynaphthalene-7-mono- or 5 : 7-disulphonic acid (*ibid.* D. R.-P. 90096; Eng. Pat. 4962 of 1895) is heated with 5 p.c. sulphuric acid at 235°; *or* when 1 : 3-dihydroxy-*β*-naphthoic acid is heated with water under pressure at 100° (Metzner, Annalen, 1897, 298, 388).

Identification.—It crystallises from water in scales, m.p. 124°, is almost insoluble in benzene, becomes rapidly brown in alkaline solution on exposure to the air, and gives with ferric chloride a yellowish-brown precipitate (Friedlaender and Rüdt, *l.c.*). The *diacetate* forms prisms, m.p. 56° (*ibid.*).

Reactions.—(1) On digestion with 60 p.c. caustic soda solution at 180°–190°, it is converted into o-*toluic* acid (Friedlaender and Rüdt, *l.c.*; Kalle, D. R.-P. 79028 of 1893).

(2) When heated with aqueous ammonia at 130°–140°, it yields 2-*amino*-4-*naphthol* and 1 : 3-*diaminonaphthalene*, but with aniline *phenyl*-2-*amino*-4-*naphthol* (Friedlaender and Rüdt, *l.c.*).

(3) With nitrosodimethylaniline in acetic acid solution it gives a violet dyestuff (*ibid.*).

(4) When heated with phthalic anhydride and either phosphoric oxide at 130°, or zinc chloride at 200°, it furnishes *naphthafluoresceïn* (Friedlaender and Rüdt, *l.c.*; Bayer, D. R.-P. 84990; Eng. Pat. 3497 of 1895).

(5) With diazotised bases it couples in alkaline or weak acid solution, giving *azo*- dyes characterised by their yellow colour (Friedlaender and Rüdt, *l.c.*).

(iii.) **1 : 4-Dihydroxynaphthalene** ([*α*-]naphthaquinol, [*α*-]naphthahydroquinone) is formed when [*α*-]naphthaquinone is reduced with hydriodic acid and phosphorus (Groves, Chem. Soc. Trans. 1873, 26, 210); with tin and hydrochloric acid, or at 140°–150° with sulphurous acid (Plimpton, *ibid.* 1880, 37, 635); or with stannous chloride and very dilute hydrochloric acid (Russig, J. pr. Chem. 1900, [ii.] 62, 32). It is best prepared by adding powdered [*α*-]naphthaquinone to a boiling mixture of tin and hydrochloric acid.

Identification.—It crystallises in needles, m.p. 176°, and is readily soluble in alcohol, ether or boiling water, but only sparingly in benzene. By chromic acid or other oxidising agents, it is converted into [*α*-]*naphthaquinone.* The *diacetate* forms tablets, m.p. 128°–130° (Korn, Ber. 1884, 17, 3025).

Alkyl derivatives. The *monomethyl ether*, obtained by etherification at the ordinary temperature with 18 p.c. methyl alcoholic hydrogen chloride, forms needles, m.p. 131°; the *monoethyl ether*, obtained by boiling the dihydroxynaphthalene with 3 p.c. ethyl alcoholic hydrogen chloride, forms needles, m.p. 105° (Badische, D. R.-P. 173730 of 1905; Eng. Pat. 7287A of 1906; *cf.* Russig, J. pr. Chem. 1900, [ii.] 62, 50). These ethers, which can also be obtained by heating 1-amino-4-naphthol hydrochloride with the corresponding alcohol under pressure at 170°–180° (Höchst, D. R.-P. 234411 of 1910), when coupled with diazotised aminosulphonic acids, furnish *ortho*-azo- dyes

(Badische, D. R.-P. 176640 of 1905; Eng. Pat. 7287 of 1906). The *dimethyl* ether forms needles, m.p. 85° (Russig, *l.c.*).

(iv.) 1 : 5-**Dihydroxynaphthalene** is formed when potassium *α*-naphthol-5-sulphonate is fused with caustic potash at 200°–250° (Cleve, Förhandl., 1875, 9, 28; Bull. Soc. chim. 1875, [ii.] 24, 513; Erdmann, Annalen, 1888, 247, 356; *cf.* Ewer and Pick, D. R.-P. 41934 of 1887); *or* when sodium naphthalene-1 : 5-disulphonate is fused with caustic soda at 220°–260° (Ewer and Pick, *l.c.*; Armstrong and Wynne, Chem. Soc. Proc. 1887, 3, 43; Bernthsen and Semper, Ber. 1887, 20, 938; Schultz, *ibid.* 3161); *or* when 1 : 5-diaminonaphthalene is either heated with 4 p.c. hydrochloric acid under pressure at 180° (Aktienges., D. P. Anm. A. 4029 of 1894), or boiled with sodium bisulphite solution and the product decomposed by alkali (Bucherer, J. pr. Chem. 1904, [ii.] 69, 84; *cf.* 70, 352).

Identification.—It crystallises from water in scales, m.p. 265° (Bentley, Robinson and Weizmann, Chem. Soc. Trans. 1907, 91, 106), sublimes in needles, is almost insoluble in benzene, reduces silver solution, and in alkaline solution becomes dark-brown on exposure to the air—a property which has suggested its use as a hair-dye (Erdmann, D. R.-P. 51073 of 1889). The *diacetate* forms feathery crystals, m.p. 159°–160° (Bernthsen and Semper, *l.c.*); the *monomethyl ether*, leaflets, m.p. 140°; and the *dimethyl ether*, needles, m.p. 183°–184° (Bentley, Robinson and Weizmann, *l.c.*).

Reactions.—(1) On oxidation with chromic acid mixture, it is converted into *juglone* (5-hydroxy-[*α*-]naphthaquinone, *cf.* Bernthsen and Semper, *l.c.*).

(2) With nitrous acid, it gives a *mono-* and a *di-nitroso-* derivative (Read, Holliday & Co., D. R.-P. 68809; Eng. Pat. 1812 of 1890).

(3) When warmed with sulphuric acid at 50°–60°, it yields a mixture of the 2- and 4-*monosulphonic acids* (Bucherer and Uhlmann, J. pr. Chem. 1909, [ii.] 80, 235), but at 100°–160° a *disulphonic acid* (*cf.* Ewer and Pick, *l.c.*; Majert, Eng. Pat. 4243 of 1887).

(4) By interaction with ammonia under pressure at 250°–300° (Ewer and Pick, D. R.-P. 45549 of 1887), or with ammonium bisulphite solution and ammonia at 125°, it gives 1 : 5-*diaminonaphthalene* (Badische, D. R.-P. 117471 of 1899; Eng. Pat. 1387 of 1900).

(5) It couples with diazotised naphthionic acid, forming an *azo-* dye which closely resembles litmus in the colours given with acids, alkalis, and carbon dioxide (Erdmann, Annalen, 1888, 247, 356), or a *disazo-* dye if the coupling be effected in alkaline solution (Badische, D. P. Anm. B. 33987; Eng. Pat. 10536 of 1903); also with diazotised *o*-aminophenolsulphonic acids in alkaline solution giving *monoazo-* dyes, distinguished by their fastness on wool after chroming (Bayer, D. R.-P. 157786; Eng. Pat. 18569 of 1902).

(v.) 1 : 6-**Dihydroxynaphthalene** is formed when sodium naphthalene-1 : 6-disulphonate is fused with caustic soda at 230°–250° (Ewer and Pick, D. R.-P. 45229 of 1887); *or* when *β*-naphthol-5-sulphonic acid is fused with caustic potash and a little water at 260° (Claus, J. pr. Chem. 1889, [ii.] 39, 316); *or* when 1 : 6-dihydroxynaphthalene-4-sulphonic acid is desulphonated by sodium amalgam (Friedlaender and Lucht, Ber. 1893, 26, 3034).

Identification.—It crystallises from benzene in small prisms or serrated scales, m.p. 135°, sublimes in scales, is only sparingly soluble in water, and with ferric chloride gives a transient blue colouration. The *diacetate* forms prisms, m.p. 73° (Claus, *l.c.*).

Reactions.—(1) With nitrous acid, it yields a *mono-* and a *di-nitroso-* derivative (Read, Holliday & Co., D. R.-P. 68809; Eng. Pat. 1812 of 1890).

(2) When heated with ammonia under pressure at 150°–300°, it is converted into 1 : 6-*diaminonaphthalene* (Ewer and Pick, D. R.-P. 45788 of 1887).

(3) It couples in alkaline solution with diazotised *o*-aminophenolsulphonic acids, forming *monoazo-* dyes, which are fast on wool after chroming (Bayer, D. R.-P. 164318; Eng. Pat. 18569 of 1902).

(vi.) 1 : 7-**Dihydroxynaphthalene** is obtained by fusing *β*-naphthol-8-sulphonic acid with caustic potash (Emmert, Annalen, 1887, 241, 371); *or* by boiling 1 : 7-dihydroxy-*β*-naphthoic acid with aniline to eliminate carbon dioxide (Friedlaender and Zinberg, Ber. 1896, 29, 40).

Identification.—It crystallises in needles, m.p. 178°, is moderately soluble in water, but readily in benzene, rapidly becomes black on exposure in alkaline solution to the air, and with ferric chloride gives at first (like *α*-naphthol) a white turbidity which with more of the reagent becomes blue (Friedlaender and Zinberg, *l.c.*). The *diacetate* forms rhombic tables, m.p. 108° (Emmert, *l.c.*).

Reactions.—(1) With nitrous acid it yields a *mononitroso-* derivative (Bayer, D. R.-P. 53915; Eng. Pat. 14230 of 1889).

(2) By interaction of its sodium derivative with carbon dioxide under pressure at 140°, it gives 1 : 7-*dihydroxy-β-naphthoic acid* (Heyden, D. R.-P. 55414 of 1890).

(3) It couples in alkaline solution with diazotised *o*-aminophenolsulphonic acids furnishing *monoazo-* dyes, which are fast on wool after chroming (Bayer, D. R.-P. 164318; Eng. Pat. 18569 of 1902).

(vii.) 1 : 8-**Dihydroxynaphthalene** is obtained when either naphthasultone or *α*-naphthol-8-sulphonic acid is fused with 75 p.c. caustic potash solution at 220°–230° (Erdmann, Annalen, 1888, 247, 356); *or* when *α*-naphthylamine-8-sulphonic acid is heated with 9 p.c. caustic soda solution under pressure at 220°–260° (Höchst, D. P. Anm. F. 6311 of 1892). It is also formed when 1 : 8-dihydroxynaphthalene-4-sulphonic acid (Bayer, D. R.-P. 67829; Eng. Pat. 13665 of 1889), *or* 1 : 8-dihydroxynaphthalene-2 : 4-disulphonic acid (Dressel and Kothe, Ber. 1894, 27, 2143), *or* naphthasultamdisulphonic acid D (Bayer, D. R.-P. 80668; Eng. Pat. 4979 of 1893) is heated with 20 p.c. sulphuric acid at 160°–200°; *or* when 1 : 8-diaminonaphthalene is heated with 17 p.c. hydrochloric acid under pressure at 180° (Aktienges., D. P. Anm. A. 4028 of 1894).

Identification.—It crystallises in long needles, m.p. 140°, or with 1 mol. H_2O in scales, oxidises rapidly when moist on exposure to the air, is only sparingly soluble in water but readily in benzene, and gives with ferric chloride a white flocculent precipitate, which rapidly becomes green. The *diacetate* forms scales, m.p. 147°–148° (Erdmann, *l.c.*).

Reactions.—(1) On oxidation with chromic acid mixture, it gives *juglone* (5-hydroxy-[α-] naphthaquinone) in small quantity (Erdmann, *l.c.*).

(2) When warmed with sulphuric acid at 50°, it is converted into a mixture of the I-, G-, and R-*disulphonic acids* (Badische, D. R.-P. 79029, 79030; *cf.* Eng. Pat. 14294 of 1891).

(3) With nitrous acid it furnishes a *mono*- and a *di-nitroso*- derivative (Bayer, D. R.-P. 51478; Eng. Pat. 14230 of 1889).

(4) By interaction of its sodium derivative with carbon dioxide under pressure at 140°, it yields 1 : 8-*dihydroxy-β-naphthoic acid* (Heyden, D. R.-P. 55414 of 1890).

(5) When boiled with 40 p.c. sodium bisulphite solution, it furnishes the corresponding *sulphite* (Badische, D. R.-P. 115335 of 1899; Eng. Pat. 1387 of 1900; Bucherer, J. pr. Chem. 1904, [ii.] 69, 87).

(6) By condensation with acyl chlorides or anhydrides in presence of zinc chloride at 140°–150°, it yields yellow or orange dihydroxyketones (*e.g.* 1 : 8-*dihydroxy*-2-*acetonaphthone*, needles, m.p. 100°–101°, and *benzonaphthone*, needles, m.p. 121°–122°) which form lakes with alumina, &c. (Lange, D. R.-P. 126199; Eng. Pat. 21970 of 1900; *cf. ibid.*, D. R.-P. 129035, 129036 of 1900).

(7) It couples in alkaline solution with diazotised bases giving 4-*monoazo*- (*cf.* Badische, D. R.-P. 51559; 52958 of 1889; Bayer, D. R.-P. 70659; Eng. Pat. 14478 of 1892), or 4 : 7-*disazo*- dyes (*cf.* Badische, D. R.-P. 52140, 53499; Eng. Pat. 6874 of 1890; Friedlaender and Silberstern, Monatsh. 1902, 23, 518).

(viii.) 2 : 3-**Dihydroxynaphthalene** has been prepared by fusing β-naphthol-3 : 6-disulphonic acid, or 2 : 3-dihydroxynaphthalene-6-sulphonic acid, with 90 p.c. caustic soda solution at 280°–320° (Badische, D. R.-P. 57525; Eng. Pat. 15803 of 1890); also by heating 2 : 3-dihydroxynaphthalene-6-sulphonic acid with 25 p.c. sulphuric acid at 200° (*ibid.*; Friedlaender and Zakrzewski, Ber. 1894, 27, 762); *or* 2-amino-3-naphthol-6-sulphonic acid with dilute mineral acid under pressure at 180°–200° (Höchst, D. R.-P. 73076 of 1893; *cf.* Friedlaender and Zakrzewski, *l.c.*).

Identification.—It forms monoclinic scales (Siegmund, Monatsh. 1908, 29, 1087), m.p. 160°–161°, is sparingly soluble in water, and gives with ferric chloride a dark-blue colouration or precipitate (Badische, *l.c.*). The *monomethyl ether* forms needles, m.p. 108°; *dimethyl ether*, needles, m.p. 115°–116°; *monoethyl ether*, m.p. 109°–110°; *diethyl ether*, m.p. 96°–97° (Friedlaender and Silberstern, Monatsh. 1902, 23, 519; Silberstern, D. R.-P. 133459 of 1901).

Reactions.—(1) When heated with 30 p.c. ammonia at 140°–150° it yields 2-*amino*-3-*naphthol*, but at 250°, 2 : 3-*diaminonaphthalene* (Höchst, *l.c.*; Friedlaender and Zakrzewski, *l.c.*). These products can be obtained at 80° by heating it with ammonium sulphite solution and ammonia (Badische, D. R.-P. 117471 of 1899; Eng. Pat. 1387 of 1900).

(2) It couples with diazotised bases giving in an acetic acid bath 1-*monoazo*- dyes, and in an alkaline bath 1 : 4-*disazo*- dyes (Friedlaender and Silberstern, *l.c.*; *cf.* Friedlaender and Zakrzewski, *l.c.*; Badische, D. R.-P. 62947 of 1891; Höchst, D. R.-P. 86937 of 1894; Bayer, D. R.-P. 99468; Eng. Pat. 28090 of 1897).

(ix.) 2 : 6-**Dihydroxynaphthalene** is obtained by fusing sodium naphthalene-2 : 6-disulphonate (*cf.* Dusart, Compt. rend. 1867, 64, 859; Darmstaedter and Wichelhaus, Annalen, 1869, 152, 306; Armstrong and Graham, Chem. Soc. Trans. 1881, 39, 140), *or* sodium β-naphthol-6-sulphonate (Armstrong and Graham, *l.c.*; Emmert, Annalen, 1887, 241, 369) with caustic potash.

Identification.—It forms rhomb-like scales, m.p. 218° (Willstätter and Parnas, Ber. 1907, 40, 1410), dissolves only sparingly in water (1 litre at 14° dissolves 1·08 grm.) or light petroleum, shows strong blue fluorescence in alkaline solution, gives with ferric chloride a yellowish-white precipitate, and has a strong caustic effect on the skin. The *diacetate* forms scales, m.p. 175° (Emmert, *l.c.*); the *dimethyl ether*, rhomb-like scales, m.p. 150° (Willstätter and Parnas, *l.c.*); the *diethyl ether* scales, m.p. 162° (Emmert, *l.c.*).

Reactions.—(1) In boiling benzene solution with lead peroxide, it is oxidised to 2 : 6-*naphthaquinone* (Willstätter and Parnas, *l.c.*).

(2) With nitrous acid it gives the 1-*nitroso*-derivative (Bayer, D. R.-P. 55126, 59268 of 1890; Eng. Pat. 14230 of 1889).

(3) When heated with ammonia under pressure at 150°–300°, it yields 2 : 6-*diaminonaphthalene* (Ewer and Pick, D. R.-P. 45788 of 1887), and with aniline at 170°, it forms *diphenyl*-2 : 6-*diaminonaphthalene* (Leonhardt, D. R.-P. 54087 of 1889; Eng. Pat. 3098 of 1890).

(4) With monohydrate at 5°, it is converted into an acid which Bayer & Co. consider to be the 4-monosulphonic acid (D. R.-P. 72222 of 1893), but Jacchia, the 1 : 5-disulphonic acid (Annalen, 1902, 323, 114); with sulphuric acid at 100° it gives a *disulphonic acid* (Griess, Ber. 1880, 13, 1959).

(5) It couples in acetic acid (Kehrmann, Ber. 1907, 40, 1962) or in alkaline solution (Bayer, D. R.-P. 164317; Eng. Pat. 18569 of 1902), furnishing 1-*monoazo*- dyes (*cf.* Höchst, D. R.-P. 86937 of 1894; Kaufler and Bräuer, Ber. 1907, 40, 3276).

(x.) 2 : 7-**Dihydroxynaphthalene** is formed when sodium naphthalene-2 : 7-disulphonate is fused with caustic soda at 290°–300° (Ebert and Merz, Ber. 1876, 9, 609; Weber, *ibid.* 1881, 14, 2206); *or* when β-naphthol-7-sulphonic acid is fused with caustic soda (Pfitzinger and Duisberg, *ibid.* 1889, 22, 398). It is also formed when 2 : 7-dihydroxynaphthalene-3 : 6-disulphonic acid is heated with 20 p.c. sulphuric acid at 200° (Bayer, D. P. Anm. F. 7243; Eng. Pat. 25074A of 1893).

Identification.—It forms needles, m.p. 190° (Clausius, Ber. 1890, 23, 520), dissolves readily in hot water, but only sparingly in benzene, and gives no colouration with ferric chloride, but blackens rapidly in alkaline solution. The *diacetate* forms scales, m.p. 136° (Clausius, *l.c.*); the *dimethyl ether*, scales, m.p. 134° (Weber, *l.c.*); and the *diethyl ether*, scales, m.p. 104° (Liebermann and Hagen, Ber. 1882, 15, 1428).

Reactions.—(1) With nitrous acid it yields the 1-*nitroso*- derivative (Leonhardt, D. R.-P.

55204; Eng. Pat. 17223 of 1889; Clausius, *l.c.*; Kaufler and Bräuer, Ber. 1907, 40, 3275; *cf.* Read, Holliday & Co., D. R.-P. 68809; Eng. Pat. 1812 of 1890), which with iron salts gives a *naphthol green* (Leonhardt, D. R.-P. 58611 of 1889).

(2) When heated with sulphuric acid at 100° it forms 2 : 7-*dihydroxynaphthalene*-3 : 6-*disulphonic acid* (Bayer, D. P. Anm. F. 7243; Eng. Pat. 25074A of 1893; *cf.* Weber, *l.c.*; Aktienges., D. R.-P. 75142; Eng. Pat. 16199 of 1893).

(3) It gives 2 : 7-*diaminonaphthalene* when heated with ammonia under pressure at 150°–300° (Ewer and Pick, D. R.-P. 45788 of 1887), or boiled with ammonium sulphite solution and ammonia (Franzen and Deibel, J. pr. Chem. 1908, [ii.] 78, 155); *phenyl*-7-*amino*-β-*naphthol* with aniline at 190° (Kalle, D. R.-P. 60103 of 1891); and the corresponding *diaryl*-2 : 7-*diaminonaphthalenes* with arylamines (aniline, &c.), and either their hydrochlorides at 140°–150° (Durand and Huguenin, D. R.-P. 40886; Annaheim, Eng. Pat. 14283 of 1886; Ber. 1887, 20, 1372), or calcium chloride at 280°–290° (Clausius, *l.c.*).

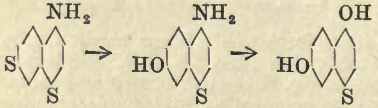
(4) It couples in alkaline solution with diazotised bases giving 1-*monoazo*- (Kaufler and Bräuer, *l.c.*; Erdmann and Borgmann, D. R.-P. 78409 of 1893; *cf.* Bayer, D. R.-P. 164318; Eng. Pat. 18569 of 1902), or 1 : 8-*disazo*- dyes (Cassella, D. R.-P. 108166; Eng. Pat. 9502 of 1899).

Dihydroxynaphthalenesulphonic Acids.

Introductory. — Dihydroxynaphthalenesulphonic acids are seldom obtained by direct sulphonation, and for their preparation recourse is had usually to α- or β-naphtholdi- or trisulphonic acids, or to α-naphthylaminedi- or trisulphonic acids. The exchange of the SO_3H, or of the NH_2 and SO_3H radicles, for OH in these acids is effected by fusion with 60–75 p.c. caustic alkali solution at high temperatures (180°–230°), with results which can be summarised thus:

(1) From *α-naphtholsulphonic acids*, the sulphonic group in the 8- position is the most easily displaced, then that in 5, but that in 2 or 4 resists displacement. From *β-naphtholsulphonic acids*, the sulphonic group in the 4-, 5-, or 8- position is easily displaced, but that in 1 or 6 resists displacement.

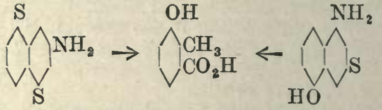
(2) With *α-naphthylaminesulphonic acids*, the order of replaceability of the SO_3H radicle by OH follows closely that observed with α-naphtholsulphonic acids. The resistance of a 4-sulphonic group to displacement by OH is displayed, for example, in the products obtained successively from α-naphthylamine-4 : 6-disulphonic acid by fusion with caustic alkali—



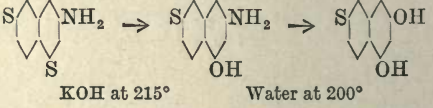
The exchange of the NH_2 radicle for OH in these acids is effected most readily when a sulphonic group is present in the 3-, 4-, or 5- position.

With β-naphthylaminesulphonic acids, the 4- or 5-sulphonic group is more easily displaced than that in the 8- position, otherwise the order of replaceability agrees with that experienced with the β-naphtholsulphonic acids. But the NH_2 radicle is not displaced by OH in the alkali fusion, and 2-aminonaphtholsulphonic acids, therefore, are the final products under ordinary conditions.

To these rules an important exception exists. Reactions which might be expected to produce 1 : 3-dihydroxynaphthalenesulphonic acids in the alkali fusion, lead almost invariably to decomposition with the formation of hydroxytoluic acids (*cf.* Kalle, D. R.-P. 91201 of 1893; Eng. Pat. 16559 of 1894; Höchst, D. R.-P. 81281; 81333 of 1893):



Turning to aminonaphtholsulphonic acids as sources of dihydroxynaphthalenesulphonic acids, those containing an α-amino- group exchange it for OH when heated with water or dilute (5 p.c.) mineral acid under pressure. With β-aminonaphtholsulphonic acids (except 2-amino-3-naphthol-6-sulphonic acid), the exchange takes place only when one of the other constituents, usually the OH radicle, is present in the 4- position.



Apart from these methods, dihydroxynaphthalenesulphonic acids have been obtained, but only in a few instances, from aminonaphtholsulphonic acids by the bisulphite method, and from [α-] or [β-]naphthaquinonesulphonic acids by reduction.

The dihydroxynaphthalenesulphonic acids and their alkali salts are easily soluble in water, the solutions when alkaline usually exhibiting fluorescence. When heated with dilute mineral acids above 200° many of them furnish the corresponding dihydroxynaphthalenes. They give colour reactions with ferric chloride and bleaching powder solutions, being characterised mainly by these and by the azo-dyes produced by coupling with certain diazotised bases. Summaries of the properties of many of the mono- and di-sulphonic acids may be found in the Patent literature (*cf.* Bayer, D. R.-P. 85241 of 1895; and 79054 of 1893 respectively).

Azo- dyes. For the production of azo- dyes, the most valuable of these products are the 1 : 8-dihydroxynaphthalene-4-monosulphonic, and the 2 : 4-, and 3 : 6-disulphonic acids, owing to the fact that the azo- dyes derived from them form lakes with chromium (aluminium or iron) mordants (*cf.* Höchst, D. R.-P. 67563 of 1890). As illustrating the resemblance between the properties of the 1 : 8- and the *ortho*- position, it may be noted that, in this series, the azo-dyes which furnish lakes are derived exclusively from the 1 : 2-, 2 : 3-, and 1 : 8- dihydroxynaphthalenesulphonic acids (*cf.* for 1 : 2-, Witt, D. R.-P. 49872 of 1889; for 2 : 3-, Bayer, D. R.-P. 82774 of 1893). The azo- dyes obtained from 1 : 3-dihydroxynaphthalenesulphonic acid are remarkable for their yellow shade (*cf.* Bayer, D. R.-P. 78877 of 1893; Eng. Pat. 3032 of 1894).

Azines. Use has been made of 1 : 2-dihydroxynaphthalenesulphonic acids for the preparation of *thiazines* (*cf.* Bayer, D. R.-P. 84232; Eng. Pat. 825 of 1893; D. R.-P. 84233; Eng. Pat. 4757 of 1893; D. R.-P. 87900; 87899; Eng. Pat. 8093 of 1893; Aktienges., D. R.-P. 83269; Eng. Pat. 23311 of 1893), and of *oxazines* (*cf.* Bayer, D. R.-P. 77120; Eng. Pat. 8093 of 1893; D. R.-P. 80744; Eng. Pat. 5056 of 1894; Dahl, D. R.-P. 84850; Eng. Pat. 5153 of 1895).

Dihydroxynaphthalenemonosulphonic Acids.

Constitution.	Preparation.	Acids, Salts and Reactions.
O : O : S		
1 : 2 : 4	(1) Reduction of [β-]-naphthaquinone-4-sulphonic acid with sulphurous acid (Witt and Kaufmann, Ber. 1891, 24, 3163) (2) Action of sodium bisulphite solution on [β-]naphthaquinone (Bayer, D. R.-P. 70867 of 1892; Eng. Pat. 825 of 1893).	*Sodium* salt, readily soluble needles; *potassium* salt sparingly soluble prisms. Does not couple with diazotised bases (*cf.* Bayer, D. R.-P. 85241 of 1895). Alkaline solution turns red on exposure to air forming 2-hydroxy-[α-]naphthaquinone.
1 : 2 : 6	Reduction of [β-]-naphthaquinone-6-sulphonic acid with sulphurous acid (Witt, Ber. 1891, 24, 3154; D. R.-P. 50506 of 1889; Paul, *cf.* J. Soc. Chem. Ind. 1897, 21, 733).	*Ammonium* salt NH_4A, readily soluble leaflets. Couples with diazotised bases, forming *azo*-dyes, which give lakes with chromium and other oxides (Witt, *l.c.*; D. R.-P. 49872 of 1889).
1 : 2 : 5 1 : 2 : 7 1 : 2 : 8	These acids obtained by reduction of the corresponding [β-]-naphthaquinonesulphonic acids (Witt, Ber. 1891, 24, 3157).	No description published.
1 : 3 : 5	2-Amino-4-naphthol-8-sulphonic acid heated with water under pressure at 180°–200° (Bayer, D. R.-P. 85241; Eng. Pat. 3580 of 1895).	*Alkali* salts form yellow solutions which show green fluorescence. Gives dirty green col. with ferric chloride. Couples with diazotised bases.
1 : 3 : 6	(1) 1-Amino-3-naphthol-6-sulphonic acid heated with water under pressure at 120° (Friedlaender and Rüdt, Ber. 1896, 29, 1613). (2) 2-Amino-4-naphthol-7-sulphonic acid heated with water under pressure at 200° (Bayer, D. P. Anm. F. 7978; Eng. Pat. 25214 of 1894.	*Alkali* salts very soluble, show green fluorescence in alkaline solution; *barium* salt, BaA_2, readily soluble needles (Friedlaender and Rüdt, *l.c.*). Couples with diazotised bases, forming *azo*-dyes (*cf.* Bayer, D. R.-P. 84991; Eng. Pat. 3580 of 1895).
1 : 3 : 7	1:3-Dihydroxynaphthalene-5:7-disulphonic acid heated with 5 p.c. sulphuric acid under pressure at 210° (Bayer, D. R.-P. 90878 of 1895).	*Alkali* salts give yellow solutions which show intense green fluorescence. Gives bluish-black col. with ferric chloride. Couples with diazotised bases, giving *azo*-dyes (*cf.* Bayer, D. R.-P. 86100; Eng. Pat. 4962 of 1895).
1 : 5 : 2 C-acid	(1) Together with the 4-acid, when 1:5-dihydroxynaphthalene is warmed with sulphuric acid at 50°–60° (Bucherer and Uhlmann, J. pr. Chem. 1909, [ii.] 80, 235; *cf.* Ewer and Pick, D. R.-P. 41934 of 1887). (2) *a*-Naphthol-2 : 5-disulphonic acid heated with 60 p.c. caustic soda at 250° (Bayer, D. R.-P. 68344 of 1889; Eng. Pat. 3397 of 1890).	*Acid sodium* salt, readily soluble leaflets; the alkaline solutions show blue fluorescence. Gives bluish-green colouration with ferric chloride. Couples with diazotised bases forming *azo*-dyes (*cf.* Bayer, *l.c.*).
1 : 5 : 3	Naphthalene-1 : 3 : 5-trisulphonic acid fused with caustic alkali (Bayer, D. R.-P. 166768; Eng. Pat. 18569 of 1902).	Couples with diazotised bases forming *azo*-dyes (Bayer, *l.c.*).
1 : 5 : 4	Together with the 2-acid (*q.v.*), when 1:5-dihydroxynaphthalene is warmed with sulphuric acid at 50°–60°.	*Calcium* salt forms a sparingly soluble double salt with calcium sulphate. Couples with diazotised bases.
1 : 5 : 7	1-Amino-5-naphthol-7-sulphonic acid boiled with sodium bisulphite solution, and product decomposed by mineral acid (Bucherer and Uhlmann, J. pr. Chem. 1909, [ii.] 80, 238).	*Acid*, scales, crystallises with ½ mol. of alcohol. Couples with diazotised bases.
1 : 6 : 3	(1) Fusion of naphthalene-1:3:6-trisulphonic acid with 90 p.c. caustic soda at 250° (Aktienges., D. R.-P. 42261 of 1886; Bayer, D. R.-P. 63015 of 1891; *cf.* Kalle, D. R.-P. 89061 of 1894). (2) 1-Amino-6-naphthol-3-sulphonic acid heated with water under pressure at 200° (Cassella, D. P. Anm. C. 5020 of 1894; *cf.* Bayer, D. R.-P. 85241; Eng. Pat. 3580 of 1895). (3) 2-Amino-5-naphthol-7-sulphonic acid heated with 40 p.c. sodium bisulphite solution, and product decomposed by mineral acid (Badische, D. R.-P. 126136, 134401 of 1899; Bucherer, J. pr. Chem. 1904, [ii.] 69, 83).	*Sodium* salt, sparingly soluble, shows in alkaline solution reddish-blue fluorescence. Gives green colouration with ferric chloride. Forms a yellow easily soluble *nitroso*-compound (Cassella, *l.c.*). Couples with diazotised bases forming *azo*-dyes (Bayer, *l.c.*; Casella, *l.c.*).

Constitution.	Preparation.	Acids, Salts and Reactions.
0:0:S		
1:6:4	Fusion of α-naphthylamine-4:6-disulphonic acid (Dahl, D. R.-P. 57114 of 1889; Eng. Pat. 735 of 1890); *or* of α-chloronaphthalene-4:6-disulphonic acid with caustic soda at 210°–220° (Rudolph, D. R.-P. 104902 of 1898).	*Acid* and *acid sodium* salt, sparingly soluble leaflets; alkaline solutions show violet fluorescence. Forms a yellow sparingly soluble *nitroso*-derivative (Rudolph, *l.c.*). Gives green col. with ferric chloride (*ibid.*). Couples with diazotised bases (Dahl, *l.c.*).
1:7:3 G-acid	Fusion of β-naphthol-6:8-disulphonic acid with caustic soda at 220°–230° (Höchst, D. P. Anm. F. 4153; Eng. Pat. 9642 of 1889; *cf.* Bayer, D. R.-P. 85241 of 1895).	*Acid sodium* salt readily soluble needles; alkaline solutions show blue fluorescence. Gives green colouration with ferric chloride. Couples with diazotised bases.
1:7:4	(1) Fusion of 2-carboxy-α-naphthol-4:7-disulphonic acid with caustic alkali at 230°–290° (Bindschedler, D. R.-P. 81938 of 1893; Eng. Pat. 4629 of 1894). (2) 1:7-Dihydroxy-2-carboxynaphthalene-4-sulphonic acid heated with 30 p.c. caustic soda under pressure at 140°–160° (*ibid.*, D. R.-P. 83965 of 1895).	*Acid* and *acid salts* readily soluble; alkaline solutions show violet fluorescence. Gives green colouration with ferric chloride. Couples with diazotised bases.
1:8:2	1-Amino-8-naphthol-7-sulphonic acid heated with lime and water under pressure at 250° (Bayer, D. P. Anm. F. 7509 of 1894).	*Acid sodium* salt needles, shows reddish-violet fluorescence in solution. Gives green colouration with ferric chloride. Couples with diazotised bases.
1:8:3 ε-acid	(1) α-Naphthylamine-3:8-disulphonic acid heated with 35 p.c. caustic soda under pressure at 220°–250° (Höchst, D. P. Anm. F. 7112 of 1892). (2) Fusion of α-naphthol-3:8-disulphonic acid with caustic alkali, or, more easily, of α-naphthol-6:8-disulphonic acid with 50 p.c. caustic soda at 170°–210° (Kalle, D. R.-P. 82422 of 1894). (3) 1-Amino-8-naphthol-3:5-disulphonic acid heated with water at 200° (Leonhardt, D. P. Anm. F. 8626; Eng. Pat. 19253 of 1895; Cassella, D. R.-P. 108848 of 1895).	*Acid sodium* salt sparingly soluble needles; alkaline solutions show blue fluorescence (Kalle, *l.c.*). Gives green colouration with ferric chloride (Kalle, *l.c.*). Couples with diazotised bases (*cf.* Bayer, D. R.-P. 85241 of 1895).
1:8:4 S-acid.	(1) Fusion of the following with caustic alkali or caustic alkali solution: α-naphthol-4:8-disulphonic acid (Bayer, D. R.-P. 54116, 67829; Eng. Pat. 13665, 18517 of 1889), *or* α-naphthol-5:8-disulphonic acid, or its sultone (Bayer, D. R.-P. 80667 of 1892; Eng. Pat. 1227 of 1894); also of α-naphthylamine-4:8-disulphonic acid under pressure (Bayer, D. R.-P. 71836 of 1890), *or* α-naphthylamine-5:8-disulphonic acid (Bayer, D. R.-P. 77285 of 1892; Eng. Pat. 1227 of 1894); also of 1-amino-8-naphthol-4-sulphonic acid (Bayer, D. R.-P. 80315 of 1893), *or* 1-amino-8-naphthol-5-sulphonic acid (Bayer, D. R.-P. 75055; Eng. Pat. 15269 of 1893; Badische, D. R.-P. 80234; Eng. Pat. 18924 of 1893). (2) 1:8-Diaminonaphthalene-4-sulphonic acid heated with milk of lime under pressure at 230° (Cassella, D. R.-P. 75962 of 1893). (3) 1-Amino-8-naphthol-4-sulphonic acid (Bayer, D. R.-P. 109102 of 1899), or 5-sulphonic acid (Bucherer, J. pr. Chem. 1904, [ii.] 69, 86), heated with sodium bisulphite solution and product decomposed by caustic alkali.	*Acid* forms three series of salts, all easily soluble; *monosodium* salt, NaH_2A, silky leaflets; *disodium* salt, Na_2HA+2H_2O, leaflets; *monobarium* salt, BaH_4A_2, needles; *dibarium* salt, $BaHA+1\frac{1}{2}H_2O$ (Bayer, D. R.-P. 67829; Eng. Pat. 13665 of 1889). Basic salts (*trisodium*, etc.) show bluish-green fluorescence in solution. Gives dirty green precipitate with ferric chloride. Couples with diazotised bases, giving many valuable *azo*-dyes which have the property of forming lakes with chromium and other oxides (*cf.* Bayer, *l.c.*; D. R.-P. 61707 of 1889; 66693; Eng. Pat. 5984 of 1891). For *monoalkyl* derivatives and the *disazo*-dyes obtained by coupling them with diazotised bases, see Bayer, D. R.-P. 73741, 78937; Eng. Pat. 3495 of 1893.
2:3:6 R-acid.	Fusion of β-naphthol-3:6-disulphonic acid with caustic soda at 240°–280° (Badische, D. R.-P. 57525; Eng. Pat. 15803 of 1890; Höchst, D. P. Anm. F. 4153; Eng. Pat. 9642 of 1889; Friedlaender and Zakrzewski, Ber. 1894, 27, 762).	*Acid sodium* salt, sp. sol. leaflets, shows reddish-blue fluorescence in alkaline solution; *barium* salt, BaA_2, sp. sol. (*cf.* Bayer, D. R.-P. 85241 of 1895). Gives intense violet col. with ferric chloride (*ibid.*). Couples with diazotised bases, giving *azo*-dyes which form lakes with metallic oxides (*cf.* Bayer, D. R.-P. 82774 of 1893).
2:7:3[1] F-acid.	Fusion of β-naphthol-3:7-disulphonic acid with caustic alkali (*cf.* Aktienges., D. R.-P. 63956 of 1891; Bayer, D. R.-P. 85241 of 1895).	*Sodium* salt, sparingly soluble crystalline powder, shows bluish-violet fluorescence in solution (*cf.* Bayer, *l.c.*). Gives deep blue colouration with ferric chloride.

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[1] The acid described as 2:6-dihydroxynaphthalene-4-sulphonic acid (Bayer, D. R.-P. 72222 of 1893) is considered by Jacchia (Annalen, 1902, 323, 131) to be a disulphonic acid.

Dihydroxynaphthalenedisulphonic Acids.

Constitution.	Preparation.	Acids, Salts and Reactions.
O:O:S:S		
1:2:3:6[1] and 1:2:6:8	(1) Acid sodium salt of 1-amino-2-naphthol-3:6-(resp. 6:8-)disulphonic acid boiled with water (Witt, Ber. 1888, 21, 3480; D. R.-P. 49857 of 1889). (2) Reduction of [β]-naphthaquinone-3:6-(resp. 6:8-)disulphonic acid with sulphurous acid (Witt, Ber. 1891, 24, 3157).	*Acid sodium* salts readily soluble leaflets; decompose very rapidly in alkaline solution (*cf.* Bayer, D. R.-P. 79054 of 1893). Do not couple with diazotised bases (Bayer, *l.c.*; *cf.* Witt, Ber. 1891, 24, 3156). Precipitate gelatin or basic aniline dyes from solution (*naphthotannins*) (*cf.* Witt, D. R.-P. 49857 of 1889).
1:3:5:7 "Yellow" acid.	(1) Mixed with 30 p.c. of "red"-acid, by heating naphthalene-1:3:5:7:tetrasulphonic acid *or* α-naphthol-3:5:7-trisulphonic acid with 60 p.c. caustic soda under pressure at 180°–200° (Bayer, D. R.-P. 79054; Eng. Pat. 25074 of 1893). (2) 2-Amino-4-naphthol-6:8-disulphonic acid heated with water under pressure at 210°–220° (Bayer, D. R.-P. 89242; D. P. Anm. F. 8154 of 1895).	*Sodium* salt, readily soluble; *potassium* salt, leaflets; alkaline solutions show green fluorescence; *barium* salt, BaA, moderately soluble needles (Friedlaender and Rüdt, Ber. 1896, 29, 1613). Gives blue colouration with ferric chloride. Couples in alkaline solution with diazotised bases, giving *azo*-dyes of yellow shade (*cf.* Bayer, D. R.-P. 78877 of 1893; Eng. Pat. 3032 of 1894).
1:5:3:7 "Red" acid.	(1) α-Naphthol-3:5:7-trisulphonic acid heated with 50 p.c. caustic soda at 150°–160° (Kalle, D. P. Anm. K. 12732 of 1895). (2) Mixed with 70 p.c. of yellow acid (*q.v.*), from naphthalene-1:3:5:7-tetrasulphonic acid.	*Potassium* and *sodium* salts readily soluble needles; in alkaline solution shows bluish-violet fluorescence (Bayer, D. R.-P. 79054 of 1893). Gives bluish-green col. with ferric chloride. Couples in acid or alkaline solution (*cf.* Bayer, *l.c.*) with 1 or 2 mols. (*cf.* Kalle, *l.c.*) of diazotised bases, giving *azo*-dyes.
1:5:(2):(4)	1:5-Dihydroxynaphthalene sulphonated with sulphuric acid at 100°–160° or with anhydro-acid in the cold (Ewer and Pick, D. R.-P. 41934 of 1887).	No description published, but acid said to couple with diazotised bases (Ewer and Pick, *l.c.*; *cf.* 2- and 4-monosulphonic acids).
1:(7):(2):(4)	Fusion of α-naphthol-2:4:7-trisulphonic acid with caustic alkali (*cf.* Höchst, D. R.-P. 67426; Eng. Pat. 18783 of 1891).	No description published.
1:7:3:6 A-acid	Mixed with 30 p.c. of the 2:3:6:8-acid (B-acid), by fusion of β-naphthol-3:6:8-trisulphonic acid with caustic alkali under pressure at 230°–240° (Höchst, D. P. Anm. F. 4154; Eng. Pat. 9642 of 1889; D. R.-P. 67563 of 1890; *cf.* Friedlaender and Silberstern, Monatsh. 1902, 23, 527).	*Sodium* salt, Na_2A, sparingly soluble needles; alkaline solutions show bluish-green fluorescence. Forms a dark blue precipitate with formaldehyde and hydrochloric acid (Friedlaender and Silberstern, *l.c.*). Gives fleeting blue col. with ferric chloride (*ibid.*). Couples with diazotised bases (Höchst, *l.c.*).
1:8:2:4 S-acid	(1) 1-Amino-8-naphthol- or naphthasultam-2:4-disulphonic acid heated with 80 p.c. caustic soda solution above 180° (Bayer, D. R.-P. 79566, 80668; Eng. Pat. 4979 of 1893; Cassella, D. R.-P. 81282; of 1893; Dressel and Kothe, Ber. 1894, 27, 2142). (2) 1-Amino-8-naphthol-5:7-disulphonic acid heated with dilute caustic soda solution above 250° (Badische, D. P. Anm. B. 16142; Eng. Pat. 18924 of 1893). (3) Fusion of α-naphthol-2:4:8-trisulphonic acid with caustic alkali at 210° (Bayer, D. R.-P. 57021; Eng. Pat. 3397 of 1890; Dressel and Kothe, Ber. 1894, 27, 2144).	*Disodium* salt readily soluble needles, showing faint blue fluorescence in solution; *trisodium* salt, $Na_3HA + 4H_2O$, readily soluble prisms, formed in alkaline solution, shows greenish fluorescence (Dressel and Kothe, *l.c.*). Forms an orange soluble *mononitroso*-compound (Cassella, *l.c.*; Dressel and Kothe, *l.c.*). Gives green colouration with ferric chloride (*cf.* Badische, *l.c.*). Couples with diazotised bases (Badische, *l.c.*). In acid solution with dichromate gives black dye on wool (Cassella, *l.c.*).
1:8:3:5 K-acid	(1) Fusion of α-naphthol-4:6:8-trisulphonic acid with 70 p.c. caustic soda solution under pressure at 170°–190° (Bayer, D. P. Anm. F. 7004; Eng. Pat. 17141c 1893; *cf.* Kalle, Eng. Pat. 1641 of 1894). (2) 1-Amino-8-naphthol-3:5-disulphonic acid heated with 7 p.c. caustic soda solution under pressure at 240° (Leonhardt, D. P. Anm. F. 8682; Eng. Pat. 21919 of 1895; Cassella, D. R.-P. 108848 of 1895). (3) 1-Amino-8-naphthol-4:6-disulphonic acid heated with 70 p.c. caustic alkali solution above 240° (Bayer, D. R.-P. 80741; Eng. Pat. 17141c of 1893).	*Disodium* salt readily soluble needles; solutions of *acid salts* show faint blue fluorescence (*cf.* Bayer, D. R.-P. 79054 of 1893). Forms a yellow readily soluble *nitroso*- derivative. Gives green colouration with ferric chloride (Bayer, *l.c.*). Couples with diazotised bases (Bayer, D. P. Anm. F. 7004; Eng. Pat. 17141c of 1803).
1:8:3:6 Chromotrope acid	(1) α-Naphthol-3:6:8-trisulphonic acid or its sultone heated with 60 p.c. caustic soda at 170°–220° (Höchst, D. R.-P. 67563 of 1890). (2) 1-Amino-8-naphthol-3:6-disulphonic acid heated with 5 p.c. caustic soda under pressure at 265° (Bayer, D. R.-P. 68721 of 1891; Eng. Pat. 11522 of 1892).	*Acid* forms four series of salts, two strongly acid, one neutral, one basic. *Disodium* salt, $Na_2H_2A + 2H_2O$, readily soluble in water, and acid towards sodium carbonate; alkaline solutions show violet-blue fluorescence. *Barium* salt, $BaH_2A + 3H_2O$, small leaflets, which in solution with sodium carbonate yields the *sodium barium* salt, $BaNaHA + 3H_2O$, in needles (Höchst, *l.c.*).

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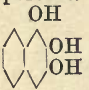
[1] The 1:2-dihydroxynaphthalene-3:6-disulphonic acid is also formed when 1:2-diaminonaphthalene-3:6-disulphonic acid is heated with dilute mineral acids (*cf.* Cassella, D. R.-P. 72584 of 1892).

Constitution.	Preparation.	Acids, Salts and Reactions.
O : O : S : S 1 : 8 : 3 : 6 (*contd.*)	(3) 1:8-Diaminonaphthalene-3:6-disulphonic acid heated with 5 p.c. caustic soda under pressure at 260°–280° (Bayer, D. R.-P. 69190 of 1891; Eng. Pat. 11522 of 1892), or with dilute mineral acids or water under pressure at 150°–160° (Cassella, D. R.-P. 75153 of 1892). (4) 8-Chloro-α-naphthol - 3 : 6 - disulphonic acid fused with caustic alkali (Badische, D. R.-P. 147852 of 1903).	Gives grass-green col. with ferric chloride (*ibid.*). Couples with 1 or 2 mols. of diazotised bases, forming ortho-*azo*- dyes (Hantower and Täuber, Ber. 1898, 31, 2156), and forms lakes, which give scarlet, claret, violet, or bluish-black shades (Höchst, *l.c.*). Is extensively used in the production of mordant *azo*-dyes. In acid solution with dichromate gives brown dye on wool (Höchst, D. R.-P. 77552 of 1891). For *chloro*-derivative and derived *azo*-dyes, see Höchst, D. R.-P. 153195 of 1903.
1 : 8 : ? : ? I-acid 1 : 8 : ? : ? G-acid 1 : 8 : ? : ? R-acid	1 : 8-Dihydroxynaphthalene sulphonated with sulphuric acid at 50° and the respective products separated by means of their barium salts of which that of I-acid is least and of R-acid most soluble (Badische, Eng. Pat. 14294 of 1891; *ibid.* D. R.-P. 79029, 79030 of 1891).	*Sodium* salts very readily soluble, show blue fluorescence in alkaline solution. Give green colourations with ferric chloride. Couple with diazotised bases, forming *azo*-dyes, which, if from I-acid are worthless, but from G-acid valuable (*cf.* Bayer, D. R.-P. 79054 of 1893).
2 : 3 : 6 : 8 B-acid	Mixed with the 1 : 7 : 3 : 6-acid, by fusion of β-naphthol-3 : 6 : 8-trisulphonic acid with caustic alkali (Höchst, D. R.-P. 67563 of 1890; *cf.* Friedlaender and Silberstern, Monatsh., 1902, 23 527).	*Sodium* salt, $Na_2A+3\frac{1}{2}H_2O$, easily soluble needles, shows bluish-violet fluorescence in alkaline solution; *barium* salt BaA, sp. sol. needles. Gives violet col. with ferric chloride, and does not form a precipitate with formaldehyde and hydrochloric acid (Friedlaender and Silberstern, *l.c.*). Couples with diazotised bases (*ibid.*).
2 : 7 : 3 : 6	(1) 2:7-Dihydroxynaphthalene heated with sulphuric acid at 100° (Aktienges., D. R.-P. 75142; Eng. Pat. 16199 of 1893; *cf.* Weber, Ber. 1881, 14, 2208). (2) β-Naphthol-3 : 6 : 7 : trisulphonic acid heated with 66 p.c. caustic soda solution under pressure at 220°–300° (Bayer, D. P. Anm. F. 7243; Eng. Pat. 25074A of 1893).	*Acid sodium* salt moderately soluble; *potassium* salt, large needles; *barium* salt, almost insoluble; salts show bluish-green fluorescence in alkaline solution (*cf.* Bayer, D. R.-P. 79054 of 1893). Forms a sp. soluble orange *nitroso*- compound. Gives deep-blue col. with ferric chloride. Couples in alkaline solution with 1 mol. of diazotised bases (Bayer, D. P. Anm. F. 7243 of 1893).

TRIHYDROXYNAPHTHALENES.

Introductory.—The trihydroxynaphthalenes have little technical interest. The methods available for their production are fusion of sulphonic acids with caustic alkali, and reduction of hydroxynaphthaquinones, but the number of isomerides they can give is limited by the small number of acids or quinones available. Only five of the fourteen isomeric trihydroxynaphthalenes have been isolated and characterised, but sulphonic acids of two others are known. The azo- dyes obtained from those that couple with diazotised bases are unimportant.



(i.) 1 : 2 : 3-**Trihydroxynaphthalene** (*Naphthapyrogallol*), obtained by boiling *iso*naphthazarin with zinc and dilute sulphuric acid (Zincke and Ossenbeck, Annalen, 1899, 307, 18), is crystalline, and gives a *triacetate*, in prisms, m.p. 250°–255° (Zincke and Noack, *ibid.* 1897, 295, 19).

(ii.) 1 : 2 : 4-**Trihydroxynaphthalene**, formed by reduction of hydroxy-[α-]naphthaquinone with tin and hydrochloric acid (Graebe and Ludwig, Annalen, 1870, 154, 324); *or* by hydrolysis of the triacetate with alcoholic hydrogen chloride (Thiele and Winter, *ibid.* 1900, 311, 346; Bayer, D. R.-P. 101607 of 1897; Eng. Pat. 10590 of 1898), crystallises in needles, m.p. 154°, and in alkaline solution absorbs oxygen giving *hydroxy*-[α-]*naphthaquinone*.

The *triacetate*, obtained by heating [α-] or [β-]naphthaquinone and acetic anhydride with a small quantity of sulphuric acid (Bayer, *l.c.*; Thiele and Winter, *l.c.*) or phosphoric acid (Bayer, D. R.-P. 107508 of 1898; Eng. Pat. *l.c.*) at 30°–40°, or zinc chloride at 50°–60° (Thiele and Winter, *l.c.*), crystallises in needles, m.p. 134°–135°.

(iii.) 1 : 3 : 5-Trihydroxynaphthalene, unknown. The **7-sulphonic acid** is formed when naphthalene-1 : 3 : 5 : 7-tetrasulphonic acid (*or* the α-naphthol-3 : 5 : 7-trisulphonic acid *or* the 1 : 3- or 1 : 5-dihydroxynaphthalenedisulphonic acid obtainable from it) is fused with caustic potash at 280° (Bayer, D. R.-P. 80464; Eng. Pat. 19624 of 1893). Its *potassium* salt separates in needles, and couples with 1 or 2 mols. of a diazotised base, forming *azo*- dyes (Bayer, D. R.-P. 87583 of 1893; Eng. Pat. 1229 of 1894).

(iv.) 1 : 3 : 6-**Trihydroxynaphthalene**,[1] obtained by fusing 1 : 6-dihydroxynaphthalene-3-sulphonic acid with caustic soda at 250°–270° (Kalle, D. R.-P. 112176 of 1899; Meyer and Hartmann, Ber. 1905, 38, 3950), forms doubly refracting crystals, m.p. 95°; a *hydrochloride* in yellow needles; and a *triacetate*, needles, m.p. 112°–113°. It couples with diazotised bases forming *azo*- dyes.

(v.) 1 : 3 : 8-Trihydroxynaphthalene, unknown. The **6-sulphonic acid**, obtained by fusing α-naphthol-3 : 6 : 8-trisulphonic acid, or 1 : 8 - dihydroxynaphthalene - 3 : 6 - disulphonic acid with caustic potash at 310°–320° (Bayer, D. R.-P. 78604; Eng. Pat. 17141C of 1893), forms easily soluble alkali salts, which show greenish-blue fluorescence in solution, and couple with 1 or 2 mols. of a diazotised base forming *azo*- dyes.

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[1] A polymeride $C_{20}H_{10}(OH)_6$, possibly a dinaphthyl derivative, of which the *hexa-acetate* in scales, m.p. 200°, is formed by boiling the aqueous solution of this trihydroxynaphthalene (Kalle, *l.c.*; Meyer and Hartmann, *l.c.*).

(vi.) 1 : 4 : 5-**Trihydroxynaphthalene** ([α-]*hydrojuglone*; *cf.* Bernthsen and Semper, Ber. 1887, 20, 941), mixed with about one-fifth the amount of [β-]hydrojuglone,[1] is present in the unripe shells of the walnut (Mylius, *ibid.* 1884, 17, 2412); the same compounds also occur in the ripe shells, and in about the same proportion, but differently combined, as they cannot be extracted by ether (Mylius, *ibid.* 1885, 18, 2568, footnote). It crystallises in scales or needles, m.p. 168°–170°; with ferric chloride gives *juglone;* and with acetic anhydride yields the *triacetate* of [β-]hydrojuglone, which forms prisms, m.p. 129°–130°.

(vii.) 1 : 6 : 7-**Trihydroxynaphthalene,** obtained when 1 : 6 : 7-trihydroxynaphthalene-3-sulphonic acid is heated with water or 5 p.c. sulphuric acid under pressure at 210°–220° (Cassella, D. R.-P. 112098; Eng. Pat. 27345 of 1898; Friedlaender and Silberstern, Monatsh. 1902, 23, 530), forms needles, m.p. 175°; its *triacetate,* needles, m.p. 143°–144°; and *trimethyl ether,* prisms, m.p. 127°–128°. It couples in the 4- position with 1 mol. of a diazotised base giving *azo-* dyes which form lakes with chromium or iron salts (Cassella, D. R.-P. 110618; Eng. Pat. *l.c.*; D. R.-P. 110904 of 1899).

The 3-sulphonic acid, prepared from β-naphthol-3 : 6 : 8-trisulphonic acid by fusion with caustic alkali (*cf.* Höchst, D. R.-P. 67426; Eng. Pat. 18783 of 1891) at 240°–250° (Friedlaender and Silberstern, *l.c.* 529), gives a *sodium* salt in sparingly soluble needles, a *barium* salt BaA$_2$ in sparingly soluble leaflets, and couples with diazotised bases forming *azo-* dyes (Höchst, *l.c.*).

AMINODIHYDROXYNAPHTHALENES.

The aminodihydroxynaphthalenes are of interest chiefly in relation to hydroxynaphthaquinoneoximes (nitrosodihydroxynaphthalenes) and have no technical value. Little is known about them, the hydrochloride and triacetyl derivative being almost the only definite substances isolated in each case.

N : O : O	[$NH_2 \cdot C_{10}H_5(OH)_2$]
1 : 2 : 3	Decomp. 230° (Friedlaender and Silberstern, Monatsh. 1902, 23, 521).
1 : 2 : 4[2] [4 : 1 : 3]	Not isolated. *Triacetyl* derivative, tablets, m.p. 155°–156° (Kehrmann and Mascioni, Ber. 1895, 28, 351; Kehrmann and Hertz, *ibid.* 1896, 29, 1419).
1 : 2 : 6	Not isolated. Obtained by reduction of azo-derivative of 2 : 6-dihydroxynaphthalene (Kehrmann and Sabo, Ber. 1907, 40, 1962).
1 : 2 : 7	Not isolated. Obtained by reduction of nitroso-2 : 7-dihydroxynaphthalene. *Triacetyl* derivative, m.p. 183° (Clausius, Ber. 1890, 23, 521; Nietzki and Knapp, *ibid.* 1897, 30, 1123).
1 : 3 : 4 [4 : 1 : 2]	Not isolated. *Triacetyl* derivative, prisms, m.p. 193° (Kehrmann, Ber. 1894, 27, 3340).
1 : 5 : 8 [5 : 1 : 4]	Not isolated. *Triacetyl* derivative, needles, m.p. 165° (Graebe, Ber. 1899, 32, 2878; Graebe and Oeser, Annalen, 1904, 335, 149).
N : O : O	[$NH_2 \cdot C_{10}H_5(OH)_2$]
1 : (6) : 8 [8 : 1 : (3)]	Unknown. The (6)-sulphonic acid, obtained by fusing 1-amino-8-naphthol-3 : 6-disulphonic acid (H-acid) with 60 p.c. caustic soda solution at 210°, is diazotisable (Bayer, D. R.-P. 75097 of 1891). The alkali salts show greenish blue fluorescence in solution.
2 : 1 : 4	Not isolated. *Triacetyl* derivative, needles, m.p. 259°–260° (Kehrmann, Ber. 1894, 27, 3343).
2 : 3 : 4 [3 : 1 : 2]	Needles, m.p. 164°. *Triacetyl* derivative, needles, decomp. above 200° (Korn, Ber. 1884, 17, 907; Zincke and Noack, Annalen, 1897, 295, 13); N-*acetyl* derivative, decomp. 170° (Kehrmann and Zimmerli, Ber. 1898, 31, 2405).
2 : (3) : 8 [7 : 1 : (6)]	Unknown. The (6)-sulphonic acid, obtained by fusing 2-amino-8-naphthol-3 : 6-disulphonic acid with caustic alkali at 240°–280°, forms sparingly soluble needles, and is diazotisable, (Höchst, D. R.-P. 53023; Eng. Pat. 15175 of 1889). The alkali salts show bluish-violet fluorescence in solution.

TETRAHYDROXYNAPHTHALENES.

1 : 2 : 3 : 4-**Tetrahydroxynaphthalene** (*leuco-*iso*naphthazarin*), obtained from *iso*naphthazarin by reduction, forms easily soluble scales, and its *tetra-acetyl* derivative, needles, m.p. 220°. It is readily oxidised to *iso*naphthazarin, and reduced to 1 : 2 : 3-*trihydroxynaphthalene* (Zincke and Ossenbeck, Annalen, 1899, 307, 16).

1 : 2 : 5 : 8-**Tetrahydroxynaphthalene** (*leuco-naphthazarin*) is obtained when naphthazarin is boiled with alcohol, stannous chloride, and hydrochloric acid (Zincke and Schmidt, Annalen, 1895, 286, 37); or when a boiling aqueous solution of 'naphthazarin melt' is reduced by iron (Badische, D. R.-P. 129074; Eng. Pat. 23887 of 1900). It forms needles, m.p. 154°, and its *tetra-acetyl* derivative, minute prisms, m.p. 277°–279° (Schunck and Marchlewski, Ber. 1894, 27, 3463; Zincke and Schmidt, *l.c.*; Liebermann, Ber. 1895, 28, 1457). It is readily oxidised to naphthazarin, and is a substantive dye which when oxidised with chromic acid on the fibre gives black shades (Badische, *l.c.*).

DIAMINODIHYDROXYNAPHTHALENES.

Several diaminodihydroxynaphthalenes have been described, but only those which furnish clues to the constitution of disazo- dyes obtained from dihydroxynaphthalenes need be mentioned here.

1 : 4-Diamino-2 : 3-dihydroxynaphthalene, obtained by reduction of disazo-dye from 2 : 3-dihydroxynaphthalene, forms *sulphate,* $B \cdot H_2SO_4$, leaflets, turning blue on oxidation, and gives iso*naphthazarin* with ferric chloride (Friedlaender and Silberstern, Monatsh, 1902, 23, 524).

1 : 6-Diamino-4 : 5-dihydroxynaphthalene, obtained by reduction of disazo-dye from 1 : 8-dihydroxynaphthalene, is very rapidly oxidised to *naphthazarin* (*ibid.* 518).

1 : 8-Diamino-2 : 7-dihydroxynaphthalene, obtained by reduction of disazo-dye from 2 : 7-dihydroxynaphthalene, gives *sulphate,* needles, which forms blue solution in alkalis (Cassella, D. R.-P. 108166; Eng. Pat. 9502 of 1899).

IX. QUINONE DERIVATIVES.

Introductory.—From the formula of naphthallene the existence of three homo- and three hetero-nucleal quinones may be predicted. Two of the homonucleal naphthaquinones together with derivatives of the third (2 : 3-) are known,

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[1] [β-]Hydrojuglone, the constitution of which is unknown, dissolves easily in chloroform, whereas [α-] hydrojuglone is insoluble in this solvent (Mylius, *l.c.*).

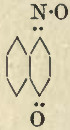
[2] An amino-1 : 3-dihydroxynaphthalene, m.p. 162°, which may have this constitution has been described by Zincke and Wiegand (Annalen, 1895, 286, 89); and a second, possibly the 2-amino-1 : 3- derivative, has been isolated by Friedlaender and Rüdt (Ber. 1896 29, 1611).

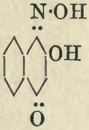
but only one of the heteronucleal compounds (2 : 6-) has been isolated.[1] A comparison shows that in physical properties 1 : 4- or [α-]naphthaquinone, but in chemical properties 2 : 6-naphthaquinone, most closely resembles ordinary *para*-benzoquinone, whereas 1 : 2- or [β-]naphthaquinone exhibits the general characters of an α- or *ortho*-diketone.

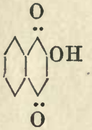
The naphthaquinones are coloured substances, and, with few exceptions, give rise to derivatives, which also are coloured, but only a small proportion of them are dyes. The 'tinctogenic' groups, which endow naphthaquinone derivatives with the property of forming coloured lakes, are associated with contiguous carbon atoms, *i.e.* are present relatively in the *ortho*-position. For quinones, these groups have been shown by Kostanecki (Ber. 1887, 20, 3147; 1889, 22, 1349) to be the following—

·C : O   ·C : N·OH   ·C : N·OH   ·C : N·OH
:C · OH   :C · OH   ·C : O   ·C : N·OH

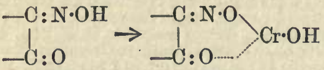
To illustrate their effect, reference may be made to the following series of [α-]naphthaquinone derivatives in which I is not a dye, but II and III form coloured lakes with basic mordants—

I. 

II. 

III. 

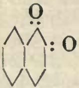
In the more recent discussion of the subject (*cf.* Tschugaeff, J. pr. Chem. 1907, [ii.] 76, 88; Werner, Ber. 1908, 41, 1062, 2383; Liebermann, *ibid.* 1436), the production of lakes by compounds of these types is referred to the formation of complex heterocyclic groups, in which the metallic base forms one component of the 5- or 6-membered ring. But cyclic structure is not of itself sufficient to develop colour with basic mordants, and in each tinctogenic complex there is present not only a salt-forming group, but a radicle, which by its 'subsidiary' valency can be linked with the metal. For example, [β-]naphthaquinoneoxime (1-nitroso-β-naphthol) is a dye, because in it, according to Tschugaeff and Werner, oxygen of the carbonyl group has residual valency, and through this residual or 'subsidiary' valency (shown in the formula by the dotted line) becomes linked to the basic radicle of the mordant:—



Oxime. Lake.

Naphthaquinonoximes, obtainable from the quinones by interaction with hydroxylamine, are usually made from the naphthols or from dihydroxynaphthalene derivatives by means of nitrous acid. As the chief interest attaching to these substances from the technical side lies in the colouring matters to which some of them give rise, they are described in this article as nitrosonaphthols, following the Patent literature, although classified as oximes.

Naphthaquinones.



(i.) 1 : 2-Naphthaquinone ([β-]naphthaquinone) is obtained by the oxidation of 1-amino-2-naphthol either with chromic acid mixture (Stenhouse and Groves, Chem. Soc. Trans. 1877, 32, 52; 1878, 33, 415; Liebermann and Jacobson, Annalen, 1882, 211, 49; Grandmougin and Michel, Ber. 1892, 25, 982; Paul, *cf.* J. Soc. Chem. Ind. 1897, 19, 733; Russig, J. pr. Chem. 1900, [ii.] 62, 56), or with ferric chloride (Groves, Chem. Soc. Trans. 1884, 45, 298; Paul, *l.c.*).

Preparation.—Freshly-prepared 1-amino-2-naphthol, obtained by reduction of Orange II (100 grms.) with sodium hyposulphite, is dissolved or suspended in sulphuric acid of sp.gr. 1·2 (200 c.c.) and oxidised in the cold by a solution of sodium dichromate (30 grms.) in water (Grandmougin, Ber. 1906, 39, 3561). Or the freshly prepared product, obtained from β-naphthol (50 grms.) by reducing its nitroso- compound with hydrogen sulphide, is dissolved in 5 p.c. sulphuric acid (1400 c.c.) and oxidised in the cold with a solution of potassium dichromate (35 grms.) in water (Lagodzinski and Hardine, Ber. 1894, 27, 3076). The yield amounts to about 25 p.c. of the weight of the Orange II (*p*-sulphobenzeneazo-β-naphthol), or to about 80 p.c. of that of the β-naphthol employed.

Identification.—It crystallises in red needles or in orange scales, decomposes with blackening at 115°–120° (Liebermann and Jacobson, *l.c.*), and resembles [α-]naphthaquinone in solubility, but differs from it by being destitute of odour and non-volatile with steam. Dilute alkalis dissolve it, forming yellow solutions, which rapidly become dark on being shaken with air.

Reactions.—(1) By sulphurous acid, or dilute hydriodic acid, it is reduced to 1 : 2-*dihydroxynaphthalene*, but stannous chloride in hydrochloric acid solution converts it into β-*dinaphthyldihydroquinone* (Stenhouse and Groves, *l.c.*: Liebermann and Jacobson, *l.c.*).

(2) With ferric chloride in 10 p.c. aqueous solution, it gives *di-β-naphthaquinone oxide* (Wichelhaus, Ber. 1897, 30, 2199); with nitric acid of sp.gr. 1·38 (Zaertling, Ber. 1890, 23, 175; *cf.* Stenhouse and Groves, *l.c.*), it yields successively 3-*nitro*-[β-]*naphthaquinone* and *phthalic acid*; but with potassium permanganate (Liebermann and Jacobson, *l.c.*) or dichromate (Boswell, J. Physical Chem. 1907, 11, 119), the product is *phthalic acid.*

(3) With phenylhydrazine it gives the *hydrazone* [O : N_2HPh=1 : 2], red needles, m.p. 138°, isomeric with benzeneazo-β-naphthol (Zincke and Bindewald, Ber. 1884, 17, 3030; Zincke and Rathgen, *ibid.* 1886, 19, 2483; Bamberger, *ibid.* 1897, 30, 514); and with hydroxylamine it forms the *monoxime*, identical with 2-nitroso-α-naphthol (Goldschmidt, *ibid.* 1884, 17, 215).

(4) When warmed in alcoholic solution with aniline it yields 2-*hydroxy*-[α-]*naphthaquinoneanil* [O : OH : NPh=1 : 2 : 4], m.p. above 240°, red needles, soluble in alkali. This anil boiled with acetic acid is converted into 2-*anilino*-[α-]*naphthaquinone*, m.p. 190°–191°, red needles, insoluble in alkali (Liebermann and Jacobson, *l.c.*; Zincke, Ber. 1881, 14, 1494), but in alcoholic solution

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[1] The compound described as 1 : 8- or *peri*naphthaquinone by Meldola and Hughes (Chem. Soc. Trans. 1890, 57, 632) is now known to be a *dinaphthaquinone* (Liebermann and Schlossberg, Ber. 1899, 32, 546; *cf.* Meldola, *ibid.* 868).

with aniline furnishes 2-*anilino-[α-]naphthaquinoneanil* [O : NHPh : NPh = 1 : 2 : 4], red needles, m.p. 187° (Zincke, *ibid.* 1882, 15, 481). From 2-anilino-[α-]naphthaquinoneanil, by heating it with aniline and aniline hydrochloride at 130°–160°, *phenylrosinduline* has been obtained (Badische, D. R.-P. 45370; Eng. Pat. 15259 of 1888; Fischer and Hepp, Ber. 1888, 21, 2622).

(5) Acetic anhydride with sulphuric acid or zinc chloride or phosphoric acid, converts it at 40°–60° into the *triacetate* of 1 : 2 : 4-trihydroxynaphthalene (Thiele and Winter, Annalen, 1900, 311, 345; Bayer, D. R.-P. 101607 of 1897; 107508; Eng. Pat. 10590 of 1898).

(6) With sodium bisulphite solution of sp.gr. 1·4 it gives 1 : 2-*dihydroxynaphthalene*-4-*sulphonic acid* at the ordinary temperature (Bayer, D. R.-P. 70867 of 1892; Eng. Pat. 825 of 1893), and, in mol. prop. with sodium thiosulphate and acetic acid, it gives 1 : 2-*dihydroxynaphthalene*-4-*thiosulphonic acid* (Bayer, D. R.-P. 71314 of 1892; Eng. Pat. *l.c.*).

(7) When heated with sulphuric acid, with or without the presence of boric acid, at 125°–150°, it is converted into *naphthaquinone black*, which dyes wool in greenish-blue to brown, but with mordants in black, shades (Heyden, D. R.-P. 113336 of 1898; Eng. Pat. 3265 of 1900).

(ii.) 1 : 4-**Naphthaquinone** ([α-]naphthaquinone) can be obtained by the oxidation of naphthalene with chromic acid in acetic acid solution (Groves, Chem. Soc. Journ. 1873, 26, 209; Plimpton, Chem. Soc. Trans. 1880, 37, 633; Japp and Miller, *ibid.* 1881, 39, 220). It is also formed when 1 : 4-diaminonaphthalene *or* α-naphthol (Miller, Ber. 1881, 14, 1602), *or* 1-amino-4-naphthol (Liebermann and Dittler, Annalen, 1876, 183, 242, 248); *or* α-naphthylamine, *or* dimethyl-α-naphthylamine, *or* naphthylamine-4-sulphonic acid (Monnet, Reverdin, and Noelting, Ber. 1879, 12, 2306) is oxidised with chromic acid mixture.

Preparation.—It is prepared conveniently from 1-amino-4-naphthol by oxidation with potassium dichromate and dilute sulphuric acid, the yield amounting to about 40 p.c. of that calculated (Liebermann and Jacobson, Annalen, 1882, 211, 61), but can be obtained in equally good yield from naphthalene by oxidation, in concentrated glacial acetic acid solution, with four times its weight of chromium trioxide dissolved in acetic acid, the mixture being kept at 15°–20° during 3 days (Miller, Ber. 1884, 17, Ref. 355). The product can be purified either by distillation with steam or by crystallisation from light petroleum (b.p. 85°–120°).

Identification.—It crystallises in yellow triclinic needles, m.p. 125°, begins to sublime below 100°, has the odour of *p*-benzoquinone, is readily volatile with steam, and dissolves easily in most organic solvents, but only sparingly in light petroleum or water.

Reactions.—(1) It is not reduced by sulphurous acid in the cold, but when heated with hydriodic acid and phosphorus or with tin and hydrochloric acid it is converted into 1 : 4-*dihydroxynaphthalene* (Groves, *l.c.*; Plimpton, *l.c.*). Partial reduction results in the formation of *naphthaquinhydrone.*

(2) In caustic soda solution it absorbs oxygen from the air forming 2-*hydroxy-[α-]naphthaquinone* (Kowalski, Ber. 1892, 25, 1659), but on oxidation with nitric acid (Liebermann and Dittler, *l.c.*), or permanganate (Japp and Miller, *l.c.*; *cf.* Boswell, J. Physical Chem. 1907, 11, 119), *phthalic acid* is formed.

(3) In acetic acid solution with chlorine it gives the *dichloride*, m.p. 176°, and with bromine the *dibromide*, m.p. 92° (Zincke and Schmidt, Ber. 1894, 27, 2757).

(4) With phenylhydrazine hydrochloride it yields the *hydrazone*, identical with benzeneazo-α-naphthol (Zincke and Bindewald, Ber. 1884, 17, 3026); and with hydroxylamine it forms the *monoxime*, identical with 4-nitroso-α-naphthol (Goldschmidt and Schmid, *ibid.* 2064).

(5) When heated with acetic anhydride and zinc chloride or sulphuric acid at 50° it furnishes 1 : 2 : 4-*trihydroxynaphthalene triacetate* (Thiele and Winter, Annalen, 1900, 311, 345; Bayer, D. R.-P. 101607 of 1897; 107508; Eng. Pat. 10590 of 1898).

(6) When warmed in alcoholic solution with aniline, it yields 2-*anilino-[α-]naphthaquinone*, red needles, m.p. 190°–191° (Plimpton, *l.c.*).

(iii.) 2 : 6-**Naphthaquinone**, obtained from 2 : 6-dihydroxynaphthalene by oxidation in boiling benzene solution with lead peroxide, forms reddish-yellow prisms, and is odourless and non-volatile, but, unlike [β-]naphthaquinone, is an oxidising agent comparable in this respect with *p*-benzoquinone (Willstätter and Parnas, Ber. 1907, 40, 1411, 3971).

HYDROXYNAPHTHAQUINONES.

(i.) 2-**Hydroxy-[α-]naphthaquinone**[1] can be obtained by boiling amino-[α-]naphthaquinoneimide (diimino-α-naphthol, *v.* 2 : 4-diamino-α-naphthol) with dilute acids (Martius and Griess, Annalen, 1865, 134, 377; Graebe and Ludwig, *ibid.* 1870, 154, 321), or with sodium carbonate solution which afterwards is acidified (Diehl and Merz, Ber. 1878, 11, 1315); *or* by heating 2-anilino-[α-]naphthaquinone (Baltzer, Ber. 1881, 14, 1900), or 2-hydroxy-[α-]naphthaquinoneanil (Liebermann and Jacobson, Annalen, 1882, 211, 80; Böniger, Ber. 1894, 27, 257) with hydrochloric acid; *or* by dissolving [β-]naphthaquinone-4-sulphonic acid in sulphuric acid and, after some hours at 25°, pouring the solution on to ice (Aktienges., D. R.-P. 100703; Eng. Pat. 26675 of 1897). It is formed, also, when an alkaline solution of [α-]naphthaquinone (Kowalski, Ber. 1892, 25, 1659) or of 1 : 2-dihydroxynaphthalene-4-sulphonic acid (Bayer, D. R.-P. 70867 of 1892; Eng. Pat. 825 of 1893), is exposed to the air; and readily by oxidizing either [β-]naphthaquinone, suspended in caustic soda solution, with hydrogen peroxide (Teichner and Weil, Ber. 1905, 38, 3376) or 1 : 2 : 4-trihydroxynaphthalene in aqueous solution with dichromate mixture at 0° (Thiele and Winter, Annalen, 1900, 311 347).

Identification.—It crystallises or sublimes in yellow needles, m.p. 190°–191°, dissolves only sparingly in boiling water, expels carbon dioxide from carbonates, and dyes wool or silk yellow.

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[1] By condensation with *o*-phenylenediamine, 2-hydroxy-[α-]naphthaquinone gives an *azine* (Kehrmann, Ber. 1890, 23, 2453), behaving as if it were 4-hydroxy-[β-]naphthaquinone. Many of the monosubstituted naphthaquinones of the 1 : 2 : 4-type exhibit a similar tautomerism (*cf.* Miller, Chem. Soc. Abstr. 1911, i. 465), although the formulæ usually assigned to them represent only one of the two isomeric forms.

The *acetate* forms yellow scales, m.p. 130° (Thiele and Winter, *l.c.*).

Reactions.—(1) On reduction with tin and hydrochloric acid, it yields 1 : 2 : 4-*trihydroxynaphthalene* (Graebe and Ludwig, *l.c.*).

(2) It couples with diazotised bases in presence of sodium acetate, forming *azo-* dyes which are remarkable because in them, the 1- or *α-* position not being available, the azo- group has taken up the alternative *ortho-*, namely the 3- or *β-* position to the hydroxyl radicle (Kehrmann and Goldenberg, Ber. 1897, 30, 2126).

3-Nitro-2-hydroxy-[α-]naphthaquinone is formed from [β-]naphthaquinone-4-sulphonic acid, or from 1-amino-2-naphthol-4-sulphonic acid by nitration in sulphuric acid solution below 50° (Aktienges., D. R.-P. 100611; Eng. Pat. 26675 of 1897). It is crystalline, and with phenylhydrazinesulphonic acid gives a yellow *azo-* dye for wool (*ibid.* D. R.-P. 102071; Eng. Pat. 676 of 1898).

2-Hydroxy-[α-]naphthaquinone-3-sulphonic acid, obtained by sulphonating 2-hydroxy-[α-]naphthaquinone with 25 p.c. anhydro- acid at 20°, forms a sparingly soluble *sodium* salt in pale-yellow scales (Atkienges., D. R.-P. 99759; Eng. Pat. 26675 of 1897), and with phenylhydrazinesulphonic acid (*ibid.* D. R.-P. 101918; Eng. Pat. 676 of 1898) or with the hydrazine from 1-amino-8-naphthol-3 : 6-disulphonic acid (*ibid.* D. R.-P. 102070; Eng. Pat. 676 of 1898), gives respectively an orange-yellow or reddish-yellow *azo-* dye for wool.

The 6-sulphonic acid is produced when a mixture of [β-]naphthaquinone-4 : 6-disulphonic acid and sulphuric acid is kept at 25° for some hours (Aktienges., D. R.-P. 100703; Eng. Pat. 26675 of 1897); or when 1 : 2-dihydroxynaphthalene-6-sulphonic acid is oxidised in caustic soda solution with hydrogen peroxide (Teichner and Weil, Ber. 1905, 38, 3376). The *sodium* salt forms red needles.

The 7-sulphonic acid (Gaess, Ber. 1899, 32, 237), which gives two *sodium* salts $NaA+3H_2O$, and Na_2A, and two *barium* salts BaA_2+2H_2O, and $BaA+3\frac{1}{2}H_2O$, forms an *azine* with *o*-phenylenediamine, reacting as if it were 4-hydroxy-[β-]naphthaquinone-7-sulphonic acid.[1]

(ii.) **5-Hydroxy-[α-]naphthaquinone** (*juglone*; *regianin*; *nucin*) occurs in the green parts and shells of the walnut (Brissemoret and Combes, Compt. rend. 1905, 141, 838; Combes, Bull. Soc. chim. 1907, [iv.] 1, 803), but in nuts not freshly gathered is replaced in part or wholly by hydrojuglone (*cf.* Mylius, Ber. 1885, 18, 2567). It can be extracted from the shells by ether (Combes, *l.c.*), and is obtained by oxidation of 1 : 4 : 5-trihydroxynaphthalene with ferric chloride (Mylius, *l.c.*), or chromic acid mixture (Bernthsen and Semper, Ber. 1885, 18, 204); *or* of 1 : 5-dihydroxynaphthalene with chromic acid mixture (*ibid.* 20, 939); *or* of 4 : 8-diamino-*α*-naphthol with ferric chloride (Friedlaender and Silberstern, Monatsh. 1902, 23, 517).

Identification.—It crystallises in yellowish-red or brown needles, m.p. 151°–154°, is almost insoluble in water, and in aqueous solution colours the skin yellow like walnut juice.

(iii.) **6-Hydroxy-[β-]naphthaquinone,** prepared by oxidising 1-amino-2 : 6-dihydroxynaphthalene with ferric chloride, forms brick-red scales, decomp. at 165° (Kehrmann, Ber. 1907, 40, 1962).

The 4-sulphonic acid closely resembles that from 7-hydroxy-[β-]naphthaquinone in mode of preparation and properties (Bayer, D. R.-P. 87900; Eng. Pat. 6035 of 1893).

(iv.) **7-Hydroxy-β-naphthaquinone,** obtained similarly from 1-amino-2 : 7-dihydroxynaphthalene (Clausius, Ber. 1890, 23, 522) forms brown needles, m.p. 194° (Nietzki and Knapp, *ibid.* 1897, 30, 1123).

The 4-sulphonic acid, prepared by oxidising 1-amino-2 : 7-dihydroxynaphthalene-4-sulphonic acid with nitrous acid (Böniger, Ber. 1894, 27, 3051) gives a *potassium* salt in brown needles, and has been employed in the production of *thiazines* (Bayer, D. R.-P. 87900; Eng. Pat. 6035 of 1893).

(v.) **8-Hydroxy-[β-]naphthaquinone** has not been described. The 4-sulphonic acid, obtained by oxidising 8-hydroxy-1 : 2-diaminonaphthalene-4-sulphonic acid with dichromate has been used for the production of *thiazines* (Bayer, D. R.-P. 87900; Eng. Pat. 6035 of 1893).

(vi.) **2 : 3-Dihydroxy-[α-]naphthaquinone** (*Isonaphthazarin*) is formed when 3-amino-2-hydroxy-[α-]naphthaquinone is heated with dilute hydrochloric acid at 180° (Diehl and Merz, Ber. 1878, 11, 1322); *or* when 1 : 4-diamino-2 : 3-dihydroxynaphthalene is oxidised by ferric chloride (Friedlaender and Silberstern, Monatsh. 1902, 23, 525); *or* when β-naphthaquinone is dissolved in dilute bleaching powder solution, which is then acidified with acetic acid and boiled with a few c.c. of hydrochloric acid (Zincke and Ossenbeck, Annalen, 1899, 307, 11; *cf.* Bamberger, Ber. 1892, 25, 134, 891; Zincke and Scharfenberg, *ibid.* 409).

Identification.—It crystallises in red needles, m.p. 280°; dissolves in caustic alkali solutions with a blue colour which disappears on exposure to the air, *o-carboxyphenylglyoxylic acid* being formed; yields 1 : 2 : 3 : 4-*tetrahydroxynaphthalene* on careful, but 1 : 2 : 3-*trihydroxynaphthalene* on vigorous reduction with zinc and dilute sulphuric acid; and is a dye for mordanted wool. Its *diacetate* forms colourless needles, m.p. 105° (Zincke and Ossenbeck, *l.c.*).

(vii.) **5 : 6-Dihydroxy-[α-]naphthaquinone** (**Naphthazarin.** *Alizarin black*; *v.* p. 569), was first obtained by heating 1 : 5-dinitronaphthalene with zinc and sulphuric acid at 200° (Roussin, Compt. rend. 1861, 52, 1033, 1177; *cf.* Liebermann, Annalen, 1872, 162, 330). It is produced on the large scale by stirring 1 : 5-dinitronaphthalene (2 pts.) into monohydrate (40 pts.), adding a solution of sulphur (1 pt.) in 40 p.c. anhydro-acid (10 pts.) below 40°, and, when a test gives a blue solution, pouring the 'naphthazarin melt' into water, removing sulphur by filtration, and boiling the filtrate until the colour has changed to red (Bayer, D. R.-P. 71386 of 1892). Substances which yield sulphur such as hydrogen sulphide, sulphur chloride, &c., can replace it as reducing agents (*ibid.* D. R.-P. 77330 of 1893; Eng. Pat. 17673 of 1892).

Naphthazarin melt contains a 'naphthazarin intermediate product' which is probably an impure form of 5-*amino*-6-*hydroxy*-[α-]*naphthaquinoneimide* (*cf.* Badische, D. R.-P. 129074; Eng. Pat. 23887 of 1900; *v.* p. 570). The blue

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[1] See footnote p. 655.

solution of this product in water, when boiled, yields naphthazarin. According to Aguiar and Bayer, the melt contains in addition a trihydroxy-[α-]naphthaquinone, producible by heating naphthazarin with sulphuric acid (Ber. 1871, 4, 439).

1:8-Dinitronaphthalene (1 pt.) also furnishes naphthazarin when heated at 120°–130° with sulphuric acid (20 pts.) and reducing agents such as aniline, phenylhydrazine, or tin, provided the melt [1] is boiled with water (Badische, D. R.-P. 76922 of 1893; Eng. Pat. 3828 of 1894; *cf.* D. R.-P. 79406 of 1894); hence it is possible in the manufacturing process to substitute the dinitration product from naphthalene for the pure 1 : 5-dinitro- derivative.[2]

As naphthazarin can be formed by boiling 1 : 4 : 5 : 6-tetra-aminonaphthalene with dilute hydrochloric acid, its constitution is known with certainty (Will, Ber. 1895, 28, 2234; Friedlaender and Silberstern, Monatsh. 1902, 23, 518).

Properties.—It sublimes in brown needles showing a green lustre, is only sparingly soluble in water, but dissolves in alkalis forming a cornflower-blue, and in sulphuric acid a magenta solution. It is an important dyestuff, giving very fast violet-black lakes with chromium salts. When warmed at 50°–70° with sodium bisulphite solution, it is converted into a soluble compound used in dyeing under the names of alizarin black S and naphthazarin S (Badische, D. R.-P. 41518; Eng. Pat. 7833 of 1887), but with concentrated sodium bisulphite solution at 100°, followed by oxidation of the resulting leuco- compound, it yields *naphthazarinsulphonic acid* (Höchst, D. R.-P. 116866 of 1889). The *diacetate*, needles, m.p. 189° (Zincke and Schmidt, Annalen, 1895, 286, 36), and the *tetra-acetate* of 1:2:5:8-tetrahydroxynaphthalene (Liebermann, Ber. 1895, 28, 1457) have been prepared from it.

By condensation of naphthazarin with salts of aromatic amines or with their sulphonic acids at 25°–40° in presence of boric acid, black dyes are formed (Badische, D. R.-P. 101525, 101152; Eng. Pat. 21297 of 1897; D. R.-P. 157684; Eng. Pat. 2468 of 1904).

Naphthazarin 'Intermediate Product,' and the derived colouring matters.

The **intermediate product** can be isolated by precipitating naphthazarin melt with zinc chloride (Höchst, D. R.-P. 111683; Eng. Pat. 16295 of 1899); *or* by oxidising the leuco-compound (*v. infra*), dissolved in caustic soda, with a rapid current of air (Badische, D. R.-P. 108551 of 1899), or a solution of the melt with hypochlorite or dichromate (*ibid.* D. R.-P. 101372; Eng. Pat. 15909 of 1898), and boiling the sodium salt thus obtained (which separates as blue needles) with acetic acid (*ibid.* D. R.-P. 108552 of 1899). By oxidation with dichromate (Badische, D. R.-P. 101372; Eng. Pat. *l.c.*); by condensation either with phenols (*ibid.* D. R.-P. 103150 of 1897; Eng. Pat. 10597 of 1898), or with aromatic amines (*ibid.* D. R.-P. 118078; Eng. Pat. 20997 of 1899; Höchst, D. R.-P. 125574; Eng. Pat. 20485 of 1899); or by sulphonation with 20 p.c. anhydro- acid (Höchst, D. R.-P. 117359 of 1899), naphthazarin melt gives respectively black, bluish-grey, green, or blue mordant dyes. Further, by reduction with stannous chloride, it is converted into the **leuco-** compound, crystallising in colourless needles (Badische, D. R.-P. 101371; Eng. Pat. 15708 of 1898), which, sulphonated with 23 p.c. anhydro- acid, gives a blue dye (*ibid.* D. R.-P. 106029; Eng. Pat. 24752 of 1898), convertible into black, green, or blue mordant dyes by boiling respectively with hydrochloric acid (*ibid.* D. R.-P. 106033; Eng. Pat. *l.c.*), or with aniline and aniline hydrochloride (*ibid.* D. R.-P. 108414; Eng. Pat. *l.c.*), or with aniline hydrochloride and water (*ibid.* D. R.-P. 108415 of 1898).

(viii.) **6 : 7-Dihydroxy-[α-]naphthaquinone,** obtained from 5-amino-2 : 3 : 8-trihydroxynaphthalene by oxidation with ferric chloride, forms reddish-brown needles, gives a green solution in caustic soda, and has only feeble dyeing properties. Its *diacetate* forms yellow needles, m.p. 65°–67° (Friedlaender and Silberstern, Monatsh. 1902, 23, 532).

(ix.) **5 : 6 : 8-Trihydroxy-[α-]naphthaquinone** (naphthapurpurin), one of the products (A) of the action of sulphuric acid in presence of boric acid on 1 : 5-dinitronaphthalene at 220° (Bayer, D. R.-P. 82574 of 1894), is obtained in a pure state either by boiling naphthazarin with an equal weight of caustic soda in 1 p.c. solution until the colour has changed to magenta (Badische, D. R.-P. 167641; Eng. Pat. 9547 of 1905), or with manganese dioxide and dilute sulphuric acid (Jaubert, Compt. rend. 1899, 129, 684). It forms reddish-brown needles, is easily soluble in the ordinary solvents, dyes wool orange-red, chroming to black (Badische, *l.c.*), and condenses with aromatic amines forming dyes, which when sulphonated give blue, green, or black shades on chromed wool (Bayer, D. R.-P. 127766 of 1900).

NAPHTHAQUINONESULPHONIC ACIDS.

[β-]Naphthaquinone-4-sulphonic acid is prepared by oxidising 2-amino-1-naphthol-4-sulphonic acid (Witt and Kaufmann, Ber. 1891, 24, 3163), or 1-amino-2-naphthol-4-sulphonic acid (Böniger, *ibid.* 1894, 27, 24) with nitric acid; *or* 1 : 2-dihydroxynaphthalene-4-sulphonic acid with nitrous acid (Bayer, D. R.-P. 83046 of 1892; Eng. Pat. 825 of 1893). It forms easily soluble salts; is converted by nitrosulphuric acid into *3-nitro-2-hydroxy-*[α-]*naphthaquinone* (Aktienges., D. R.-P. 100611; Eng. Pat. 26675 of 1897), or by sulphuric acid at 25° into *2-hydroxy-*[α-] *naphthaquinone* (*ibid.* D. R.-P. 100703; Eng. Pat. *l.c.*); and gives *thiazines* by condensation with aromatic nitroso- compounds (Bayer, *l.c.*), or with thiosulphonated arylamines (Sandoz, D. R.-P. 109273 of 1893; Eng. Pat. 3886 of 1894), also *oxazines* with aminonaphtholsulphonic acids (Dahl, D. R.-P. 82740; Eng. Pat. 5153 of 1895).

The 4 : 6- and 4 : 7-disulphonic acids, obtained by oxidising 1-amino-2-naphthol-4 : 6-

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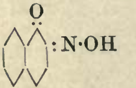
[1] The naphthazarin melt from 1:8-dinitronaphthalene contains an intermediate product different from, but probably isomeric with, that furnished by 1:5-dinitronaphthalene.

[2] When heated in sulphuric acid solution at 130° with hydrogen sulphide, 1:5-dinitronaphthalene (Badische, D. R.-P. 134705; Eng. Pat. 6053 of 1900; Höchst, D. R.-P. 138105 of 1900), and 1:8-dinitronaphthalene (Badische, D. R.-P. 114264 of 1899; Eng. Pat. 890 of 1900) give products which, unlike naphthazarin, develop blue and violet shades on wool without a mordant.

and 4 : 7-disulphonic acids respectively with nitric acid (Böniger, Ber. 1894, 27, 3052), form *thiazines* by condensation with thiosulphonated arylamines (Sandoz, D. R.-P. 116765 of 1894).

By oxidising the corresponding aminonaphtholsulphonic acids, the β-naphthaquinone-6-, 7-, and 8-mono-, and 4 : 8- and 6: 8-disulphonic acids have been obtained, which furnish *thiazines* by condensation with aromatic nitroso- compounds (Bayer, D. R.-P. 84233; Eng. Pat. 4757 of 1893).

NAPHTHAQUINONEOXIMES.



(i.) **2-Nitroso-α-naphthol** ([α-] naphthaquinone-2-oxime) can be obtained from [β-]-naphthaquinone by boiling it in alcoholic solution with hydroxylamine hydrochloride (Goldschmidt, Ber. 1884, 17, 215); *or* from 1-hydroxy-β-naphthoic acid by means of nitrous acid (Reverdin and de la Harpe, *ibid.* 1893, 26, 1280); *or,* mixed with the 4-oxime (*q.v.*), from α-naphthol by interaction with nitrous acid (Fuchs, Ber. 1875, 8, 626; Worms, *ibid.* 1882, 15, 1816; Ilinski, *ibid.* 1884, 17, 2589; Henriques and Ilinski, *ibid.* 1885, 18, 706). It crystallises in yellow needles, m.p. 152° (Goldschmidt), soluble in the ordinary organic solvents or in hot water; forms coloured salts and ethers, the *potassium* and *ammonium* salts being green, and the *methyl* (m.p. 95°) and *ethyl* (m.p. 101°) *ethers,* greenish-yellow (Fuchs, *l.c.*).

Reactions.—(1) Concentrated nitric acid in acetic acid solution converts it into 2 : 4-*dinitro-α-naphthol*; potassium ferricyanide in alkaline solution oxidises it rapidly to 2-*nitro-α-naphthol* (Fuchs, *l.c.*).

(2) With sodium bisulphite solution it yields 2-*amino*-1-*naphthol*-4-*sulphonic acid* (Böniger, Ber. 1894, 27, 29).

(3) Like nitroso-β-naphthol it gives [β-] *naphthaquinonedioxime* with hydroxylamine (Goldschmidt and Schmid, Ber. 1884, 17, 2066), forms metallic salts (Ilinski, *ibid.* 1884, 17, 2592), and is a mordant dye (*cf.* Aktienges., D. R.-P. 66786 of 1891).

2-Nitroso-1 : 8-dihydroxynaphthalene (Erdmann, Annalen, 1888, 247, 358) gives black lakes (Bayer, D. R.-P. 51478; Eng. Pat. 14230 of 1889).

2-Nitroso-α-naphthol-4-sulphonic acid gives a *naphthol-green* with ferric chloride (Gans & Co. D. R.-P. 28065; Eng. Pat. 2269 of 1884; Hoffmann, Ber. 1885, 18, 46).

(ii.) **4-Nitroso-α-naphthol** ([α-]naphthaquinone-4-oxime) is formed when [α-]naphthaquinone in alcoholic solution is boiled with hydroxylamine hydrochloride (Goldschmidt and Schmid, Ber. 1884, 17, 2064), *or,* mixed with the 2-oxime, by the interaction of α-naphthol with nitrous acid (Fuchs, *ibid.* 1875, 8, 626; Worms, *ibid.* 1882, 15, 1816). The best yield, viz. 40 grms. of the colourless 4-oxime and 50 grms. of the yellow 2-oxime from 100 grms. of α-naphthol, is obtained by boiling a solution of α-naphthol (1 pt.) and zinc chloride (1 pt.) in alcohol (6 pts.) with aqueous sodium nitrite (0·5 pt.) during 2–3 hours, the product which separates consisting of the 4-oxime mixed with the zinc salt of the 2-oxime (Henriques and Ilinski, Ber. 1885, 18, 706; *cf.* Ilinski, *ibid.* 1884, 17, 2590). It crystallises in needles, m.p. 190° (Friedlaender and Reinhardt, Ber. 1894, 27, 240), dissolves easily in alcohol or ether, gives a *methyl ether,* m.p. 98°–100° (Ilinski, *l.c.*), and is destitute of tinctorial power (Kostanecki, *ibid.* 1887, 20, 3147).

Reactions.—(1) Concentrated nitric acid in acetic acid solution converts it into 2 : 4-*dinitro-α-naphthol*; potassium ferricyanide in alkaline solution oxidises it very slowly to 4-*nitro-α-naphthol* (Fuchs, *l.c.*).

(2) Like the 4-oxime and [β-]naphthaquinone-1-oxime, it gives 2-*anilino*-[α-]*naphthaquinone-anil,* m.p. 187°, when boiled with aniline and acetic acid (Brömme, Ber. 1888, 21, 393).

4-Nitroso-α-naphthol-2-sulphonic acid does not give a naphthol-green with ferrous sulphate, but is readily converted into 2:4-dinitro-α-naphthol by dilute nitric acid (Conrad and Fischer, Annalen, 1893, 273, 110).

4-Nitroso-α-naphthol-2: 5-disulphonic acid is formed when α-nitronaphthalene-3 : 8-disulphonic acid is warmed with concentrated caustic soda solution. Its *potassium* salt $K_2A+1\frac{1}{2}H_2O$, forms yellow, and *basic potassium* salt green, needles; the *amino-* acid, obtained from it by reduction, furnishes 1-*amino*-4-*naphthol* on desulphonation with sodium amalgam (Friedlaender, Ber. 1895, 28, 1535).

5-Nitro-4-nitroso-α-naphthol (5-nitro-[α-] naphthaquinoneoxime) is produced when 1 : 8-dinitronaphthalene is heated with 12–23 p.c. anhydro- acid at 40°–50° (Badische, D. R.-P. 90414; Eng. Pat. 14955 of 1896; Graebe, Ber. 1899, 32, 2877; Friedlaender, *ibid.* 3528; Friedlaender and Scherzer, *cf.* J. Soc. Chem. Ind. 1900, 19, 339). It crystallises in yellow needles, and is soluble in alkalis giving yellow solutions which become red when heated with zinc dust (Badische, *l.c.*).

Reactions.—(1) By potassium ferricyanide it is oxidised to 4 : 5-*dinitro-α-naphthol* (Friedlaender, *l.c.*); by dilute nitric acid to 2 : 4 : 5-*trinitro-α-naphthol* (Friedlaender and Scherzer, *l.c.*); and by potassium permanganate to 3-*nitrophthalic acid.*

(2) On reduction with ammonium sulphide or stannous chloride, it gives 4 : 5-*diamino-α-naphthol,* but with tin and hydrochloric acid 5-*amino*-1 : 4-*dihydroxynaphthalene* (Graebe and Oeser, Annalen, 1904, 335, 152).

The 2 : 7-disulphonic acid, formed by the action of very dilute caustic soda solution [1] on 1 : 8-dinitronaphthalene-3 : 6-disulphonic acid at the ordinary temperature, gives a yellow *potassium* salt K_2A+2H_2O and a green *basic potassium* salt. With dilute nitric acid it furnishes a crystalline yellow nitro- dye with the loss of one of the SO_3H groups (Kalle, D. R.-P. 113063 of 1899).

7-Nitro-4-nitroso-α-naphthol (7-nitro-[α-] naphthaquinone-4-oxime), obtained when 1 : 6-dinitronaphthalene is heated with 15–17 p.c. anhydro- acid at 40°–50°, crystallises in yellow needles, is soluble in alkalis, and on oxidation gives 4-*nitrophthalic acid* (Graebe, Annalen, 1904, 335, 144).

8-Nitro-4-nitroso-α-naphthol (8-nitro-[α-] naphthaquinone-4-oxime), obtained by heating

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[1] If concentrated caustic soda solution is used, the product is a 1 : 8-dinitrosodihydroxynaphthalene-3 : 6-disulphonic acid, the *sodium* salt Na_3A+3H_2O of which crystallises in needles (Kalle, *l.c.*).

1 : 5-dinitronaphthalene with 12–23 p.c. anhydro-acid at 40°–50° (Badische, D. R.-P. 91391; Eng. Pat. 14955 of 1896; *v.* 5-nitro-compound for other references) forms yellow crystals; these dissolve in alkalis giving yellow solutions which become green when boiled with zinc dust (Badische, *l.c.*).

Reactions.—(1) By potassium ferricyanide it is converted into 4 : 8-*dinitro-α-naphthol* (Friedlaender, Ber. 1899, 32, 3529), but by dilute nitric acid into 2 : 4 : 8-*trinitro-α-naphthol* (Friedlaender and Scherzer, *cf.* J. Soc. Chem. Ind. 1900, 19, 339; Graebe and Oeser, Annalen, 1904, 335, 154).

(2) On reduction with tin and hydrochloric acid, it furnishes 1 : 5-*diamino*-8-*naphthol* (Graebe and Oeser, *l.c.*).

(iii.) **1-Nitroso-β-naphthol** ([β-]naphthaquinone-1-oxime) is obtained by the action of nitrous acid on β-naphthol (Fuchs, Ber. 1875, 8, 1026; Stenhouse and Groves, Chem. Soc. Trans. 1877, 32, 47; Ilinski, Ber. 1884, 17, 2584; Groves, Chem. Soc. Trans. 1884, 45, 295; *cf.* Köhler, D. R.-P. 25469 of 1883). As the sparingly soluble reddish-brown zinc salt, it is formed when a solution of sodium nitrite (2 pts.) is added to a hot solution of β-naphthol (4 pts.) and zinc chloride (3 pts.) in alcohol (24 pts.), and the mixture boiled for a short time, the product being converted into the oxime by digestion with caustic soda solution and acidification of the filtrate (Henriques and Ilinski, Ber. 1885, 18, 705). As a greenish-yellow precipitate, it is produced when 10 p.c. sulphuric acid (700 c.c.) is added gradually to a solution of β-naphthol (50 grms.), caustic soda (14 grms.), and sodium nitrite (25 grms.) in water (1500 c.c.) containing one-third its weight of ice (Lagodzinski and Hardine, Ber. 1894, 27, 3076). It crystallises from alcohol in anhydrous orange-brown thin plates or short thick prisms, m.p. 109·5°, dissolves only very sparingly in hot water, and when pure is readily volatile with steam (Ilinski, *l.c.*).

Salts.—The *cupric* salt CuA_2 (Knorre, Ber. 1887, 20, 283), and *ferric* salt FeA_3, are insoluble in water or in 50 p.c. acetic acid (Ilinski and Knorre, *ibid.* 1885, 18, 2728); and the *cobaltic* salt CoA_3, is only very slightly soluble in boiling 50 p.c. acetic acid (*ibid.* 699). Since Hg, Pb, Cd, Al, Cr, Ni, Zn, Mn, Mg, Gl, &c., are not precipitated by it in acetic acid solution, nitroso-β-naphthol can be employed for the quantitative separation of Cu, or Fe, or Co, from any of the metals named (*cf.* Knorre, Zeitsch. angew. Chem. 1893, 6, 264). The *barium, potassium* KA, and *sodium* salts are green (Ilinski, Ber. 1884, 17, 2885).

Reactions.—(1) With dilute nitric acid (Stenhouse and Groves, *l.c.*) or potassium ferricyanide it gives 1-*nitro-β-naphthol.*

(2) By concentrated sodium bisulphite solution below 50°, it is converted into a crystalline bisulphite *compound*, which, unlike nitroso-β-naphthol, couples with diazotised bases forming *azo-* dyes (Dahl, D. R.-P. 79583 of 1893; D. R.-P. 95758 of 1897; *cf.* Ashworth and Bürger, Eng. Pat. 11556 of 1893). When decomposed by hydrochloric acid this compound furnishes 1-*amino*-2-*naphthol*-4-*sulphonic acid* (Böniger, Ber. 1894, 27, 23).

(3) Dissolved in hot methyl alcohol (Goldschmidt and Schmid, Ber. 1884, 17, 2067) or in cold caustic soda solution (Kehrmann and Messinger, *ibid.* 1890, 23, 2815), it yields [β-]*naphthaquinonedioxime*, m.p. 180°–181°, with hydroxylamine hydrochloride, but if the alkali solution be warm, the product is the *anhydride*, m.p. 78° (Kehrmann and Messinger, *l.c.*).

(4) Under the name 'Gambin R.' it has been introduced as a mordant dye for cotton (Aktienges., D. R.-P. 66786 of 1891).

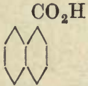
1-Nitroso-β-naphthol-6-sulphonic acid, formed by the action of nitrous acid on β-naphthol-6-sulphonic acid (Meldola, Chem. Soc. Trans. 1881, 39, 40), needles, gives a *barium* salt BaA_2+H_2O, in orange needles; a green *basic barium* salt $BaA+H_2O$; a *basic sodium* salt Na_2A+2H_2O, in green needles (Hoffmann, Ber. 1891, 24, 3471), and coloured metallic salts with Co, Ni, and Fe, from which the metal is not precipitated by alkalis or alkali carbonates. With ferric chloride and sodium carbonate it forms the *iron sodium salt* $Fe(NaA)_3$ (Gans, D. R.-P. 28065; Eng. Pat. 2269 of 1884; Hoffmann, Ber. 1885, 18, 46; *l.c.*), which, under the name *naphthol-green*, has been introduced as a green dye for wool (Gans, D. R.-P. 28901 of 1884; *cf.* Ulrich, J. Soc. Chem. Ind. 1890, 8, 1126).

1-Nitroso-2 : 6-dihydroxynaphthalene (Bayer, D. R.-P. 55126, 59268 of 1900; Eng. Pat. 14230 of 1889); 1-nitroso-2 : 7-dihydroxynaphthalene or *dioxin* (Leonhardt, D. R.-P. 55204; Eng. Pat. 17223 of 1889); and nitroso-2 : 8-dihydroxynaphthalene (Bayer, D. R.-P. 53915; Eng. Pat. 14230 of 1889) are mordant dyes, the two former giving green shades with iron salts.

X. Carboxy-Derivatives.

The naphthoic acids are technically unimportant, as are their derivatives with the exception of the hydroxynaphthoic acids.

Naphthoic Acids.



α-Naphthoic acid can be prepared by heating α-naphthonitrile with hydrochloric acid at 200° (Boessneck, Ber. 1883, 16, 639), or with 15 p.c. alcoholic soda at 160° (Bamberger and Philip, *ibid.* 1887, 20, 242), but most easily by boiling it with a mixture of sulphuric and acetic acids (Rabe, *ibid.* 1898, 31, 1898). It crystallises in needles, m.p. 160°, b.p. 300°, dissolves only sparingly in hot water, and on nitration yields both the 5- and the 8-*nitro-α-naphthoic acids* (Ekstrand, J. pr. Chem. 1888, [ii.] 38, 156). The *barium* salt BaA_2+4H_2O, and the *calcium* salt CaA_2+2H_2O, crystallise in needles; the *nitrile*, needles, m.p. 34°, b.p. 299°.

β-Naphthoic acid is obtained when β-naphthonitrile is boiled with alcoholic potash (Vieth, Annalen, 1876, 180, 305), or with a mixture of sulphuric and acetic acids (Baeyer and Besemfelder, *ibid.* 1891, 266, 187). It crystallises in silky needles, m.p. 184°, dissolves only sparingly in hot water, and yields *trimellitic acid* on oxidation with alkaline permanganate (Ekstrand, J. pr. Chem. 1891, [ii.] 43, 427). The *barium* salt BaA_2+4H_2O, and *calcium* salt CaA_2+3H_2O, crystallise in very sparingly soluble needles; the *nitrile* forms scales, m.p. 66·5°, b.p. 306·5°.

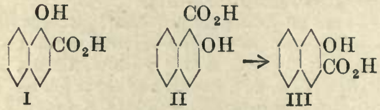
Hydroxynaphthoic Acids.

Introductory.—Two general methods have been used for the production of hydroxynaphthoic acids—

(1) Fusion of sulphonated naphthoic acids with caustic alkali;

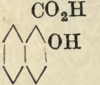
(2) Interaction of the sodium salts of the naphthols or dihydroxynaphthalenes with carbon dioxide under pressure at a suitable temperature.

The acids formed from the naphthols are—



The α- acid (II) from β-naphthol is obtained at 120°–140°, and the β- acid (III) at 200°–250°, a transformation which affords the only example in the naphthalene series of the entry of a radicle into the 3- position to produce a 2 : 3- disubstitution derivative.

The hydroxynaphthoic acids have found only a limited use in the manufacture of dye-stuffs. They give both normal and basic salts, and with ferric chloride usually a blue colouration. The order of stability of the acids and of their sulphonic derivatives may be inferred from the following facts: Acid II loses carbon dioxide more readily than acid I, and both by coupling furnish azo- dyes which do not contain the carboxyl group. Acid III and its derivatives, on the contrary, do not suffer this decomposition, although they, too, lose carbon dioxide when boiled with sodium bisulphite solution (Bucherer, *cf.* J. Soc. Chem. Ind. 1902, 21, 1272; J. pr. Chem. 1905, [ii.] 71, 445), a reaction which has thrown light on the constitution of some of the sulphonic acids of the group (Bucherer, *cf.* J. Soc. Chem. Ind. 1903, 22, 945).



(i.) **2-Hydroxy-1-naphthoic acid** is obtained by acting on dry sodium β-naphtholate with solid, liquid, or gaseous carbon dioxide under pressure in the cold, and subsequently heating the sodium β-naphthyl carbonate thus produced at 120°–140° (Schmitt, D. R.-P. 31240 of 1884; Schmitt and Burkard, Ber. 1887, 20, 2701; Heyden, D. R.-P. 38052 of 1886). The *acid* crystallises in needles, m.p. 156°–157°, but when slowly heated begins to decompose at 124°–128°, and is converted quantitatively into β-naphthol and carbon dioxide by prolonged boiling with water (Schmitt and Burkard, *l.c.*). It couples with diazotised bases, but the products are *azo-* derivatives of β-naphthol (Nietzki and Guitermann, Ber. 1887, 20, 1275).

The 6-sulphonic acid is formed by sulphonating 2-hydroxy-1-naphthoic acid with 20 p.c. anhydro- acid at 40°. It loses carbon dioxide forming *β-naphthol-6-sulphonic acid,* either when warmed in aqueous solution at 60°, or when coupled with diazotised bases (Seidler, D. R.-P. 53343 of 1889).

(ii.) **8-Hydroxy-1-naphthoic acid,** formed, together with the *anhydride* or lactone (m.p. 108)°, by boiling diazotised α-naphthylamine-8-carboxylic acid with dilute sulphuric acid, crystallises in needles, m.p. 169° (Ekstrand, Ber. 1886, 19, 1138); it does not readily reform the lactone.

(iii.) **1-Hydroxy-2-naphthoic acid** is obtained by acting on dry sodium α-naphtholate with carbon dioxide under pressure at 120°–145° (Heyden, D. R.-P. 38052 of 1886), or with solid, liquid, or gaseous carbon dioxide in the cold and subsequently heating the sodium α-naphthyl carbonate thus produced at 120°–140° (Schmitt, D. R.-P. 31240 of 1884; Schmitt and Burkard, Ber. 1887, 20, 2699). The *acid* crystallises in needles, m.p. 187°, is only very sparingly soluble in water (0·058 grm. in 100 c.c. at 17°), and gives with ferric chloride a blue colouration. The *sodium* salt $NaA+H_2O$, scales, and the *ammonium* salt NH_4A, needles, are readily soluble in hot water (Schmitt and Burkard, *l.c.*).

Reactions.—(1) Nitrous acid reacts with it, forming 2-*nitroso-α-naphthol* with the elimination of carbon dioxide (Reverdin and de la Harpe, Ber. 1893, 26, 1280); nitric acid converts it into 2 : 4-*dinitro-α-naphthol* (Nietzki and Guitermann, Ber. 1887, 20, 1275).

(2) It couples with diazotised bases forming para- *azo-* dyes (Nietzki and Guitermann, *l.c.*; Bischoff, Ber. 1890, 23, 1910; *cf.* Nietzki, D. R.-P. 44170; Eng. Pat. 17583 of 1887; D. R.-P. 46203 of 1888; Höchst, D. R.-P. 48357 of 1888).

The 4-sulphonic acid is obtained by warming 1-hydroxy-2-naphthoic acid with monohydrate at 60°–70° until sulphonation is complete (Dahl, D. R.-P. 51715 of 1889; *cf.* König, Ber. 1889, 22, 787). The *acid* H_2A+5H_2O, crystallising in small needles, shows blue fluorescence in alkaline solution.

Reactions.—(1) Nitric acid converts it successively into 4-*nitro*-1-*hydroxy*-2-*naphthoic acid* and 2 : 4-*dinitro-α-naphthol* (König, Ber. 1890, 23, 806).

(2) It couples with diazotised bases forming *azo-* dyes, which, owing to elimination of carbon dioxide, are derivatives not of β-naphthoic acid, but of α-naphthol-4-sulphonic acid (König, Ber. 1890, 23, 806; *cf.* Dahl, *l.c.*; Bayer, D. R.-P. 38802; Eng. Pat. 14424 of 1885).

The 4 : 7-disulphonic acid is the main product of the sulphonation of 1-hydroxy-β-naphthoic acid with 20 p.c. anhydro- acid at 100° (König, Ber. 1889, 22, 787; Seidler, D. R.-P. 56328 of 1889). The acid H_3A+4H_2O, needles, shows bluish-green fluorescence in alkaline solution.

Reactions.—(1) When boiled with 3 p.c. hydrochloric acid it yields *α-naphthol*-4 : 7-*disulphonic acid,* but when heated with dilute sulphuric acid (b.p. 160°) at 140° it gives 7-*sulpho*-1-*hydroxy*-2-*naphthoic acid* (Friedlaender and Taussig, Ber. 1897, 30, 1460).

(2) On fusion with caustic alkali at 220°–240°, it forms 4-sulpho-1 : 7-dihydroxy-2-naphthoic acid (Friedlaender and Zinberg, Ber. 1896, 29, 38), and at a higher temperature 1 : 7-*dihydroxynaphthalene*-4-*sulphonic acid* (Bindschedler, D. R.-P. 81938 of 1893; Eng. Pat. 4629 of 1894).

(3) It couples with diazotised bases forming *azo-* dyes of α-naphthol-4 : 7-disulphonic acid, owing to elimination of carbon dioxide (König, Ber. 1890, 23, 810; *cf.* Bindschedler, D. R.-P. 96930; Eng. Pat. 4630 of 1894).

(iv.) **2-Hydroxy-3-naphthoic acid** is obtained by allowing the calculated quantity of carbon dioxide to act on dry sodium β-naphtholate at at 200°–250° under pressure (Heyden, D. R.-P. 50341; Eng. Pat. 9612 of 1889; Schmitt and Burkard, Ber. 1887, 20. 2702). It crystallises in yellow scales, m.p. 216°, dissolves only very sparingly in hot water, and is characterised by its great stability, being decomposed, with loss of carbon dioxide, only when boiled with sodium bisulphite solution (Bucherer, J. pr. Chem. 1905, [ii.] 71, 445). Its normal salts are yellow, but the basic *sodium* salt, like the *acetyl* derivative, m.p. 176°–177° (Grädenwitz, Ber. 1894, 27, 2624), is colourless.

Reactions.—(1) On oxidation with potassium permanganate in alkaline solution it gives *o-carboxyphenylglyoxylic acid* (Schöpff, Ber. 1893, 26, 1123) and *phthalic acid* (Schmid, *ibid.* 1114).)

(2) When heated with ammonia under pressure at 260°–280° it is converted into 2-*amino*-3-*naphthoic acid* (Möhlau, Ber. 1893, 26, 3067).

(3) With nitrous acid it yields 1-*nitroso*-2-*hydroxy*-3-*naphthoic acid* (Kostanecki, Ber. 1893, 26, 2898).

(4) It couples with diazotised bases, forming *azo-* dyes, without elimination of the carboxyl group (Kostanecki, *l.c.*: *cf.* Aktienges., D. R.-P. 77286; Eng. Pat. 15789 of 1892; Griesheim, D. R.-P. 171904; Eng. Pat. 7839 of 1905; Merz, D. R.-P. 213499 of 1907; Eng. Pat. 16372 of 1908).

The 6-sulphonic acid (L- acid), and the 8-sulphonic acid (S- acid), obtained by sulphonating 2-hydroxy-3-naphthoic acid with monohydrate at 60° or above, are separated as calcium salts, that of the L-acid being the more soluble in hot water (Gesellsch., D. R.-P. 69357 of 1892; Schmid, Ber. 1893, 26, 1118; Hirsch, *ibid.* 1177), or as acid sodium salts, that of the L-acid being the less soluble (Bucherer, *cf.* J. Soc. Chem. Ind. 1903, 22, 945). The L-acid couples readily, but the S- acid only slowly with diazotised bases.

The 6 : 8-disulphonic acid is the chief product of the sulphonation of 2-hydroxy-3-naphthoic acid (Gesellsch., D. R.-P. 67000; Eng. Pat. 14161 of 1892), or of L- acid or S- acid (Schmid, *l.c.*), with 24 p.c. anhydro-acid at 125–150°.

Reactions.—(1) By fusion with caustic soda at 210°–240° it is converted into 3-*sulpho*-1 : 7-*dihydroxy*-6-*naphthoic* or *nigrotic acid* (Gesellsch., *l.c.*; *cf.* D. R.-P. 71202 of 1892; Schmid, *l.c.*).

(2) When heated with ammonia solution under pressure at 240°–280°, it gives 6-*sulpho*-2-*amino*-8-*hydroxy*-3-*naphthoic acid* (Gesellsch., D. R.-P. 69740 of 1892).

Of the remaining hydroxynaphthoic acids four have been obtained by fusing the isomeric sulphonaphthoic acids with caustic potash (Battershall, Annalen, 1873, 168, 121; Stumpf, *ibid.* 1877, 188, 1), and two from the corresponding naphthylaminecarboxylic acids (Friedlaender, Heilpern and Spielfogel, *cf.* J. Soc. Chem. Ind. 1898, 17, 836).

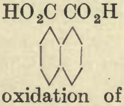
DIHYDROXYNAPHTHALENECARBOXYLIC ACIDS.

Introductory. — The dihydroxynaphthalenecarboxylic acids have little technical importance. *Five*, namely those containing the radicles OH : OH : CO_2H in the 1 : 2 : 3-, 1 : 4 : 2-, 1 : 7 : (?)-, 1 : 8 : 2-, and 2 : 7 : (3)- positions, have been obtained by interaction of the heated sodium salts of the respective dihydroxynaphthalenes with carbon dioxide under pressure (*cf.* Möhlau, Ber. 1893, 26, 3067; 1895, 28, 3093; Schmid, *ibid.* 1893, 26, 1117; Heyden, D. R.-P. 55414 of 1890), and *two*, containing these radicles respectively in the 1 : 7 : 6- (*infra*) and 2 : 6 : 3-positions, by fusion of the isomeric sulpho-2-hydroxy-3-naphthoic acids, S and L, with caustic alkali (*cf.* Schmid, *l.c.*; Gesellsch., D. R.-P. 69357 of 1892). Of these acids four, *viz.* the 1 : 7 : 6-, 1 : 8 : 2-, 2 : 6 : 3-, and 2 : 7 : (3)-derivatives, couple with diazotised bases forming *azo-* dyes.

1 : 7-*Dihydroxynaphthalene*-2-*carboxylic acid.* The 4-sulphonic acid is produced by fusing 4 : 7-disulpho-1-hydroxy-2-naphthoic acid with 80 p.c. caustic soda solution at 190° (Bindschedler, D. R.-P. 84653; Eng. Pat. 4630 of 1894), or with caustic soda at 220°–240° (Friedlaender and Zinberg, Ber. 1896, 29, 38). It couples with diazotised bases (Bindschedler, *l.c.*), and is converted into 1 : 7-*dihydroxynaphthalene*-4-*sulphonic acid* when heated with 30 p.c. caustic soda at 140°–160° (Bindschedler, D. R.-P. 83965 of 1893), but into the 2-*carboxylic acid* when either boiled with 20 p.c. hydrochloric acid (Bayer, D. R.-P. 89539 of 1894), or heated at 140° with 50 p.c. sulphuric acid (Friedlaender and Zinberg, *l.c.*).

1 : 7-*Dihydroxynaphthalene*-6-*carboxylic acid.* The 3-sulphonic acid (**nigrotic acid**, *cf.* Bucherer, J. pr. Chem. 1907, [2] 75, 287), obtained by fusing 6 : 8-disulpho-2-hydroxy-3-naphthoic acid with caustic soda at 210°–240° (Gesellsch., D. R.-P. 67000; Eng. Pat. 14161 of 1892; Schmid, Ber. 1893, 26, 1119) shows yellowish-green fluorescence in alkaline solution. It couples with diazotised bases forming black or grey *azo-* dyes (Gesellsch., D. R.-P. 71202 of 1892; D. R.-P. 75258; Eng. Pat. 14253 of 1892; D. R.-P. 80912, 84546; Eng. Pat. 4460 of 1894).

NAPHTHALENEDICARBOXYLIC ACIDS.



The naphthalenedicarboxylic acids have no technical value, but **naphthalene-1 : 8-dicarboxylic acid** (*naphthalic acid*), obtained by the oxidation of acenaphthene with chromic acid mixture (Behr and Van Dorp, Annalen, 1874, 172, 266; Anselm, Ber. 1892, 25, 652), is of interest chiefly on account of the readiness with which, like *ortho*-dicarboxylic acids, it is converted into an *anhydride* (m.p. 274°) or *imide* (m.p. 300°); and of the resemblance which this *peri*-anhydride shows to phthalic anhydride (Terisse, Annalen, 1885, 227, 135) in forming a *fluoresceïn* by condensation with resorcinol.

W. P. W.

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NAPHTHASE *v.* Azines.

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NAPHTHAZINES *v.* Azines.

NAPHTHIONIC RED or **ARCHIL SUBSTITUTE** *v.* Azo- colouring matters.

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NAPHTHOPHENAZINE *v.* Azines.

NAPHTHYLHYDRAZINE *v.* Hydrazines.

NAPHTHYLHYDRAZONES *v.* Hydrazones.

NAPLES YELLOW *v.* Antimony.

NARCEÏNE *v.* Vegeto-alkaloids.

NARCOFORM, NARCYL, and **NARGOL** *v.* Synthetic drugs.

NARCOTINE *v.* Vegeto-alkaloids.

NARINGIN $C_{21}H_{26}O_{11}$. A glucoside obtained from the blossoms of *Citrus decumana* (Murr.). It is a white substance which dissolves in alcohol and in warm water, and crystallises with

4 mols. H_2O, sp. rotatory power in aqueous solution $[\alpha]_D=84 \cdot 5°$; in alcoholic solution $[\alpha]_D=87 \cdot 6°$. By hydrolysis is resolved into *iso*dulcit and *naringenin* $C_{15}H_{12}O_5$, a white crystalline substance, m.p. 248° with decomposition. Gives a deep-brown-coloured solution with ferric chloride, and is readily soluble in alcohol, ether, and benzene. Naringenin is readily decomposed when boiled with conc. KOH, into phloroglucinol and *naringenic acid* C_9H_8O, a white crystalline powder, m.p. 207°, soluble in water, giving a red-brown-coloured solution with ferric chloride. Its aqueous solution treated with sodium amalgam gives *hydronaringeninic acid* ($C_9H_{10}O_3$), m.p. 126° (W. Will, Ber. 20, 294) (*v.* GLUCOSIDES).

NATROLITE. One of the commonest of the several minerals belonging to the zeolite group of hydrated silicates. Its composition is $Na_2Al_2Si_3O_{10},2H_2O$, and it crystallises in the orthorhombic system, sometimes as square prisms, but more often as fine needles. It is usually found as radiating fibrous masses in the steam-cavities of volcanic rocks. Sp.gr. 2·25. Colour, usually white; lustre, vitreous. Compact, radially-fibrous material with concentric yellow bands, from Hohentwiel in Würtemberg, has occasionally been cut and polished for ornamental purposes. L. J. S.

NATRON. A mineralogical term (from the ancient νίτρον, soda) for the hydrated sodium carbonate $Na_2CO_3,10H_2O$, crystallising in the monoclinic system. Since this hydrate crystallises only at temperatures below 20°, it is only under exceptional conditions that it is likely to be found in the natron or soda lakes of desert regions; and if formed it would soon effloresce into the monohydrate Na_2CO_3,H_2O, known as thermonatrite. According to Dana it exists only in solution. The native soda met with in the regions of natron lakes consists for the most part of the salt $Na_2CO_3 \cdot NaHCO_3,2H_2O$ known as trona, together with thenardite (Na_2SO_4) and halite (NaCl) (*v.* TRONA). L. J. S.

NEAPOLITAN YELLOW *v.* ANTIMONY.

NEAT'S FOOT OIL. Neat's foot oil (*Oleum bubulum* of the B.P.) is obtained from the feet of cattle by boiling with water. In this country the preparation of neat's foot oil is chiefly carried out in small establishments, in which the by-products and waste material of the slaughter-houses are worked up ('tripe shops'). The feet are carefully scraped and washed, the hoofs are cut off, and after the hair has been removed, they are boiled with water in jacketed pans heated by steam, the water being kept simmering for 8–10 hours. The oil rises to the top, and is skimmed off from time to time by means of suitable skimmers.

On a large scale, neat's foot oil is obtained as a by-product in the centres of the meat-packing trade (Chicago, South America). There the feet are taken in their fresh state from the slaughter-houses and sawn by a circular saw into suitable sizes for further working up. The chief object of sawing off the feet is to separate the more costly shin bones from the feet proper, which latter yield the genuine neat's foot oil. The fatty matter contained in the shin bones approaches somewhat in consistence horse- or beef-marrow fat, as the case may be. When kept separate it is sold as 'bone oil.' This oil must not be confounded with neat's foot oil, nor with bone fat. It is, however, customary in America to recover the oil from the shin bones, together with the neat's foot oil, by boiling the shin bones with the feet. Therefore American oil has a higher solidifying-point than that prepared in this country. The feet are scalded by immersion in boiling water from 10 to 15 minutes in order to loosen the hoofs, which are removed.

The oil is skimmed off as it rises to the surface, filtered roughly through a fine wire screen, separated from water as far as possible, and then run into vessels provided with close steam coils. Steam is passed through the coils and the water still contained in the oil thereby driven off, whilst at the same time organic impurities (albumen) become coagulated. The dried oil is finally obtained in a perfectly limpid state by filtering.

Neat's foot oil is pale yellow and has a bland taste. For the chemical and physical characters of the oil, *see* OILS, FIXED, AND FATS, tables. Properly prepared oil contains only a very small amount of free fatty acids. On standing, the oil deposits 'stearine.' This 'stearine' is frequently removed by filtering at a low temperature; this is done especially in the preparation of neat's foot oil for the leather industries, in which oil of a low 'cold test' is required. Owing to its comparatively high price neat's foot oil is largely adulterated with vegetable oils, fish oils, and even mineral oils. For the detection of the adulterants, *see* Lewkowitsch, Chem. Techn. ii. 403.

Neat's foot oil is a valuable lubricating oil for clocks, guns, sewing machines, and other delicate machinery. It is largely used in the leather industries ('fat liquor'). J. L.

NEEDLE-ORE or **AIKINITE** $PbCuBiS_3$.

NEMALITE *v.* BRUCITE.

NEODYMIUM. Sym. Nd. At.wt. 144·3. The fractionation of the cerite earths by Mosander in 1842 led to the separation of a new oxide, to the supposed element of which the name '*Didymium*' was given on account of the constant association of this substance with the metal lanthanum.

In 1879 the didymium earths yielded another element, samarium (Lecoq de Boisbaudran, Compt. rend. 88, 323), and six years later Auer von Welsbach succeeded in resolving 'didymium' into two components *neodymium* and *praseodymium* by the systematic fractional crystallisation of the double ammonium and sodium nitrates (Monatsh. 1885, 6, 477).

Occurrence.—In the rare minerals cerite, orthite, ytterbite, aeschynite, monazite, and samarskite.

Separation. (I.) *Fractional precipitation methods* depending on differences in basic strength (*v.* LANTHANUM).

(II.) *Crystallisation methods.*—The rare earth nitrates in aqueous solution are acidified with one-tenth of their weight of nitric acid and treated with the calculated amount of ammonium nitrate, the liquid being then evaporated to the crystallising-point and left for 24 hours. The mother liquor is again concentrated to the crystallising-point and the process repeated 6–8 times. The fractions thus obtained are again systematically crystallised and the cycle of operations repeated many times until finally the lanthanum ammonium nitrate separates in the least soluble fractions, followed successively by the praseodymium and neodymium double salts. The course of the separation is to some extent indicated by the colour differences of the various fractions; those richest in lanthanum are colourless, then follow successively green fractions containing chiefly praseodymium and some colourless fractions in which the neutral tint is due to the complementary colours of praseodymium and neodymium salts. The more soluble fractions show the pink colour of neodymium salts, and finally the uncrystallisable mother liquors contain the very soluble salts of samarium and the terbium and yttrium metals. Owing to the presence of these soluble salts the neodymium fractions do not crystallise readily, and it is therefore convenient to remove the yttrium earths by a basic process and then convert the crude neodymium salt into double sodium nitrate. The crystallisation of this double salt furnishes fractions still containing praseodymium, and this component is the more readily separated from neodymium by the addition of lanthanum, with which it subsequently crystallises in the least soluble fractions.

Although the proportions of neodymium and praseodymium present in the rare earths vary within wide limits, yet ‘didymium’ solutions generally have a pink colour owing to the predominance of the former component.

Various modifications of von Welsbach's process have been introduced. After removing the main portion of the lanthanum the separation of praseodymium is accelerated by the addition of pure cerous ammonium nitrate, the cerous and praseodymium double salts crystallising together (Schéele, Ber. 1899, 32, 409; *cf.* Dennis and Chamot, J. Amer. Chem. Soc. 1897, 19, 799).

The manganous double nitrates, when crystallised from strong nitric acid give only a small amount of the middle fractions containing mixed praseodymium and neodymium salts, and bring about a sharp separation between the latter metal and samarium (Lacombe, Bull. Soc. chim. 1904, [iii.] 31, 570).

The magnesium double nitrates

$$2R(NO_3)_3,3Mg(NO_3)_2,24H_2O$$

have been employed in acid, neutral and slightly basic solutions. In this process a preliminary separation is sometimes effected by means of moderately concentrated potassium carbonate when lanthanum and praseodymium are concentrated in the precipitate whilst neodymium, samarium, and the yttrium metals accumulate in the filtrate (Demarçay, Compt. rend. 1900, 130, 1019, 1185; Drossbach, Ber., 1902, 35, 2826; Muthmann and Weiss, Annalen, 1904, 331, 1).

Fractionation of the oxalates has been used in freeing praseodymium from lanthanum, and neodymium from samarium (Schéele, *l.c.*; R. T. Meyer, Zeitsch. anorg. Chem. 1904, 41, 94).

Purification of neodymium and praseodymium. Neodymium is freed from samarium and the yttrium metals by continued crystallisation of the double nitrates and finally by fractional precipitation with ammonia.

The *m*-nitrobenzenesulphonates have been suggested as a means of obtaining pure neodymium preparations (Holmberg, Bihang. Sv. Vet. Akad. Handl. 1903, 28, II. No. 5; Chem. Centr. 1906, ii. 1595).

Fractional precipitation of neodymium chloride with hydrogen chloride serves to free neodymium from lanthanum (Baskerville and Stevenson, J. Amer. Chem. Soc. 1904, 26, 54).

Praseodymium sulphate is approximately twice as soluble in water as neodymium sulphate at temperatures ranging from 10° to 70°, and this difference has been utilised in separating the two elements (Muthmann and Rölig, Ber. 1898, 31, 1718).

It is scarcely possible to free praseodymium from last traces of lanthanum, but the following means have been recommended: crystallisation of oxalates (Feit and Przibylla, Zeitsch. anorg. Chem. 1905, 43, 202); crystallisation of citrates (Baskerville and Turrentine, J. Amer. Chem. Soc. 1904, 26, 46; Zeitsch. anorg. Chem. 1905, 45, 86; *cf.* R. J. Meyer, *ibid.* 1904, 41, 94); fusion of nitrates with potassium nitrate when praseodymium dioxide and basic lanthanum nitrate are produced, the latter being extracted with cold aqueous ammonium nitrate; oxidation with potassium permanganate and mercuric oxide followed by the gradual addition of cerous chloride when the higher oxides of praseodymium and cerium are precipitated, the lanthanum remaining in solution (Orloff, Chem. Zeit. 1907, 31, 115).

Metallic neodymium, sp.gr. 6·9563, m.p. 840°, which is obtained by electrolysing the fused chloride (Annalen, 1902, 320, 231; 1904, 331, 1), has a pale-yellow tinge; when heated at 220° in hydrogen it absorbs the gas forming the hydride NdH_3 or NdH_2.

Neodymium carbide NdC_2, yellow hexagonal plates, sp.gr. 5·15, produced by heating the oxide with sugar carbon in the electric furnace (900 ampères, 50 volts) is decomposed by water evolving approximately 66 p.c. of acetylene, 6 p.c. of olefines, and 28 p.c. of paraffins (Moissan, Compt. rend. 1900, 131, 595).

Neodymium sulphide Nd_2S_3, olive green, sp.gr. 5·179, obtained by passing hydrogen sulphide over the heated sulphate or sulphur vapour over the carbide (Ber. 1899, 32, 3413).

Neodymium fluoride NdF_3, lilac crystalline powder, precipitated by hydrofluoric acid from a warm solution of the nitrate (Ber. 1908, 41, 634).

Neodymium chloride $NdCl_3$, a crystalline pink hygroscopic mass prepared by (1) dehydrating the hydroxide in a current of hydrogen chloride; (2) heating the oxide or sulphate in chlorine and sulphur chloride (Matignon, Compt. rend. 1901, 133, 289; 1904, 138, 631); (3) decomposition of the sulphide with hydrogen chloride (Muthmann and Stützel, Ber. 1899, 32, 3413). The anhydrous salt absorbs from 2 to 12 molecular proportions of ammonia, and is slowly converted by dry air into the oxychloride NdOCl. The hexahydrate $NdCl_3,6H_2O$ separates from aqueous or aqueous-alcoholic solution in pink rhombic crystals (Ann. Chim. Phys. 1906, [vii.] 8, 243; Ber. 1902, 35, 2622).

Neodymium bromide and **iodide** are produced respectively by warming the anhydrous chloride in hydrogen bromide and iodide; the latter is a black crystalline mass (Compt. rend. 1905, 140, 1637).

Neodymium hydroxide $Nd(OH)_3$, obtained as a bluish-white precipitate from soluble neodymium salts by the action of caustic alkalis or ammonia (Zeitsch. anorg. Chem. 1905, 43, 267).

Neodymium oxide (*neodymia*) Nd_2O_3, a pale blue powder with violet tinge, prepared by heating the hydroxide, oxalate, nitrate, &c. (Monatsh. 1885, 6, 477; Amer. Chem. J. 1898, 20, 345; Compt. rend. 1898, 126, 1039; Annalen, 1904, 331, 1; J. Amer. Chem. Soc. 1904, 26, 54; Bull. Soc. chim. 1904, [iii.] 31, 570). Higher oxides have been described: NdO_2 by Brauner (Zeitsch. anorg. Chem. 1902, 32, 1) and Nd_4O_7 by Waegner (*ibid.* 1904, 42, 118).

Neodymium nitrate $Nd(NO_3)_3,6H_2O$ (for isodimorphism with bismuth nitrate, *v.* Bodman, Ber. 1898, 31, 1237) furnishes the following double nitrates—

$$2Nd(NO_3)_3,3Mg(NO_3)_2,24H_2O,$$
$$Nd(NO_3)_3,2NH_4NO_3,4H_2O,$$
$$\text{and } Nd(NO_3)_3,2RbNO_3,4H_2O$$

(Zeitsch. anorg. Chem. 1911, 69, 221).

Neodymium chromate, moss green mass (Chem. Zeit. 1907, 31, 562).

Neodymium carbonate $Nd_2(CO_3)_3$, a pale red precipitate readily soluble in excess of alkali carbonates forming double carbonates

$$Nd_2(CO_3)_3,R_2CO_3,$$

the solutions of which are blue and exhibit absorption spectra differing as to the position and intensity of the bands from those of simpler neodymium salts.

Neodymium oxalate $Nd_2(C_2O_4)_3,10H_2O$ with the exception of thorium oxalate is the least soluble in acids of any of the rare earth oxalates.

Neodymium acetylacetonate

$$Nd[CH(CO{\cdot}CH_3)_2]_3$$

violet crystalline mass, m.p. 144°–146°; its molecular weight in ethyl sulphide is double that indicated by the foregoing formula.

The *absorption spectrum* of neodymium is much more complex than that of praseodymium. A 10 p.c. neodymium chloride solution shows upwards of 17 bands, and 29 (range $\lambda742$–$\lambda328$) have been noticed on dilution (Le Radium, 1909, 6, 215; Compt. rend, 1898, 126, 1039; Proc. Amer. Phil. Soc. 1908, 47, 276).

For *spark* and *arc spectra v.* Exner and Haschek, Sitzungsber. Wien. 1899, II*a*. 108, 1088; Die Wellenlängen der Bogenspektra, 1904; Zeit. wiss. Photograph. Photophys. Photochem. 1906, 3, 411, 4, 16.

Thermochemistry of neodymium compounds (*v.* Matignon, Compt. rend. 1905, 141, 53).

Physiological action of neodymium salts (*v.* Amer. J. Physiol. 1906, 16, 314; Proc. Phys. Soc. 1910, 68).

‘ *Didymium* ’ *salicylate* (*Dymal*)

$$[Nd,Pr]{\cdot}[C_6H_4(OH){\cdot}CO_2]_3$$

a reddish-white substance, has been employed as a dusting powder having non-irritant, non-poisonous and antiseptic properties (Kopp, Therapeutische Monatsh. 1901, 2). G. T. M.

NEOGEN. An alloy resembling silver in colour, said to have the following composition (Sauvage, Dingl. poly. J. 215, 377):

Cu	Zn	Ni	Sn	Al	Bi
58·0	27·0	12·0	2·0	0·5	0·5

NEON. Sym. Ne. At.wt. 20·2 (Watson, *v. infra*). An inert gas, discovered by Ramsay and Travers in the lighter portions of gas obtained by fractionating 15 litres of crude argon (Proc. Roy. Soc. 1898, 63, 438; Phil. Trans. 1901, 47). The method employed in the separation of neon from the accompanying helium and argon is fully described in Travers’ Study of Gases, 212–218. To obtain a gas rich in neon (and helium), the gas escaping from an air liquefier is used. This gas is chiefly nitrogen; it is liquefied and a current of air blown through the liquid. The first portion of the liquid to evaporate contains nearly all the neon and helium present. After removing oxygen and nitrogen, the argon is separated by fractional evaporation at the temperature of liquid air. To separate neon from helium effectively, fractionation must be carried out at the temperature of liquid hydrogen (*cf.* Watson, Chem. Soc. Trans. 1910, 97, 810). Neon and helium may be separated from the remaining inert gases by absorbing the latter in charcoal at the temperature of liquid air (Valentiner and Schmidt, Sitzungber. K. Akad. Wiss. Berlin, 1905, 38, 816).

Neon is much more abundant in the atmosphere than krypton and xenon; 1 million volumes of air contain 15 volumes of neon (Claude, Compt. rend. 1909, 148, 1454; *cf.* Watson, Chem. Soc. Trans. 1910, 97, 810; Ramsay, Proc. Roy. Soc. 1905, 76, A, 111; 1908, 80, A, 599). It also occurs in the gases evolved from many thermal springs (Moureu and Biquard, Compt. rend. 1906, 143, 180).

Neon is a colourless, odourless, tasteless gas. Next to helium and hydrogen, it is the least easily condensable gas known. Its critical temperature is below −210°; at the temperature of liquid hydrogen it solidifies. The critical pressure is 29 atmospheres, and the triple-point pressure for the system solid-liquid-gas is 35 cm. (Onnes, Proc. K. Akad. Wetensch. Amsterdam, 1909, 12, 175). At N.T.P. 1 litre of neon weighs $0{\cdot}9002\pm0{\cdot}0003$ grams (Watson, Chem. Soc. Trans. 1910, 97, 832). The compressibility of the gas has been studied by Burt (Trans. Faraday Soc. 1910, 6, 19). The refractive index of neon at N.T.P. for the green mercury line ($\lambda=5461$) is 1·0000672 (Cuthbertson and Cuthbertson, Proc. Roy. Soc. 1910, 83, A, 149); for its viscosity, *v.* Rankine (Proc. Roy. Soc. 1910, 83, A, 516). Neon is slightly soluble in water, the absorption coefficient at 20° being 0·0147 (Antropoff, *ibid.* 1910, 83, A, 474).

When neon is shaken in a tube with mercury, a red glow is observed, which is as bright at 120–200 mm. as at 760 mm. On long shaking, the glow ceases to appear; but the property is restored by sparking the gas. Moisture must be absent; hydrogen does not seriously affect the glow, which is more pronounced in a silica tube than in one of glass (Collie, Proc. Roy. Soc. 1909, 82, A, 378). For the spectrum of neon, *v.* Baly (*ibid.* 1903, 72, 84; Phil. Trans. 1903, A, 202, 183); Liveing and Dewar (Proc. Roy. Soc. 1901, 68, 389); Purvis (Proc. Camb. Phil. Soc. 1909, 15, 45).

Neon is monatomic, since the ratio of its specific heat is 1·66 (Ramsay and Travers).

NEPHRITE *v.* JADE.

NEROL $C_{10}H_{18}O$ is a terpene alcohol, first isolated by Hesse and Zeitschel (J. pr. Chem. 1902, [ii.] 66, 481) from the neroli oil of orange blossom oil. It is also contained in petit-grain oil (Soden and Zeitschel, Ber. 1903, 36, 265); in

Bergamot, Java Cananga, and in French lavender and other ethereal oils (Elze, Chem. Zeit. 1910, 34, 538, 857, 1029; Soden and Treff, Ber. 1904, 37, 1094).

Preparation.—South American petit-grain oil is saponified and then carefully distilled with steam or under reduced pressure. The higher boiling-point fractions contain the nerol together with geraniol and terpineol; the two former are separated from the latter by converting them into their acid phthalic esters. After purifying and saponifying, the mixture is treated with powdered anhydrous calcium chloride with which geraniol gives a solid product, whereas nerol is unaffected and can be washed out with light petroleum (D. R. P. 150495; Soden and Zeitschel, *l.c.*). In a similar manner nerol can be prepared from *Helichrysum angustifolium* and other species of *Helichrysum* from which larger yields are said to be obtained (D. R. P. 209382; Chem. Zentr. 1909, i. 1785). Nerol of the same composition and properties has also been obtained by heating linalool with acetic anhydride and sodium acetate, or with formic acid, or a mixture of sulphuric and acetic acids, the nerol being separated from the resulting product as above (D. R. PP. 165894; 165895; 165896; Zeitschel, Ber. 1906, 39, 1780, 1792).

The nerol obtained by any of the above methods still contains geraniol from which it can be finally purified by treatment with diphenyl carbamide chloride in the presence of pyridine. The geranyl and neryl diphenyl urethanes thus formed are separated by fractional crystallisation from light petroleum.

Neryl diphenyl urethane, m.p. 52°–53°, when treated with an alcoholic solution of potassium hydroxide, yields pure nerol (Soden and Treff, Chem. Zeit. 1903, 27, 897; Ber. 1906, 39, 906).

Properties.—Nerol is a colourless oil, b.p. 226°–227°/755 mm., 125°/25 mm., sp.gr. 0·8813 at 15°, and having a delicate fresh rose smell (Austerweil and Cochin, Compt. rend. 1910, 151, 440) on account of which it has been employed for the manufacture of artificial perfumes (D. R. P. 155287; J. Soc. Chem. Ind. 1903, 819). Nerol has been found to have a toxic action on mice (Hildebrandt, Beitr. Chem. Physiol. Path. 1903, 4, 251). Nerol is probably a space isomeride of geraniol; when oxidised with chromic acid it yields a substance with the odour of methylheptanone, and, probably, citral *b*, mixed with a little citral *a*. Citral *b* when reduced forms nerol. On prolonged shaking nerol forms terpin hydrate (Zeitschel, Ber. 1906, 39, 1780).

Nerol tetrabromide $C_{10}H_{18}OBr_4$, obtained by adding the calculated quantity of bromine to a solution of nerol in chloroform, evaporating and recrystallising from ethyl acetate, forms long, silky needles, m.p. 118°–119° (Soden and Treff, Ber. 1906, 39, 906).

The aliphatic esters of nerol have a similar smell to nerol; the *acetate*, b.p. 93°–94°/3 mm., 134°/25 mm., sp.gr. 0·916 at 15°, saponification number 286·2, and the *formate*, b.p. 119°–121°/25 mm., sp.gr. 0·928 have been prepared (Soden and Zeitschel, *l.c.*; Soden and Treff, *l.c.*).

Nerolidol $C_{10}H_{26}O$ is probably an aliphatic sesquiterpene alcohol. It is contained in neroli, and rose oils, and is, possibly, identical with or very similar to farnesol. It forms a colourless oil possessing a faint but permanent pleasant odour, has b.p. 128°–129°/6 mm., 164°–165°/25 mm., 276°–277°/760 mm., sp.gr. 0·880; $[\alpha]_D + 13·32°$ (Hesse and Zeitschel, *l.c.*), b.p. 149°/4 mm., sp.gr. 0·894 at 15°, $\alpha \pm 0°$ (Soden and Treff, Ber. 1904, 37, 1094). It forms an addition product with 6 atoms of bromine.

NEROLI *v.* OILS, ESSENTIAL.

NEURIDINE, NEURINE *v.* PTOMAÏNES.

NEURODIN *v.* SYNTHETIC DRUGS.

NEURONAL. Trade name for bromo-diethylacetamide (*v.* SYNTHETIC DRUGS).

NEUTRAL RED. *Toluylene red v.* AZINES.

NEUTRAL VIOLET *v.* AZINES.

NEURALTEIN. Trade name for the sodium salt of sulphomethylphenetidine (*v.* SYNTHETIC DRUGS).

NEW BLUE. *Naphthylene blue, Fast blue 2 B or R, Meldola's blue, New methylene blue v.* OXAZINE COLOURING MATTERS.

NEWKIRKITE. A variety of manganite (*q.v.*).

NICHOLSON'S BLUE *v.* TRIPHENYLMETHANE COLOURING MATTERS.

NICKEL. At.wt. 58·68; sym. Ni.

History.—This metal was discovered by Cronstedt in 1751, who isolated it from an ore containing arsenide of nickel NiAs, a copper coloured mineral called by the German miners *kupfer-nickel* or false copper, because of its resemblance to the colour of certain copper ores.

Occurrence.—Nickel is always present in meteoric iron, which is composed mainly of a nickel iron alloy containing 6–7 p.c. nickel, and in addition a small quantity of a complex alloy containing a constituent with about 40 p.c. nickel (Smith, Proc. Roy. Soc. A, 1907, 79, 132). It is also a constituent of the solar atmosphere.

The ores of nickel are widely distributed and have been worked for some time in many countries, especially in Saxony, Norway, and Sweden, Austria, Spain, Russia, the United States, and to some extent in different parts of Great Britain. Nickel exists in these countries usually associated with cobalt, as *kupfer-nickel* NiAs, *nickel-glance* $Ni(AsS)_2$, *nickel-blende* or *millerite* NiS, *cobalt-speiss* $(CoNiFe)As_2$, magnetic pyrites, &c.

The ores that have been found in the above countries are generally very complex in composition, containing, besides nickel and cobalt, copper, antimony, arsenic, iron, manganese, sulphur, &c. This fact renders the extraction of metallic nickel from such ores both expensive and troublesome.

The principal sources of nickel at the present time, however, are (1) mixed silicate of nickel and magnesium named after its discoverer *Garnierite*, and (2) nickeliferous magnetic, or copper, pyrites. The former (1) occurs in New Caledonia as a green- or brown-coloured ore which is found in veins in serpentine and other rocks. Similar silicates have since been found in other localities, but only in small quantities. The ore usually contains about 10 p.c. of nickel, and the following composition may be regarded as typical: 9–17 p.c. NiO; 41–46 p.c. SiO_2; 5–14 p.c. Fe_2O_3; 1–7 p.c. Al_2O_3; 6–9 p.c. MgO; 8–16 p.c. H_2O.

The nickeliferous magnetic pyrites (*pyroholite*) are found in Norway, Sweden, Saxony, Pennyslvania, &c., but the principal deposits occur at Sudbury in Ontario, these being now the chief source of the nickel of commerce. They occur chiefly as lenticular deposits in diorite dykes in rocks of the Huronian and Laurentian formations, these deposits being occasionally over 300 feet in length and 100 feet in thickness. The average amount of nickel is about 3 p.c., but the percentage apparently increases with the depth of the deposit, some of the lower deposits giving from 8 to 10 p.c. of nickel.

Extraction.—The method of extraction of nickel varies with the nature of the ore, and differs in detail in different works, but the general principle is as under. In the case of sulphide ores containing chiefly iron sulphide with a smaller quantity of nickel sulphide, and also probably some copper sulphide, the treatment consists of the following processes: (*a*) the removal of earthy materials and excess of sulphur with the production of a matte consisting of the sulphides of the metals; (*b*) the refining of the matte, that is the removal of the iron; (*c*) the conversion of the refined nickel sulphide, or nickel-copper sulphides into nickel, or if desired into an alloy of nickel and copper.

(*a*) If the percentage of sulphur is high the ores are subjected to a preliminary roasting either in heaps, stalls, kilns, or reverberatory furnaces. When roasted in heaps, the ore is broken and piled on a bed of wood above a layer of fine ore; the whole heap is covered with fine ore, and a central chimney is left. Such a heap may contain from 600 to 3000 tons, and the roasting may take from 6 to 20 weeks. If the percentage of sulphur is low this roasting may not be necessary. The resulting mass consists chiefly of sulphides of the metals, together with oxide of iron and gangue. This is next smelted with a suitable flux in special water-jacketed blast furnaces. These usually vary from 10 to 20 feet in height, and are capable of working from 100 tons of ore daily. If oxide of iron is in excess a silicious flux is added such as an acid slag, but if the iron present is insufficient to form a slag, a basic slag is added. During the smelting the iron passes into the slag, the nickel and copper remaining in the matte as sulphides, but it is necessary still to leave a quantity of iron sulphide in the matte, as otherwise considerable loss of nickel will result. A matte thus produced from Sudbury ore may contain from 15 to 25 p.c. nickel, and from 25 to 35 p.c. of iron, together with some copper, present almost entirely as sulphides. Arsenic, if present, is partly volatilized and partly passes into the matte. The slag consists chiefly of silicate of iron, the Sudbury slag containing from 27 to 38 p.c. silica, and from 40 to 46 p.c. ferrous oxide. When poor ores are employed it may be necessary to concentrate the matte by repeating these processes.

(*b*) The removal of the iron, or the refining of the matte may be effected in reverberatory furnaces, or more speedily and effectively in Bessemer converters. When reverberatory furnaces are employed, two refining processes may be necessary. The matte is partially roasted and afterwards the temperature is raised and sand added to slag the iron. A refined matte containing about 0·5 p.c. iron is thus obtained. The converters employed resemble ordinary Bessemer converters with a quartz lining, and are capable of holding from 1 to 6 tons of matte, which is either previously melted or run in directly from the furnace in which it is produced. Fine sand is added during the blow in order to slag the iron and to preserve the converter lining. When the process is complete the blast is stopped and the slag and matte poured into separate pots. The refined matte consists almost entirely of sulphides of copper and nickel, and a very small quantity (about 0·3 p.c.) of iron. The slag, however, which is chiefly silicate of iron may contain from 2 to 10 p.c. of nickel, and is added to the ore charges.

(*c*) The refined matte is next converted into metallic nickel. If copper is absent the matte is crushed and roasted, at first at a dull red and later at a bright heat. After this roasting it is ground fine, sieved and again roasted at a bright red heat with the production of an oxide of nickel containing less than 0·005 p.c. sulphur. This is mixed with meal or sugar syrup, moulded into cubes, dried and heated with carbon in crucibles or in a muffle furnace for about 24 hours. The temperature of reduction is not sufficient to effect fusion of the nickel, and if molten nickel is required a flux is added and a higher temperature employed. When copper is present separation of the sulphides is necessary. To effect this the matte may be first fused with sodium sulphate and coal; the molten mass separates into two layers, the upper layer—'*tops*'—consisting chiefly of sulphides of sodium, iron, and copper, and the lower—'*bottoms*'—being chiefly sulphide of nickel. The 'bottoms' together with those obtained from a further treatment of the tops are again similarly smelted with sodium sulphate and coal, and the resulting concentrated 'bottoms,' consisting almost entirely of nickel sulphide treated as above. For treatment of the copper-nickel matte the Mond process (Eng. Pat. 23665, Dec. 10, 1895) is also employed. This is dependent on the formation of the volatile compound $Ni(CO)_4$ by the action of carbon monoxide on nickel, and its subsequent decomposition by increase of temperature. The matte is dead roasted in rotating reverberatory furnaces and completely converted into oxides; the resulting mass is finely ground and leached with dilute sulphuric acid in lead vats at a temperature of about 85°, and much of the copper is thus extracted. After drying the mass is reduced by heating in a current of water gas, the temperature being maintained at about 250°, whereby reduction of any oxide of iron is obviated, and the reduced nickel is obtained in a reactive condition. The nickel is then converted into nickel carbonyl in volatilising towers by the action of carbon monoxide at a temperature of about 50°. The gas is obtained partly from the later decomposition of carbonyl and partly from the unused water gas. The nickel carbonyl produced is drawn into towers heated by gas burners in an outer annular space to about 200°, and containing nickel pellets kept in motion. The gas passes up the towers depositing nickel on the pellets, and the carbon monoxide is drawn off through a cooled tube again to pass through the volatilisers. The pellets are drawn off from below, screened, and the smaller ones added with fresh charges at the top of the reduction towers, the larger ones being used for commerce. Before the reduced matte in the volatilisers is completely exhausted the action becomes very slow, and the matte is then again roasted, leached, and reduced. The nickel thus obtained is of a very high degree of purity, some specimens containing over 99·5 p.c. nickel, the chief impurity being a very small quantity of iron.

Various other methods for treatment of the refined mattes have been proposed, many dependent on the fact that by chlorinating, roasting, or by treatment with chlorides and superheated steam, the copper, cobalt, &c., are more readily converted into chloride than is the nickel, and are hence removable by lixiviation (J. Soc. Chem. Ind. 1906, 115). These methods are best adapted for ores with low copper percentage. When it is desired to produce a copper-nickel alloy direct from the matte, the latter is first dead roasted for complete elimination of sulphur. This is frequently done in two operations, the material being finely powdered after the first roasting. The resulting mixture of copper and nickel oxides is then made into cubes with syrup, &c., and heated with powdered charcoal in crucibles or is smelted with charcoal in suitable furnaces.

In the case of arsenical ores such as kupfernickel, &c., the treatment is similar to that of the sulphides, *i.e.* the ores are roasted, whereby the iron is oxidised while the nickel remains as arsenide. The coarse '*speiss*,' as this regulus is termed, is then smelted to slag the iron, the processes being repeated until the refined speiss contains little or no iron. This is then dead roasted with, if necessary, the addition of carbonaceous material and later saltpetre in order (1) to reduce arsenate, and (2) to complete the oxidation of arsenides. The oxide of nickel so obtained is treated as above.

The New Caledonian ores consist chiefly of silicate of nickel, and for its extraction these ores are first converted into sulphides by smelting in shaft furnaces with calcium sulphide (obtained from alkali waste) or with a mixture of calcium sulphate and coal. The ore, gypsum, and coal are first ground to powder and compressed into bricks; during the smelting the gypsum is reduced to sulphide, which interacts with the nickel silicate forming nickel sulphide and calcium silicate. The coarse matte thus obtained may contain 50–55 p.c. nickel, 25–30 p.c. iron, and 16–18 p.c. sulphur, and is then treated similarly to the mattes from sulphide ores (*v. supra*).

Wet methods. Wet methods are not used to any extent for the extraction of nickel direct from the ores, but are frequently used for its extraction from the speiss or matte produced as above. Very many variations of the method in general use have been proposed, but little information is forthcoming regarding the technical or commercial success of many of these. The general method involves first the dead roasting of the matte or speiss (in the case of the latter, carbonaceous material and an oxidiser may be added to effect the complete removal of the arsenic) the temperature being raised towards the end in order to obtain as much of the iron as possible in the ferric condition. The mixture of oxides thus produced is brought into solution by means of hydrochloric acid and precipitation of iron, as ferric oxide in the case of a matte and a mixture of oxide and arsenate in the case of a speiss, is effected by bleaching powder. Copper is precipitated as sulphide by hydrogen sulphide, and excess of the latter removed by boiling. The liquid is then neutralised and cobalt precipitated by bleaching powder, and finally the nickel is thrown down as hydroxide by means of milk of lime. It is afterwards dried and reduced to metal as above.

Various liquids have been used or suggested as solvents for the nickel in the roasted mattes, &c., *e.g.* sulphuric acid, ferric sulphate solution (Emmens, Min. Industry, 1894, 463), magnesium chloride solution or ammonia solution with air blast (McIvor and Fradd, J. Soc. Chem. Ind. 1906), ferric chloride (D. R. P. 100142). A method due to Herrenschmidt for the treatment of New Caledonian ores consists of treatment with concentrated ferrous sulphate solution, manganese cobalt and nickel dissolving as sulphates and the iron being precipitated as oxide. The three metals are precipitated as sulphides, by sodium sulphide, the manganese converted into calcium manganite by milk of lime and air blast and the precipitate of cobalt and nickel sulphides is converted into sulphates in a reverberatory furnace, from which, after conversion into chlorides, the cobalt is precipitated as sesquioxide. Another wet process (D. R. P. 68559) proposes precipitation of iron by copper carbonate, then copper by nickel hydroxide, and then separation of the cobalt and nickel.

Electrolytic methods for treatment of the mattes, &c., have been proposed and attempted. The methods are usually dependent on the use of the mattes or of the nickel-copper alloys produced from them as anodes in an acid electrolyte with low currents. In this case copper only is deposited, nickel passes into solution, while silver, platinum, &c. (occasionally present in Sudbury ores) pass into an anode slime. The liquid is drawn off and after precipitation of copper and iron present the nickel is separated either by electrolysis with a carbon anode and nickel cathode or by precipitation as hydroxide and subsequent reduction as above.

Properties of nickel.—Nickel is a lustrous silver-white metal having a slight steel-grey tinge which is very observable when it is compared with silver. It is sufficiently hard to take a fine polish. Pure nickel was prepared by Winkler by electrolysis of an alkaline solution containing ammonium sulphate and subsequent heating in hydrogen (Zeitsch. anorg. Chem. 1894, 8, 1).

Nickel is magnetic at ordinary temperatures, but at high temperatures it forms a non-magnetic variety; the transition temperature appears to be about 350°; it has a density of 8·8 at 15° and a specific heat 0·108. Its hardness is 3·5, specific resistance 6·4 (micro ohms / c.c.), breaking weight 42 kilos. per sq. mm., and melting-point 1470° (Copaux, Compt. rend. 1905, 140, 657). At a white heat it can be welded with itself, with iron, or with various alloys. Its tensile strength exceeds that of iron.

Nickel may be distilled in the electric furnace, the distillate having the same properties as the finely divided metal. It is not so volatile as manganese, but is more volatile than iron or chromium (Moissan, Compt. rend. 1906, 142, 425).

Pure nickel is not a readily oxidisable metal, and its resistance to the action of the atmosphere, and also to the action of both fresh and salt water, admits of its being ranked in these respects with the precious metals. If heated, nickel wire burns in oxygen like iron, it also becomes incandescent in nitric oxide at 200°, and when prepared by reduction is pyrophoric. It decomposes steam at a red heat, but then only slowly. It dissolves slowly in dilute sulphuric and hydrochloric acids, rapidly in nitric acid or *aqua regia*. In contact with concentrated nitric acid it becomes passive like iron; when dropped into fuming nitric acid it may be violently attacked, may become passive, or may be disintegrated to a grey magnetic powder (Hollis, Proc. Camb. Phil. Soc. 1904, 12, 253). Acetic, citric, tartaric, and oxalic acids have little or no action on nickel unless they are left in contact with the metal for a long time. Caustic soda or other alkalis may be fused in nickel vessels without any change taking place.

Hydrogen is occluded by nickel at temperatures above 200°, in quantity increasing with temperature, but very different values have been obtained for the actual amount (*cf.* Bayer and Altmayer, Ber. 1908, 41, 3062; and Sieverts, Zeitsch. physikal. Chem. 1907, 60, 129). Nickel also appears capable of absorbing its own monoxide, its tenacity and malleability being thereby reduced. Carbon monoxide and nickel cyanide are also absorbed by molten nickel with deleterious effects. To purify such nickel a process due to Fleitmann is frequently employed. It consists in adding to the fused nickel contained in a fireclay crucible, a small quantity ($\frac{1}{8}$–$\frac{1}{20}$ p.c.) of metallic magnesium. The effect of this appears to be the reduction of the oxides and the decomposition of the cyanide with formation of nickel and *volatile* magnesium cyanide. Nickel so treated can be rolled into very thin sheets, and in this condition has been welded on to sheet iron or steel to be used for the manufacture of culinary and other utensils. It can be drawn into wire and cast or forged (D. R. PP. 6365, 7569, 9405, 13304, 14172, 23500, 28460, 28924). Manganese added to the extent of 1–3 p.c. is also stated to act as a purifier and to improve the quality of the metal.

Nickel may be deposited as a brilliant metallic layer by electrolysing a solution of the double sulphate of nickel and ammonia

$$NiSO_4,(NH_4)_2SO_4,6H_2O.$$

When nickel is prepared by reducing the oxide along with carbon, the metal is somewhat brittle, and when broken the fracture has a dull-grey colour and crystalline structure.

Alloys. Nickel readily forms alloys with a variety of metals. With copper and zinc the alloys are known under a very great variety of names, *e.g. German silver*, *nickel silver*, *China silver*, *Nevada silver*, *Potosi silver*, *silveroid*, *argentan*, *packfong*, *electrum*, &c.; and on the Continent as *maillechort*, *argiroide*, *neu-silber*, *weisskupfer*. All copper-nickel alloys appear to consist of mixed crystals, no compound being formed, the freezing-point curve falling regularly from that of nickel to that of copper (Guertler and Tammann, Zeitsch. anorg. Chem. 1907, 32, 25). The addition of nickel, even in small quantity, greatly reduces the conductivity of the copper and increases its hardness. The alloy containing 2–3 p.c. nickel has been found well adapted for metal work which has to be exposed to high temperatures, *e.g.* boiler tubes; alloys of 25 p.c. nickel are also used for firebox plates.

Constantan is an alloy of 60 p.c. copper and 40 p.c. nickel used largely for electric resistances owing to its very small temperature coefficient; it is also used with copper as a thermoelectric couple for moderate temperatures.

Manganin used similarly for resistance boxes contains about 12 p.c. nickel, with 4 p.c. manganese and 84 p.c. copper, whilst another somewhat similar alloy, *nickeline*, contains about 25 p.c. nickel, 74·5 p.c. copper, and 0·5 p.c. iron.

The German silver alloys are not definite compounds but consist of homogeneous mixed crystals. They form very valuable alloys, being ductile, hard, tough, capable of welding and hammering, and they withstand atmospheric influences. They are usually prepared by melting together an alloy of copper and nickel with one of copper and zinc. The composition of German silver varies very greatly, the percentage of copper ranging from 40 to 65 p.c., that of nickel from 6 to 31 p.c., and that of zinc from 18 to 30 p.c.; small quantities of iron, lead, or cobalt being occasionally present. The Birmingham extra-white metal contains 50 p.c. copper, 30 p.c. nickel, and 20 p.c. zinc; the German silver used as a base for electroplating contains about 57 p.c. copper, 7 p.c. nickel, and 36 p.c. zinc. German silver can be soldered, a solder commonly used containing 47 p.c. copper, 12 p.c. nickel, and 41 p.c. zinc.

Platinoid is a German silver of 60 p.c. copper, 14 p.c. nickel, 24 p.c. zinc, with 1–2 p.c. tungsten, largely used for electric resistances. Aluminium to the extent of about 3 p.c. is sometimes added to improve the quality, such an alloy being used for the German silver parts of typewriters. The coinage of Switzerland up to the 20-centime piece consists of a German silver alloy with silver added; and other nickel alloys are largely used in many countries for coinage.

Added to iron or steel nickel improves the quality for many purposes, the alloy being known as nickel steel (*see* IRON).

Many of the alloys with iron are remarkable for possessing a very low coefficient of expansion. The alloy containing 46 p.c. of nickel and 0·15 p.c. carbon has a coefficient of expansion equal to that of glass, and is used under the name of *platinite* for fusing into glass, in place of the far more expensive platinum. The alloy containing 36 p.c. nickel and about 0·2 p.c. carbon has a coefficient of expansion almost zero, and is very largely used in scientific instruments under the name of *invar*—a coefficient as low as 0·0000008 can be guaranteed by the manufacturers.

Much work on alloys of nickel with various metals has been done, and a number of references are given below: with boron (Moissan, Compt. rend. 1896, 122, 424; and Jassoneix, *ibid.* 1907, 145, 240); with tin and with antimony (Vigouroux, *ibid.* 1907, 144, 639, 145, 246, 429; 1908, 147, 976); with antimony (Lossew, Zeitsch. anorg. Chem. 1906, 49, 58); with tin (Guillet, Compt. rend. 1907, 144, 752); with arsenic (Granger and Didier, *ibid.* 1900, 130, 914; Friederich and Bennigson, Metallurgie, 1907, 200); with silicon (Guertler and Tammann, Zeitsch. anorg. Chem. 1906, 49, 93; Vigouroux, Compt. rend. 1907, 142, 1270); with copper (Guertler and Tammann, Zeitsch. anorg. Chem. 1906, 49, 93; 1907, 52, 25); with aluminium (Groyer, *ibid.* 1908, 57, 113). *Cf.* also Voss, *ibid.* 1908, 57, 34.

Uses of nickel.—The chief use of nickel is in the manufacture of alloys, and in the preparation of nickel sulphate for use in electroplating.

Vessels of pure nickel for laboratory purposes are an excellent substitute for those made of iron or copper. Basins may be used for boiling with caustic alkalis or alkaline carbonates, and crucibles may be employed for fusing minerals or salts with caustic alkalis or nitrates of the alkalis. Water-baths, spatulas, and tongs of nickel are very serviceable.

Oxides of nickel. The chief oxides of nickel are the monoxide NiO and the sesquioxide Ni_2O_3.

Nickel monoxide NiO occurs native as *bunsenite*, and may be prepared by strongly heating the hydroxide $Ni(OH)_2$, carbonate $NiCO_3$, or nitrate $Ni(NO_3)_2$. It is a green crystalline powder, which turns yellow on heating. It is easily reduced to the metal when heated in hydrogen. The *hydroxide* $(NiOH)_2$ is formed as an apple-green precipitate, when a nickel salt is treated with alkali hydroxide.

The salts of nickel are derived from the monoxide. They are in general yellow when anhydrous, emerald-green when hydrated or in solution.

Nickel sesquioxide Ni_2O_3 is a black powder obtained by gently heating the nitrate or carbonate in air. It is decomposed by heat, and is probably nickelous nickelite $NiO\cdot NiO_2$.

Nickel trihydroxide $Ni(OH)_3$ is obtained as a black precipitate when a nickel salt is warmed with alkali hypochlorite or chlorine passed through the hydroxide $Ni(OH)_2$ suspended in water. According to Bellucci and Clavari, however, this precipitate is the hydrated dioxide $NiO_2\cdot xH_2O$ (Gazz. chim. ital. 1905, 14, ii. 234; Atti. R. Accad. Lincei, 1907, [v.] 16, i. 647).

The *peroxide* NiO_2 is obtained in a hydrated form by the action of hydrogen peroxide on nickel salts (Pellini and Meneghini, Zeitsch. anorg. Chem. 1908, 60, 178), and an oxide regarded as NiO_4 was obtained by Hollard (Compt. rend. 1903, 136, 229).

Nickel carbonyl, $Ni(CO)_4$. When carbon monoxide is passed over reduced nickel at 30°–80°, combination occurs, and a volatile carbonyl is formed (Mond, Langer and Quincke, Chem. Soc. Trans. 1890, 749). It is a colourless liquid, boiling at 43·2° and solidifying at −25°; its sp.gr. is 1·3185 at 17°. At 50° it has the normal vapour density. The carbonyl is soluble in organic media; its vapour is very poisonous. For its reactions, see Dewar and Jones, *ibid.* 1904, 203; Proc. Roy. Soc. 1903, 71, 427; and *v.* CARBONYLS, Vol. I, p. 687.

Nickel arsenide NiAs occurs as *kupfernickel* (*v. supra*). The *phosphide* Ni_2P is obtained in grey needles when nickel and phosphorus are heated in the electric furnace (Maronneau, Compt. rend. 1900, 130, 656; cf. Granger, *ibid.* 1896, 122, 1484; 1896, 123, 176).

Nickel boride NiB is prepared in the electric furnace, and forms brilliant prismatic crystals of sp.gr. 7·39 (Moissan, Compt. rend. 1896, 122, 424). It is decomposed when fused with alkali.

Nickel silicide Ni_2Si is prepared by heating an excess of nickel with silicon in the electric furnace until the greater part of the metal has been volatilised; and then dissolving away the remaining metal with dilute nitric acid. It is a steel-grey, metallic-looking powder of sp.gr. 7·2, and is attacked by *aqua regia* and by hydrofluoric acid (Vigouroux, Compt. rend. 1895, 121, 686).

SALTS OF NICKEL.

Nickel bromide $NiBr_2$ is produced when finely divided nickel is heated in bromine vapour. It sublimes in golden scales. The bromide is very hygroscopic, and forms a trihydrate $NiBr_2,3H_2O$. The accepted equivalent of nickel rests largely upon the results obtained by Richards and Cushmann (Zeitsch. anorg. Chem. 1898, 16, 167; 1899, 20, 352) in their analyses of anhydrous nickel bromide.

Nickel carbonate $NiCO_3$ is obtained by heating a solution of nickel chloride with calcium carbonate at 150°. It forms pale-green, microscopic rhombohedra. A hexahydrate $NiCO_3,6H_2O$ is produced by mixing nickel nitrate solution with sodium bicarbonate and saturating the cold solution with carbon dioxide. It readily loses water. The pale green precipitates obtained by adding alkali carbonate to a nickel salt are basic carbonates of variable composition.

Nickel chloride $NiCl_2$ is formed when finely divided nickel is warmed in chlorine. It can be sublimed, and forms golden scales. It dissolves in water with the evolution of heat, and a green hexahydrate $NiCl_2,6H_2O$ can be crystallised out from the solution. The anhydrous chloride readily absorbs ammonia, forming an almost white compound $NiCl_2,6NH_3$, which dissolves easily in water. Nickel chloride is soluble in alcohol.

Nickel cyanide $Ni(CN)_2$ is obtained as an apple-green precipitate by adding potassium cyanide to a solution of a nickel salt. It is easily soluble in excess of potassium cyanide, and from the solution the double salt $Ni(CN)_2\cdot 2KCN$ can be crystallised. This salt is readily decomposed by dilute acids; no double cyanides are known corresponding to ferro- and ferri-cyanides.

Nickel fluoride NiF_2 forms green prisms (Poulenc, Compt. rend. 1892, 114, 1426); it is soluble in water and forms a trihydrate $NiF_2,3H_2$.

Nickel iodide NiI_2 forms black scales; the hexahydrate $NiI_2,6H_2O$ is a bluish-green, very hygroscopic crystalline substance.

Nickel nitrate $Ni(NO_3)_2,6H_2O$ is a green salt which crystallises in monoclinic tablets. It dissolves in twice its weight of cold water and is also soluble in alcohol. Tri- and mono-hydrates are also known.

Nickel nitrite $Ni(NO_2)_2$ is of little importance itself. It forms a double salt $Ni(NO_2)_2\cdot 4KNO_2$ which is easily soluble in water, and a triple nitrite $2KNO_2\cdot Ca(NO_2)_2\cdot Ni(NO_2)_2$, which is a yellow crystalline substance only sparingly soluble in water. Similar salts are known with barium and strontium, and hence the alkaline earth metals must be absent when nickel and cobalt are to be separated by the cobaltinitrite method.

Nickel sulphate $NiSO_4$ is formed in solution when nickel, or the hydroxide or carbonate is dissolved in dilute sulphuric acid. At ordinary temperatures the salt crystallises as the green heptahydrate $NiSO_4,7H_2O$, isomorphous with magnesium sulphate. At 50°–70° the hexahydrate $NiSO_4,6H_2O$ separates, in monoclinic crystals, and a hydrate of the same composition separates at ordinary temperatures from acid solutions, but the crystals are tetragonal pyramids.

The hydrated sulphate loses water at 100°, forming the monohydrate $NiSO_4,H_2O$, and at 280° the yellow anhydrous sulphate is left. The latter absorbs ammonia, forming a pale violet powder of the composition $NiSO_4{\cdot}6NH_3$. The compound $NiSO_4{\cdot}4NH_3,2H_2O$ crystallises in dark-blue tetragonal prisms from concentrated solutions of the sulphate in ammonia.

The solubility of nickel sulphate in water, expressed as parts of the anhydrous salt per hundred parts of water, is as follows:—

Temp.	2°	16°	23°	41°	50°	60°	70°
$NiSO_4$	30·4	37·4	41·0	49·1	52·0	57·2	61·9

Nickel sulphate forms numerous double sulphates with the sulphates of other metals. Of these, the most important is *nickel ammonium sulphate* $NiSO_4{\cdot}(NH_4)_2SO_4,6H_2O$, which is largely used in the process of nickel plating and in other processes in which a salt of nickel is employed. It is obtained by dissolving either nickel or nickel monoxide in sulphuric acid, and adding ammonium sulphate to the concentrated acid solution. It is purified by recrystallisation and forms short, monoclinic prisms. The solubility, expressed as parts of $NiSO_4{\cdot}(NH_4)_2SO_4$ per hundred parts of water, is as follows:—

Temp.	3·5°	16°	20°	30°	40°	50°	68°	85°
Salt	1·8	5·8	5·9	8·3	11·5	14·4	18·8	28·6

Nickel monosulphide NiS occurs in nature as *millerite*, sometimes in brass-yellow rhombohedra, but usually in capillary crystals. It is obtained in a black, hydrated form when a nickel salt is precipitated by ammonium sulphide. For its behaviour towards acids, *v. infra*, *Detection and estimation*. For the subsulphide Ni_2S, *v.* Mourlot, Compt. rend. 1897, 124, 768, and for the sesquisulphide, *v.* Dewar and Jones, Chem. Soc. Trans. 1904, 211.

Detection and estimation. Nickel salts colour the borax bead red in the oxidising flame. The sulphide is black, and cannot be precipitated in the presence of mineral acids, but when once precipitated, it dissolves very slowly in dilute hydrochloric acid.

Nickel may be estimated as the metal, as the monoxide, as nickel dimethyl glyoximate or as nickel dicyanodiamidine; it may also be estimated volumetrically. For details of these methods, and for the separation of nickel from other metals, *v.* ANALYSIS.

Atomic weight. The equivalent of nickel has been determined by the analysis of the bromide to be 29·34 (*v. supra*, p. 669; for other methods, *v.* Russell, Chem. Soc. Trans. 1863, 58; 1869, 292; Winkler, Zeitsch. anorg. Chem. 1893, 4, 10, 462; 1894, 8, 1, 291). From its specific heat, and the isomorphism of nickel salts with those of other metals, it follows that the atomic weight of nickel is twice its equivalent, or 58·68. The carbonyl is the only compound of nickel of known vapour density.

NICOTIDINE *v.* BONE OIL; also VEGETO-ALKALOIDS.

NICOTINE *v.* VEGETO-ALKALOIDS.

NICOTINIC ACID *v.* BONE OIL.

NIGELLA SEEDS or **BLACK CUMMIN.** The seeds of *Nigella sativa* (Linn.), a ranunculaceous plant growing on the Mediterranean coasts, and in Egypt, Trans-Caucasia, and India, were found by Reinsch, in 1841, to yield 35·8 p.c. of fat oil, 0·8 p.c. of volatile oil, and only 0·6 p.c. of ash. He gave the name of *nigellin* to a bitter extract resembling turpentine, yet soluble in water as well as in alcohol, though not in ether.

By submitting 25 lbs. of fresh seed to distillation, Flückiger obtained a nearly colourless essential oil, but in smaller quantity than Reinsch. It has a slight odour, somewhat resembling that of parsley oil, with a magnificent bluish fluorescence, as already remarked by Reinsch. In a column 50 mm. long this oil deviates the ray of polarised light 9·8° to the left. Its sp.gr. is 0·8909. The chief part of it, when heated with calcium chloride in a current of dry carbonic acid, distils at 256°. Its composition corresponds with the formula $2C_{10}H_{16},H_2O$. The residual portion, which is almost entirely devoid of rotatory power, after having been rectified by means of sodium, consists of terebenes $C_{10}H_{16}$. The fat oil, extracted by means of boiling ether from seed grown in Germany, previously finely powdered (necessarily including some essential oil which imparted to the other its fluorescence), is a fluid fat which does not congeal at 15°: it consists chiefly of olein, together with a considerable amount of a solid fatty acid, probably a mixture of palmitic and myristic acids.

It is stated in the Pharmacopœia of India that Nigella seeds are carminative, and they were formerly so regarded in Europe. In the East, generally, they are used as a condiment to food, and in Greece, Turkey, and Egypt, they are frequently strewed over the surface of bread and cakes in the same manner as anise or sesame. The fixed oil of the seeds is also expressed for use.

NIGER SEED OIL is obtained from the *achenes* of *Guizotia abyssinica* (Linn.), Cass. (*Guizotia oleifera*, D.C.), a plant indigenous to Abyssinia, and largely cultivated not only in East Africa, but also in the East and West Indies. The *achenes* contain from 40 to 45 p.c. of oil. For the chemical and physical characters of this oil, *see* tables OILS, FIXED, AND FATS.

Niger seed is crushed in Hull and Marseilles, and has been used lately to an increased extent as a substitute for linseed oil in soap-making, &c.

J. L.

NIGHT BLUE. A colouring matter obtained by the action of *p*- tolyl - *α* - naphthylamine on tetramethyl-diamino-benzophenone. Resembles Victoria blue *v.* TRIPHENYLMETHANE COLOURING MATTERS.

NIGRISIN is the commercial name for a basic grey dyestuff formed when aqueous or alcoholic solutions of nitrosodimethylaniline hydrochloride are boiled. It forms a black powder soluble in water to a reddish-grey solution which is changed to blue-grey on addition of acid. 1 litre of water at 100° dissolves 80 grams of nigrisin. In sulphuric acid it forms a pure grey solution, which, on addition of water, turns to red- then blue-grey. It is oxidised by nitric acid and reduced by stannous chloride and hydrochloric acid, and by zinc dust and acid. Potassium dichromate produces a brown precipitate soluble in acetic or tartaric acid with a grey-blue, in hydrochloric acid with a red-blue colour. Nigrisin is distinguished by its purity of shade, strong colouring power, fastness, and the variety of compound shades which it is capable of yielding when mixed with other dyestuffs (Baumann, Bull. Soc. Ind. Mulhouse, 1890, 65).

Nigrisin does not require a mordant for dyeing bleached cotton, and full shades are obtained with 1–3 p.c. of the dye. Cotton mordanted with antimony tannate also takes the dye well; in this case the material is padded in a solution containing 2–10 grams of the dye per litre. It is then dried and steamed, or before drying it may be passed through 0·5 p.c. solution of potassium dichromate at 60°, when an insoluble chromate of the colour-base is formed.

Nigrisin is formed and simultaneously fixed upon the fibre when cotton is printed with the following mixture and then steamed for about 3 minutes: 100 grams of nitrosodimethylaniline hydrochloride, 1 litre of warm water, 1¼ litre of starch paste thickening, 1¼ gum tragacanth paste (6 : 100). In the presence of an organic acid a grey (similar to that formed by nigrisin on unmordanted cotton) is produced. If the organic acid is replaced by tannin, and after steaming it is fixed with tartar emetic and washed, a deep rich-grey is obtained. By varying the conditions of dyeing and by the introduction of reducing agents, white and colour discharge effects upon a grey ground are obtained (Federmann, Bull. Soc. Ind. Mulhouse, 1909, 79, 251). The grey colour mixtures can also be made to give blacks (Brandt, J. Soc. Chem. Ind. 1900, 1106).

NIGROSINES *v.* Indulines.

NILE BLUES *v.* Oxazine colouring matters.

NIOBITE *v.* Columbite; also Columbium.

NIOBIUM *v.* Columbium.

NIRVANIN is the diethylglycocoll compound of 5-amino-2-hydroxybenzoic methyl ester. It forms a hydrochloride of neutral reaction, which produces complete anæsthesia of a longer duration than that caused by cocaïne (Einhorn and Heinz, Pharm. J. 1889, 62, 95), *v.* Synthetic drugs.

NITON. Sym. Nt. At.wt. and mol.wt. 222·4. The name given by Gray and Ramsay (Proc. Roy. Soc., 1911, A, 84, 536) to the gaseous emanation of radium discovered by Dorn (Naturforsch. Ges. für Halle a S. 1900). Niton, which has only been obtained in minute quantities, is prepared by heating a compound of radium or by dissolving it in water and pumping off the gases slowly produced. Oxygen, hydrogen, carbon dioxide, and nitrogen are successively removed by means of heated copper, copper oxide, phosphoric pentoxide, fused potassium hydroxide and heated lithium respectively, the niton left is then liquefied at −150° to −170°, and the helium present, together with a little niton, is pumped off (Debierne, Compt. rend. 1909, 148, 1264; Rutherford, Phil. Mag. 1908, 16, 300).

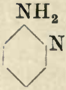
Niton is a member of the family of inert gases. Its density, measured by means of a microbalance sensitive to 2×10^{-6} mgm. with about $\frac{1}{1400}$ mgm. of material, gave a value of 223 for the molecular weight (Gray and Ramsay, *l.c.*; Compt. rend. 1910, 151, 126), but the value 222·4 is preferred for theoretical reasons. The direct density measurements are confirmed by the effusion experiments of Debierne (Compt. rend, 1910, 150, 1740), and the diffusion experiments of Perkins (Amer. J. Sci. 1908, [iv.] 25, 461), which gave the values 220 and 235 respectively for the molecular weight (for other determinations, *v.* Rutherford and Brooks, Trans. Roy. Soc. Canada, 1901; Curie and Danne, Compt. rend. 1903, 137, 1314; Bumstead and Wheeler, Amer. J. Sci. 1904, [iv.] 17, 97; Makower, Phil. Mag. 1905, [vi.] 9, 56; Chaumont, Le Radium, 1909, 6, 106). Niton therefore occupies the position in group O of the Periodic Scheme in the same series as, and immediately preceding, radium (*cf.* Gray and Ramsay, Chem. Soc. Trans. 1909, 95, 1073; Rankine, Phil. Mag. 1911, [vi.] 21, 45).

Niton undergoes a rapid diminution in volume to one-half the original amount when it is isolated. The gas, both before and after this change, obeys Boyle's Law. Niton is condensed to a solid at the temperature of liquid air. Both liquid and solid niton are phosphorescent. The critical temperature is 104·5°, the critical pressure 62·5 atmos., and the boiling-point is −62° (Rutherford and Soddy, Phil. Mag. 1903, [iv.] 5, 561; Rutherford, *ibid.* 1909, [vi.] 17, 723; Gray and Ramsay, Chem. Soc. Trans. 1909, 95, 1073; Laborde, Compt. rend. 1909, 148, 1591). Niton possesses a definite spectrum (Ramsay and Collie, Proc. Roy. Soc. 1904, 73, 470; 1908, 81, A, 210; Rutherford and Royds, Phil. Mag. 1908, [vi.] 16, 313; Royds, *ibid.* 1909, [vi.] 17, 202; Proc. Roy. Soc. 1908, [vi.] 82, 22; Watson, *ibid.* 1909, A, 83, 50).

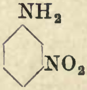
In the presence of niton, slow decomposition of water, ammonia, hydrogen chloride, and the oxides of carbon occurs (Ramsay, Chem. Soc. Trans. 1907, 91, 931; Cameron and Ramsay, *ibid.* 1907, 91, 1593; 1908, 93, 966, 992; Perman, *ibid.* 1908, 93, 1775; Usher, *ibid.* 1910, 97, 389; Rutherford and Royds, Phil. Mag. 1908, [vi.] 16, 812; Curie and Gleditsch, Compt. rend. 1908, 147, 345). Niton spontaneously decomposes, producing helium and other substances. For radioactive properties of niton, *v.* Radioactivity.

β-NITRANILINE RED *v.* Azo- colouring matters.

NITRANILINES. By the direct nitration of aniline, a mixture of *o*-, *m*-, and *p*-nitranilines is produced. Aniline is dissolved in 6 to 8 times the calculated quantity of nitric acid, mixed with an equal volume of sulphuric acid, the temperature being kept below 0°. The liquid is poured on to ice, and diluted with ice-water until *o*-nitraniline ceases to be precipitated. After filtration, the liquid is neutralised with sodium carbonate, and the *m*- and *p*-nitranilines separated by fractional precipitation, *p*-nitraniline being first precipitated as a yellowish-brown powder, and then the *m*- compound, which is pure yellow (Nietzki and Benckiser, Ber. 1885, 18, 295; Pinnow and Müller, *ibid.* 1889, 24, 150; Bruns, *ibid.* 1895, 28, 1954).

_o_-Nitraniline  may be prepared by the reduction of *o*-dinitrobenzene with ammonium sulphide (Körner, Gazz. chim. ital. 4, 305; *cf.* Rinne and Zincke, Ber. 1874, 7, 1374); by heating *o*-dinitrobenzene (Laubenheimer, *ibid.* 1878, 11, 1155; de Bruyn, Rec. trav. chim. 13, 121), *o*-nitrophenol (Merz and Ris, Ber. 1886, 19, 1751), *o*-nitroanisole (Salkowski, Annalen, 174, 278), or *o*-bromonitrobenzene (Walter and Zincke, Ber. 1872, 5, 114) with alcoholic ammonia; by heating *o*-nitrobenzanilide with dilute sodium hydroxide (Hübner, Annalen, 208, 278; Lellmann, *ibid.* 221, 6); by treating an aqueous solution of *o*-phenylenediamine with sodium peroxide (O. Fischer and Trost, Ber. 1893, 26, 3084); by treating oxanilide with strong sulphuric acid, nitrating the oxanilidedisulphonic acid thus formed, and decomposing the dinitro-oxanilidedisulphonic acid by boiling with water (Wülfing, D. R. PP. 65212, 66060; Frdl. iii. 44, 45). It is manufactured by gradually adding 40 kilos. of acetanilide to 80 kilos. of sulphuric acid (66°B.) with constant stirring, and keeping the temperature below 50°. A mixture of 36 kilos. of nitric acid (36°–37°B.) and 40 kilos. of sulphuric acid (66°B.) is then run in, the temperature being kept between 40° and 50°. Next day the liquid is poured into 200 litres of hot water, *o*- and *p*-nitroacetanilide being precipitated. The nitroacetanilides are deacetylated by heating an aqueous suspension with steam until complete solution occurs; the liquid is cooled to 50° and then poured on ice, *o*-nitraniline being precipitated. The *p*- compound is obtained by adding 180 kilos. of soda lye (36° B.) to the mother liquors and cooling with ice; yield 25 p.c. ortho- and 60 p.c. para- (Pokorný, Bull. Soc. Ind. Mulhouse, 1894, 280; Turner, Ber. 1892, 25, 985; Meldola, Chem. Soc. Trans. 1883, 427; Körner, Gazz. chim. ital. 4, 305).

o-Nitraniline crystallises in orange-yellow needles, m.p. 71·5°; 1 litre of water dissolves 1·256 grams at 25°; dielectric constant (*v.* Löwenherz, Zeitsch. physikal. Chem. 25, 407). Electrolytic reduction in sodium carbonate solution yields *o*-phenylenediamine (Rohde, Zeitsch. Elektrochem. 7, 339); this can also be effected by boiling with zinc and water. By boiling with ethyl chlorocarbonate, *o*-nitrophenylurethane is produced (Rudolph, Ber. 1889, 12, 1295), and with phthalic chloride *o*-nitrophthalanil is the product (Pawlewski, *ibid.* 1895, 28, 118). 3-chloro-6-nitraniline (*v.* Bad. Anil. Soda Fab. D. R. P. 206345; Chem. Soc. Abstr. 1909, i. 297).

_m_-Nitraniline  may be prepared by the reduction of *m*-dinitrobenzene with ammonium sulphide (Muspratt and Hofmann, Annalen, 57, 215; Körner, Gazz. chim. ital. 4, 305; Beilstein and Kurbatow, Annalen, 176, 44), with stannous chloride (Anschütz and Heusler, Ber. 1886, 19, 2161), or with iron and sulphuric or hydrochloric acids (Wülfing, D. R. P. 67018; Frdl. iii. 47); by treating *m*-nitrobenzanilide with dilute alkalis (Hübner, Annalen, 208, 278); by treating an aqueous solution of *m*-phenylenediamine with sodium peroxide (O. Fischer and Trost, Ber. 1893, 26, 3084).

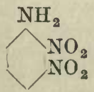
m-Nitraniline crystallises in large yellow needles, m.p. 114° (Hübner, Annalen, 208, 298), b.p. 285°, sp.gr. 1·430 (Schröder, Ber. 1879, 12, 563). Soluble in hot water and the usual organic solvents (Carnelly and Thomson, Chem. Soc. Trans. 1883, 786). Electrolytic reduction in alkaline solution yields *m*-azoaniline (Elbs and Kopp, Zeitsch. Elektrochem. 1895, 5, 108; Wülfing, D. R. P. 108427; Chem. Zentr. 1900, i. 1175); reduction with sodium stannite in alkaline solution yields di*meta*diaminoazoxybenzene (Meldola, Chem. Soc. Trans. 1896, 7), and in hot alkaline solution *m*-azoxyaniline is formed (Poirrier and Rosenstiehl, D. R. P. 44045; Frdl. ii. 436). By boiling with phthalic chloride, *m*-nitrophthalanil is produced (Dobreff, Ber. 1895, 28, 939; Pawlewski, *ibid.* 1894, 27, 430; 1895, 28, 1118). For methylation, *v.* Staedel and Bauer, *ibid.* 1886, 19, 1939; chlorination, *v.* Körner and Contardi, Atti. R. Accad. Lincei. 1909 [v.], 18, i. 93; bromination, *ibid.* 1908 [v.], 17, i. 465; iodination, *ibid.* ii. 679).

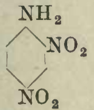
_p_-Nitraniline  may be prepared by heating *p*-nitrophenol (Merz and Ris, Ber. 1886, 19, 1753), or *p*-chloronitrobenzene (Engelhardt and Latschinow, Zeitsch. Chem. 1870, 232; Clayton Aniline Co., D. R. P. 148749; Chem. Soc. Abstr. 1904, i. 393) with strong aqueous ammonia; by boiling *p*-nitrobenzanilide with dilute potassium hydroxide (Hübner, Annalen, 208, 278); by oxidising *p*-nitrosoaniline (O. Fischer, *ibid.* 286, 154); by treating an aqueous solution of *p*-phenylenediamine with sodium peroxide (O. Fischer and Trost, Ber. 1893, 26, 3084); by nitrating benzylidineaniline with equal quantities of sulphuric and nitric acids, and dissolving out the product with water (Bayer and Co., D. R. P. 72173; Frdl. iii. 48); and by nitrating acetanilide (*v. o-Nitraniline*).

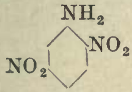
p-Nitraniline crystallises in long yellow needles, m.p. 147° (Hübner, *l.c.*); sp.gr. 1·424 (Schröder, Ber. 1879, 12, 563); readily soluble in hot water and the usual organic solvents (Carnelly and Thomson, Chem. Soc. Trans. 1883, 786). Electrolytic reduction in the presence of sulphuric acid yields *p*-diaminobenzene sulphate (Noyes and Dorrance, Ber. 1895, 28, 2349), but in the presence of sodium carbonate *p*-phenylenediamine is the product (Rohde, Zeitsch. Elektrochem. 7, 339). *p*-Phenylenediamine is also formed by reduction with zinc and water, or with hyposulphurous acid (Goldberger, Oester. Chem. Zeit. 3, 470). By heating with ethyl chlorocarbonate, *p*-nitrophenylurethane is formed (Hager, Ber. 1884, 17, 2625); and with phthalic chloride *p*-nitrophthalanil (Dobreff, *ibid.* 1895, 28, 939; Pawlewski, *ibid.* 1894, 27, 3430; 1895, 28, 1118).

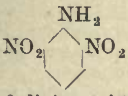
For chlorination, *v.* Flürscheim, Chem. Soc. Trans. 1908, 1772; oxidation with hypochlorites, *v.* Bayer & Co., D. R. P. 83525; Frdl. iv. 1017;

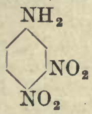
AZO- derivatives of the nitranilines, *v.* AZO-COLOURING MATTERS; constitution of the nitranilines, *v.* Hirsch, Ber. 1903, 36, 1898; absorption spectrum, *v.* Baly, Edwards and Stewart, Chem. Soc. Trans. 1906, 514; mercury salts, *v.* Jackson and Peakes, Amer. Chem. J. 1908, 39, 567; condensation products with chloral, *v.* Wheeler and Weller, J. Amer. Chem. Soc. 1902, 24, 1063.

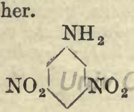
2 : 3-**Dinitraniline**  may be prepared by heating 2 : 3-dinitracetanilide with sulphuric acid (Wender, Gazz. chim. ital. 19, 226); orange-yellow needles, m.p. 127°; soluble in alcohol.

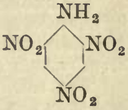
2 : 4-**Dinitraniline**  may be prepared by heating 2 : 4-dinitrosuccinanil (Gottlieb, Annalen, 85, 24) or 2 : 4-dinitracetanilide (Rudnew, Zeitsch. Chem. 1871, 202) with potassium hydroxide; by heating 1-chloro-2 : 4-dinitrobenzene (Engelhardt and Latschinow, *ibid.* 1870, 233), 1-bromo-2 : 4-dinitrobenzene (Clemm, J. pr. Chem. [ii.] 1, 145), 2 : 4-dinitroanisol, (Salkowski, Annalen, 174, 263), or 2 : 4-dinitrophenol (Barr, Ber. 1888, 21, 1542) with alcoholic ammonia. Yellow crystals, m.p. 176°; insoluble in water, soluble in alcohol and ether. On reduction with ammonium sulphide, *o*- and *p*-nitrophenylenediamines are produced (Kehrmann, Ber. 1895, 28, 1707); by boiling with alcoholic potassium cyanide, 2 : 4-dinitroaminophenol is formed (Lippmann and Fleissner, Monatsh. 7, 95), and with potassium hydroxide, 2 : 4-dinitrophenol (Willgerodt, Ber. 1876, 9, 979). For derivatives, *v.* Jaeger, Proc. K. Akad. Wetensch. Amsterdam, 1906, 9, 23.

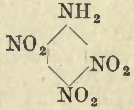
2 : 5-**Dinitraniline**  may be prepared by heating 2 : 5-dinitracetanilide with sulphuric acid (Wender, Gazz. chim. ital. 19, 233); orange-yellow needles, m.p. 137°; readily soluble in alcohol.

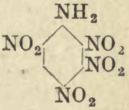
2 : 6-**Dinitraniline**  may be prepared by heating 2 : 6-dinitroanisol (Salkowski, Annalen, 174, 273) or 1-iodo-2 : 6-dinitrobenzene (Körner, J. 1875, 345) with alcoholic ammonia; yellow needles, m.p. 138°; soluble in alcohol.

3 : 4-**Dinitraniline**  may be prepared by heating 3 : 4-dinitracetanilide with sulphuric acid (Wender, Gazz. chim. ital. 19, 233); citron-yellow needles, m.p. 154°; soluble in alcohol, almost insoluble in ether.

3 : 5-**Dinitraniline**  may be prepared by reducing 1 : 3 : 5-trinitrobenzene with ammonium sulphide (Bader, Ber. 1891, 24, 1653); yellow needles, m.p. 159°; soluble in alcohol and ether, almost insoluble in benzene.

2 : 4 : 6-**Trinitraniline**, *Picramide*  may be prepared by heating 1-chloro-2 : 4 : 6-trinitrobenzene with ammonia (Pisani, Annalen, 92, 326) or by nitrating *o*- or *p*-nitranilines (Witt and Witte, Ber. 1908, 41, 3090); dark yellow needles, m.p. 188°. By reduction with tin and hydrochloric acid 2 : 4 : 6-triaminophenol is formed (Hepp, Annalen, 215, 350; Salkowski, *ibid.* 174, 261). By heating with potassium hydroxide, picric acid is produced (*q.v.*).

2 : 4 : 5-**Trinitraniline**  is obtained by nitrating *m*-nitracetanilide (Witt and Witte, *l.c.*), m.p. 183°.

2 : 3 : 4 : 6-**Tetranitraniline**  is prepared by nitrating *m*-nitraniline, 2 : 3- or 2 : 4-dinitranilines (Flürscheim and Simon, Chem. Soc. Proc. 1910, 81); yellow crystals, m.p. 212°.

NITRATED OILS *v.* OILS, FIXED, AND FATS.

NITRATINE, *Soda-nitre*, or *Chile saltpetre* (Span. *Salitre sodico*). Sodium nitrate ($NaNO_3$) is by far the most abundant of the few naturally-occurring mineral nitrates. In the provinces of Tarapaca and Antofagasta, in northern Chile, the nitrate deposits occur along a narrow belt of country where the westwardly sloping pampas abut against the coast range at an altitude of about 3000 feet. This district extends from the town of Tarapaca in the north to that of Taltal in the south—a distance of nearly 400 miles—and embraces an area of over 8000 square miles. The salt bed has a thickness of 1 to 6 feet and is overlain by 2 to 20 feet of gypsum, clay, sand, and gravel. The crude salt, called 'caliche,' is granular in texture and more or less cavernous; its colour is white, violet, bright yellow, or brown. It consists of from 20 to 60 p.c. of sodium nitrate, together with much sodium chloride and sulphate, and smaller amounts of soluble calcium and magnesium salts, potassium perchlorate, iodides, iodates, borates, &c. In the purification of the salts by re-crystallisation, iodine is a valuable by-product.

Chile saltpetre is largely used as a fertiliser, and for the preparation of potassium nitrate and nitric acid, used for the manufacture of explosives, &c. The quantity annually exported is about two million tons, valued at about £9 per ton.

See G. P. Merrill, The Non-Metallic Minerals, 2nd ed. New York, 1910; Estadística Minera de Chile en 1906 i 1907, Santiago de Chile, 1909, vol. iii. For references to the literature, *v.* F. W. Clarke, Data of Geochemistry (Bull. U. S. Geol. Survey, No. 330), 1908. L. J. S.

NITRE. *Potassium nitrate v.* POTASSIUM.

NITRE, CUBIC, *v.* SODIUM AND NITRATINE.

NITRIC ACID *v.* NITROGEN.

NITRIFICATION *v.* SOILS.

NITRILES. Prussic acid, being tautomeric in character, gives rise to two classes of esters, the *normal cyanides* or *nitriles* and the *isocyanides, isonitriles* or *carbylamines.*

The **nitriles** all contain the $-C{\equiv}N$ group, and they can be regarded either as hydrocarbons with one hydrogen atom replaced by the CN group, or as acids in which the COOH group has been converted into the CN group; *e.g.* CH_3CN is known either as methyl cyanide or as acetonitrile. The nitriles were discovered in 1834 by Pelouze, who obtained propionitrile by distilling barium ethyl sulphate with potassium cyanide.

Methods of preparation.—(a) *Aliphatic nitriles.*

(1) By heating alkyl halides (preferably iodide) with potassium cyanide in alcoholic solution at 100°.

(2) By distilling the salts of alkyl-sulphuric acids with potassium cyanide. (In each of these methods a little *iso*cyanide is also produced.)

(3) By heating alkyl *iso*cyanides to 250°.

(4) By treating cyanogen chloride with zinc alkyl. (In the above four methods the carbon chain is lengthened.)

(5) By the dry distillation of the acid amide or of the ammonium salt of the acids with phosphorus pentoxide or other dehydrating agent.

(6) By passing the acids together with a stream of ammonia through a red-hot tube.

(7) By converting the aldehydes into aldoximes, which are then dehydrated by acetic anhydride.

(8) By treating primary amines containing more than five carbon atoms with potassium hydroxide and bromine.

(b) *Aromatic nitriles.* By methods 3, 5, and 7.

(4) By diazotising a primary aromatic amine and decomposing the diazo- chloride thus formed with cuprous cyanide or with potassium cyanide and copper sulphate.

(5) By the action of potassium hydroxide and bromine on the primary arylalkylamines.

(6) By distilling the acids with potassium or lead thiocyanate.

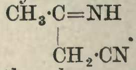
(7) By replacing the hydrogen atoms of the hydrocarbons directly with $-CN$ by passing cyanogen into the boiling hydrocarbon mixed with aluminium chloride.

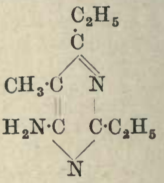
(8) By desulphurising the mustard oils with metallic copper.

(9) By heating the diarylthioureas with zinc dust.

(10) By distilling the formanilides with strong hydrochloric acid or with zinc dust.

(11) By distilling the alkali benzene sulphonates with potassium cyanide or with potassium ferrocyanide.

Properties (*aliphatic* and *aromatic*).—The nitriles are colourless volatile oils, which have an ethereal odour, are not very soluble in water, and distil unchanged. They are easily hydrolised by acids or alkalis into ammonia and the corresponding acid, the temperature required to effect this change being higher in the aromatic than in the aliphatic series. If an alcoholic solution of hydrochloric or sulphuric acid is used to carry out the hydrolysis, the ester is produced. In this case the triple link between carbon and nitrogen is completely destroyed, but there are many instances in which the nitriles behave as unsaturated compounds, the reactions being additive. Thus nitriles, when heated with water at 180°, or when treated with alkaline hydrogen peroxide at 40°, combine with a molecule of water to form acid amides. Similarly with acids they form diacylamines; with acid anhydrides, triacylamines; with sulphuretted hydrogen, thioamides; with hydroxylamine, amidoximes; with nascent hydrogen, amines (Mendius Reaction); with hydrochloric acid, iminochlorides or imino-ethers, depending on the use of aqueous or alcoholic solutions. In common with other unsaturated compounds, the nitriles form polymerisation products. By treatment with sodium in ether, bimolecular indifferent substances are produced; thus aceto-nitrile yields the imino-nitrile of acetoacetic acid  $\begin{array}{l}CH_3{\cdot}C{=}NH\\ \quad|\\ CH_2{\cdot}CN\end{array}$. On treatment with sodium in the absence of any solvent, trimolecular compounds are produced; in the case of the aliphatic series these are strongly basic substances, amino-pyrimidines, propionitrile yielding amino-methyl-diethyl-pyrimidine



(*v.* PYRMIDINES), while the aromatic nitriles yield cyanuric compounds containing the tricyanogen ring. From dicarboxylic acids two nitriles can be produced, the half-nitrile or nitrilic acid and the dinitrile, *e.g.* oxalic acid yields the dinitrile, oxalonitrile, which is dicyanogen, and the half-nitrile, oxalonitrilic acid, which is cyanoformic acid, and is known only in the form of esters. Similarly phthalic acid yields the dinitrile, phthalonitrile and the half-nitrile *o*-cyanobenzoic acid, which on heating changes into phthalimide (*v.* PHTHALIC ACID). For individual aliphatic nitriles, *v.* arts. METHYL, ETHYL, &c., and acids from which they are derived.

Benzonitrile, *Phenyl cyanide,* $C_6H_5{\cdot}CN$ occurs in coal tar oil (Krämer and Spilker, Ber. 1890, 23, 83). It may be prepared by the prolonged heating of phenyl *iso*cyanide at 200°–220° (Weith, Ber. 1873, 6, 213); by the dry distillation of ammonium benzoate (Fehling, Annalen, 49, 91); or by distilling the aqueous solution with baryta (Laurent and Gerhardt, J. 1849, 327; Wöhler, Annalen, 192, 362), lime (Anschütz and Schültz, *ibid.* 196, 48), phosphorus pentoxide (Buckton and Hoffmann, *ibid.* 100, 115), phosphorus pentachloride (Henke, *ibid.* 106, 276), or phosphorus pentasulphide (Henry, Ber. 1869, 2, 307); by distilling benzaldoxime with acetic anhydride (Lach, *ibid.* 1884, 17, 474); by diazotising aniline, and decomposing the diazobenzene chloride thus formed with potassium cyanide and copper sulphate (Sandmeyer, *ibid.* 2563); by distilling benzoic acid with potassium thiocyanate (Letts, *ibid.* 1872, 5, 673); by passing cyanogen into boiling benzene in the presence of aluminium chloride (Desgrez, Bull. Soc. chim. [iii.] 13, 735); by heating benzene and cyanogen chloride or bromide in the presence of aluminium chloride (Friedel and Crafts, Ann. Chim. Phys. [vi.] 1, 528; Merz and Weith, Ber. 1877, 10, 756); by the interaction of potassium fulminate and benzene in the presence of aluminium chloride (Scholl, Ber. 1899, 32, 3496); by treating potassium benzoate with cyanogen bromide (Cahours, Annalen, 108, 319); by desulphurising phenyl mustard oil with metallic copper (Weith, Ber. 1873, 6, 213); by distilling formanilide in a stream of hydrogen over heated zinc (Gasiorowski and Merz, *ibid.* 1885, 18, 1002); by heating potassium benzene sulphonate (Merz, Zeitsch. Chem. 1868, 33), or triphenylphosphate (Scrughan, Annalen, 92, 318; Heim, Ber. 1883, 16, 1771) with potassium cyanide; by treating benzamide, potassium cyanate or thiocyanate with benzoyl chloride (Limpricht, Annalen, 99, 117; Schiff, *ibid.* 101, 33); by heating chloro- or bromobenzene with potassium ferrocyanide at 400° (Merz and Weith, Ber. 1875, 8, 918; 1877, 10, 749); by heating iodobenzene and silver cyanide at 300° (Merz and Schelnberger, Ber. 1875, 8, 1630); by treating a mixture of brombenzene and cyanogen chloride in ethereal solution with sodium (Klason, J. pr. Chem. [ii.] 35, 83); by the interaction of ethylene dicyanide and benzoic acid (Matthews, J. Amer. Chem. Soc. 1898, 20, 650); by heating hippuric acid either alone or better with anhydrous zinc chloride at 240° (Limpricht and Uslar, Annalen, 88, 133; Gössmann, *ibid.* 100, 74); by passing dimethylaniline through a heated tube (Nietzki, Ber. 1877, 10, 474); and by the interaction of magnesium nitride and benzoic anhydride (Emmerling, *ibid.* 1896, 29, 1635).

Benzonitrile is a colourless oil, having an odour resembling that of benzaldehyde, b.p. 190·7° (corr.), sp.gr. 1·0101 at 15°/15° (Perkin, Chem. Soc. Trans. 1896, 1244; Kopp, Annalen, 98, 373), m.p. −12·9° (Schneider, Zeitsch. physikal. Chem. 19, 157); soluble in alcohol and ether, and in 100 parts of boiling water. On boiling benzonitrile with potassium hydroxide it is hydrolysed to benzoic acid and ammonia, while by digesting it for many hours with dilute potassium hydroxide at 40°, benzamide is produced (Rabaut, Bull. Soc. chim. [iii.] 21, 1075). Benzylamine is formed by reduction with alcoholic hydrochloric acid and zinc (Mendius, Annalen, 121, 144). According to Sabatier and Senderens (Compt. rend. 1905, 140, 482), hydrogenation in the presence of reduced nickel at 200° yields toluene and ammonia; but Frebault (*ibid.* 1036) states that by embedding the nickel in iron filings to ensure an even temperature, at 250° the products are benzylamine, dibenzylamine and possibly a trace of tribenzylamine. Chlorine in the presence of sunlight yields benzonitrile hexachloride (Matthews, Chem. Soc. Trans. 1900, 1273).

Benzonitrile oxide, *v.* Wieland, Ber. 1907, 40, 1667; Werner and Buss, Ber. 1894, 27, 2193. Addition compounds with platinous chloride, *v.* Hofmann and Bugge, *ibid.* 1907, 40, 1772; Ramberg, *ibid.* 2578).

The *iso***cyanides** contain the group $-N{=}C$ (Nef, Annalen, 1892, 270, 267; 1895, 287, 265). They were first prepared in 1866 by Gautier by treating alkyl iodides with silver cyanide. Later Hofmann obtained them by the interaction of potassium hydroxide, chloroform and primary amines. They are also formed in small quantity in some of the methods for preparing the nitriles (*v. supra*).

The *iso*cyanides are colourless, volatile liquids, having a most disagreeable odour, and are readily soluble in alcohol and ether, sparingly so in water. Though the *iso*cyanides are not basic, yet they combine with hydrochloric acid in ethereal solution to form compounds of the type $2R{\cdot}NC,3HCl$, but these substances are unstable to water. The *iso*cyanides are more easily hydrolysed than the nitriles, dilute acids or water at 180° effecting this, the products being formic acid and primary amines. Glacial acetic acid converts them into alkylformamides by the addition of one molecule of water. On reduction there are formed secondary amines, one of the groups being methyl.

Alkyl *iso*cyanides *v.* arts. METHYL, ETHYL, &c.

Phenyl *iso*cyanide, *Phenylcarbylamine*

$$C_6H_5{\cdot}N{=}C$$

may be prepared by the interaction of aniline, chloroform, and potassium hydroxide in alcoholic solution at 50° (Hofmann, Annalen, 144, 117; Nef, *ibid.* 270, 274); or by the action of chloroform and dry powdered caustic alkali on aniline in the absence of any solvent (Biddle and Goldberg, *ibid.* 310, 7); by the action of chloroform, carbon tetrachloride, hexachlorethane, bromoform, iodoform, or chloral on phenyl hydrazine in the cold (Brünner and Vuilleumier, Chem. Zentr. 1908, ii. 588).

Phenyl *iso*cyanide, when freshly prepared, is a green liquid; after a few minutes it changes to a pale blue, then to a dark blue liquid, and finally, after some months to a brown resin, b.p. 165° (with decomposition), sp.gr. 0·9775 at 15°/15°. By passing dry hydrogen chloride into a dry ethereal solution of phenyl *iso*cyanide the hydrochloride $2C_6H_5{\cdot}NC,3HCl$ is formed; this is decomposed by water (Nef, Annalen, 270, 303). By passing chlorine into the dry ethereal solution a chloride is obtained; this chloride can also be prepared by passing chlorine into phenyl mustard oil (Nef, *ibid.* 282), and on treatment with water at 100°, *sym*-diphenylurea, carbon dioxide, hydrochloric acid, and aniline are the products. Bromide, *v.* Lengfield and Stieglitz, Amer. Chem. J. 17, 101. Phenyl *iso*cyanide is readily hydrolysed by dilute acids into aniline and formic acid. Glacial acetic acid converts it into formanilide, and a trace of acetanilide; thioacetic acid yields acetanilide (Pawlewski, Ber. 1899, 32, 1425). It combines with sulphur, yielding phenyl mustard oil (Weith, *ibid.* 1873, 6, 210); with sulphuretted hydrogen it yields thioformanilide. By heating phenyl *iso*cyanide at 200°–220°, benzonitrile is produced (Weith, *ibid.* 213). Addition compounds with platinous chloride, *v.* Hofmann and Bugge, Ber. 1907, 40, 1772; Ramberg, *ibid.* 2578.

NITROBENZENE *v.* BENZENE.

NITROCELLULOSES *v.* EXPLOSIVES.

NITROCINNAMIC ACID *v.* CINNAMIC ACID.

NITROCRESOL *v.* NITROPHENOLS AND THEIR HOMOLOGUES.

NITRO DYES *v.* AURANTIA; NAPHTHALENE; and PICRIC ACID.

NITROGEN. Symbol N. At.wt. 14·01. Nitrogen was discovered in 1772 by Rutherford, Professor of Botany in the University of Edinburgh. He found that when a small animal was allowed to breathe air in a confined space for a time, and the carbon dioxide thereby produced removed by absorption, a gas still remained which was incapable of supporting respiration. Lavoisier first established the individuality of this gas, and clearly demonstrated its existence in the atmosphere. From its incapacity to support life he gave it the name of *azote;* the name nitrogen, denoting that the gas is an essential constituent of nitre, was subsequently given to it by Chaptal.

Occurrence.—Nitrogen is one of the most widely diffused of the elements, and occurs free in the air, of which it constitutes four-fifths by volume, or, more accurately, 78·06 p.c. (Leduc, Compt. rend. 1896, 123, 805). Volcanic gases contain considerable quantities of nitrogen, and the air-bladders of certain fishes, the bone-cavities of many birds, as well as the cavities of plants, all contain the gas in the free state. It occurs in many meteorites. The nebulæ consist, in part, of free nitrogen, and it is contained in the atmosphere of the sun.

Nitrogen, in a state of combination with oxygen, exists in the air as nitric and nitrous acids, and, combined with hydrogen, as ammonia. According to Hayhurst and Pring (Chem. Soc. Trans. 1910, 868) nitrous gases are present in the atmosphere, in quantities which vary from time to time, and are usually greater at high than at low altitudes, to the extent of about 1 in 3,000,000. These compounds are consequently present in rain-water. Nitrogen is an essential constituent of animal and vegetable organisms, and is found in many minerals, but chiefly in saltpetre or potassium nitrate, and Chile saltpetre or sodium nitrate.

PREPARATION.—(A) *From the Atmosphere.*

(α) By chemical separation of the oxygen with some reagent with which it easily reacts—

(1) By passing air over reduced iron (Brunner).

(2) With hydrogen over platinum sponge (Dumoulin).

(3) Over heated copper turnings (Dumas and Boussingault), or better, mixed with ammonia gas (Lupton, Chem. News, 1876, 33, 90), or with hydrogen (Hulett, J. Amer. Chem. Soc. 1906, 27, 1415).

(4) By absorption with alkaline pyrogallol (Liebig, Annalen, 1851, 77, 107).

(5) With copper and aqueous ammonia (Berthelot, Bull. Soc. chim. [ii.] 13, 314).

(6) With manganous and ferrous hydroxides (Flight, Chem. News, 1882, 45, 105).

(7) With phosphorus.

In these cases, after removal of carbon dioxide and water vapour, the gas obtained is at the most 99 p.c. pure, as the inert gases are still present.

Amongst the many patents for the production of nitrogen on this principle are those of Frank and Caro (nitrogen from combustion gases, *e.g.* from gas producers, D. R. P. 204882, May 22, 1907), Cyanide Ges. m.b. H. (D. R. P. 218671, Nov. 25, 1908; from air passed over copper in specially designed apparatus), Kassner (D. R. PP. 233383, and 234849, May 29, 1910, by absorbing the oxygen with calcium plumbate, alkali manganate, &c.), and Acker (Nitrogen Co. New York, Eng. Pat. 24413, 1910).

(β) By fractional distillation of liquid air. The bulk of the uncondensed gas is nitrogen, and the vapour boiling off from the liquid is mainly the more volatile nitrogen, the liquid after standing in a Dewar flask for some time being practically pure oxygen (*v.* Stock and Nielson, Ber. 1906, 39, 3393).

For the distillation of mixtures of liquid nitrogen and oxygen, *v.* Baly (Phil. Mag. 1900, [v.], 49, 517), Inglis and Coates (Chem. Soc. Trans. 1906, 886), Inglis (Phil. Mag. 1906, [vi.] 11, 640).

Erdmann (Ber. 1906, 39, 1207) describes a commercial method for condensing large quantities of nitrogen, in practically pure condition.

Many forms of apparatus designed for the production of nitrogen by this means have been patented. Of these the best known is the

LINDE NITROGEN SEPARATOR.

In the article OXYGEN, vol. iv., Fig. 1 illustrates the Linde oxygen separator, and in the description of that apparatus it is shown how it is possible to obtain pure liquid oxygen at the bottom of the rectification column, whilst the nitrogen vapours leaving the top of the column can never contain less than 7 p.c. of oxygen. Reference is also made to a modification of the Linde process due to Claude, by means of which small quantities of pure nitrogen may be obtained from an oxygen separator. For the production of pure nitrogen in large quantities, Linde employs a modified construction of his separator, which is illustrated diagramatically in Fig. 1.

In this apparatus, as in the oxygen one, the circular upper portion of the casing is made of wood and contains in its centre the rectification column A, whilst the base, constructed of wood in the form of a hexagon, contains the vaporising or distilling chamber B. All clearance spaces are packed with sheep's wool, or other suitable insulating material in order to prevent the penetration of heat from the outside. C is the counter-current interchanger, constructed in the form of a large copper spiral pipe, and containing three smaller pipes of different sizes *d*, *e*, and *f*. The vertical pipe C is an extension of the main spiral pipe to the top of the rectification column A. The pipe coil d_1 shown in the vaporising chamber is connected at one extremity with pipe *d* contained in the counter-current interchanger. The other extremity of this pipe is connected to the inlet of the valve box G to the outlet of which another pipe d_2 is connected, as shown. This pipe is carried upwards and enters the rectification column near the middle, where it is fitted as shown with a rose-end, the function of which will be explained later. The coil f_1, also shown in the vaporising chamber, is connected at one extremity with the pipe *f* contained in the counter-current interchanger. The other extremity of this pipe is connected to the inlet of the valve box H to the outlet of which another pipe f_2 is connected, as shown. This pipe is carried upwards and enters the rectification column near the top, where it is fitted, as shown, with a rose-end, the function of which will be described later. The short pipe e_1 communicates at one end with the top of the vaporising chamber and is connected at the other end to the extremity of the pipe e contained in the counter-current interchanger.

Two gas compressors are employed in conjunction with the separator, one working at high pressure and the other at low pressure. A fore-cooler as described in connection with the oxygen separator (*v.* OXYGEN) may also advantageously be used. This fore-cooler is kept cold by means of a carbonic acid or ammonia machine, and is interposed between the compressors and the separator, so that the compressed gases leaving the compressors at normal atmospheric temperatures, become reduced to a temperature well below the freezing-point of water before they enter the separator. With this preliminary description of the essential parts, the working of the apparatus can now be readily followed.

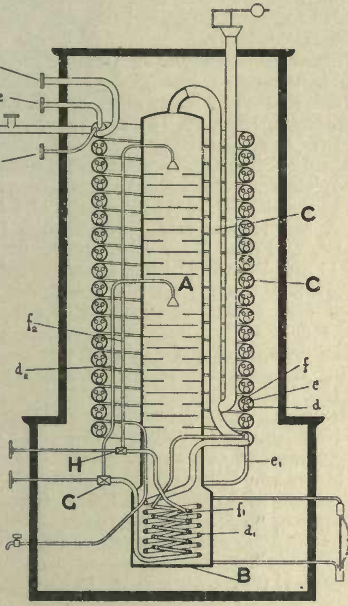


FIG. 1.

There are, as in the case of all such apparatus, two stages in the working.

First, the preliminary cooling down and production of liquid, and *second* the separation of pure nitrogen.

The preliminary cooling may be effected by charging the vaporiser B with liquid air, separately produced; or air at normal atmospheric temperature (or less where a fore-cooler is employed) and at a pressure of about 2000 lbs. per square inch is conveyed from the high-pressure gas compressor through the small pipe f of the counter-current interchanger. (Although only one pipe f is shown, several of these are generally employed.) This compressed air then passes through the pipe coil f_1 in the vaporiser B to the inlet of the valve box H. At this point, by the adjustment of the valve spindle, the air is caused to expand from a high to a low pressure and is discharged at this low pressure through the rose-ended pipe f_2 into the top of the rectification column. This expanded air fills the column and flows away through the outlet C into the counter-current interchanger in a reverse flow to the incoming high pressure air, leaving the apparatus through the pipe C. As a branch of this pipe is coupled to the intake of the high-pressure compressor, it is obvious that the same air circulates through the apparatus with a regenerative cooling effect, until a temperature is ultimately reached at which the expanded air begins to liquefy and collect in that state round the coils in the vaporiser B. The quantity of liquid thus collected is registered outside the apparatus by means of an ordinary coloured liquid which is contained in a glass tube j enclosed in a pressure-equalising circuit, as indicated.

When the vaporiser B is nearly filled with liquid, the second stage is reached in which the apparatus can be employed for the continuous production of nitrogen.

During the production of liquid in the vaporiser B, separation of oxygen and nitrogen has been taking place, first through simple fractional evaporation, and subsequently through rectification, as fully described under OXYGEN.

The nitrogen issuing from the pipe C has also been getting steadily purer in quality owing to the fact that it has been undergoing continuous treatment in an enclosed circuit. For the continuous production of pure nitrogen, it is, however, necessary to introduce a supplementary supply of liquid air, and as it is impossible by simple rectification to disengage nitrogen vapours from liquid air with less than 7 p.c. of oxygen, further treatment of the nitrogen has obviously to be employed in order to eliminate the residual oxygen. This is effected in the following manner:—

The air to be treated is supplied by the low-pressure compressor, already referred to, at normal atmospheric temperature (or less), and at a pressure of about 60 lbs. per square inch through the pipe d of the counter-current interchanger. This low-pressure air, thus cooled nearly to its temperature of condensation, then passes through the pipe coil d_1 in the vaporiser B, where its latent heat is transferred to the surrounding liquid, and it is itself entirely condensed, whilst at the same time evaporating an approximately equal quantity of the surrounding liquid. The pressure is then reduced by means of the valve G, and the liquid at atmospheric pressure is discharged into the lower part of the rectification column through the rose-ended pipe d_2. It is there rectified by the ascending vapours from the chamber B to a content of 7 p.c. of oxygen, whilst the liquid descending into the vaporising chamber is nearly pure oxygen. The nitrogen containing 7 p.c. of oxygen rises to the top of the column and is discharged from the apparatus through the pipe C and the main pipe C of the counter-current interchanger. Now, as already explained, a branch of the pipe C is coupled to the intake of the high-pressure compressor. Part of the outflowing nitrogen, therefore enters that compressor, and passing through the high-pressure circuit in the manner already described, is liquefied and discharged at the top of the rectification column through the rose-ended pipe f_2. This liquid containing 7 p.c. of oxygen is, according to Baly's experiments (*v.* Fig. 3, OXYGEN), able to purify the vapours encountered by it down to about 2 p.c. of oxygen. Part of these are again drawn into the high-pressure system and condensed, and flowing into the column, continue automatically to displace oxygen from the rising vapours until pure nitrogen only is discharged from the pipe C. Part of this nitrogen continues to circulate through the high-pressure system for scrubbing purposes, but the major part is collected for use through the vertical branch on the pipe C. Oxygen vapours are abstracted from the apparatus through the pipes e_1 and e.

It is found that an installation of this description will produce approximately one cubic metre of nitrogen per ½ I.H.P.

(B) *By Chemical Means.*—(1) By passing chlorine through a strong solution of ammonia

$$8NH_3+3Cl_2=6NH_4Cl+N_2.$$

The ammonia must be in excess, otherwise nitrogen chloride may be formed. Anderson (Chem. News, 5, 246) states that so obtained the nitrogen always contains oxygen. Ammonia is removed by passing through sulphuric acid.

(2) By adding metallic zinc to fused ammonium nitrate.

(3) By heating ammonium nitrite, or a mixture of ammonium chloride, and potassium nitrite: $NH_4NO_2=2H_2O+N_2$. This method gives nitric oxide in small quantity. If this is removed by ferrous sulphate solution, some is always evolved again on shaking, whilst with potassium permanganate oxygen is liberated in varying quantities (*v.* Knorre, Chem. Zentr. 1903, [i.] 125). The best method of procedure is to take 1 part $NaNO_2$, 1–2 parts $(NH_4)_2SO_4$, and 1 part $K_2Cr_2O_7$, warm the solution, and wash the gas evolved with a solution of 5 vols. saturated $K_2Cr_2O_7$ solution and 1 vol. concentrated H_2SO_4.

(4) By heating ammonium dichromate, or a mixture of ammonium chloride and potassium dichromate $(NH_4)_2Cr_2O_7=Cr_2O_3+4H_2O+N_2$.

(5) By heating glycerol (2 parts) and NH_4NO_3 (1 part) (Mai, Ber. 1901, 34, 3805).

The reaction commences at 190°, but once started proceeds without further heating till the temperature has fallen to 150°. A few drops of sulphuric acid cause the reaction to proceed more regularly and at a lower temperature. CO_2 is present in small quantity. The yield of nitrogen is nearly theoretical.

(6) By heating a mixture of dry ammonium nitrate and ammonium chloride

$$4NH_4NO_3+2NH_4Cl=Cl_2+12H_2O+5N_2.$$

(7) By passing a mixture of (*a*) nitric oxide, or (*b*) nitrous oxide, with ammonia over heated copper gauze or platinised asbestos. The nitrogen is purified by passing through dilute H_2SO_4, over fused KOH, through concentrated H_2SO_4, and finally over red-hot copper gauze (Baxter and Hickey, Amer. Chem. J. 1905, 33, 300).

(8) By decomposing chamber crystals with ammonium sulphate at 130° (Pelouze, Ann. Chim. Phys. 1841, [iii.] 2, 49)

$$2NO_2{\cdot}SO_3H+(NH_4)_2SO_4=3H_2SO_4+2H_2O+2N_2$$

It is also formed in other chemical decompositions, notably by the action of hypochlorites and hypobromites on ammonia and acid amides, and of nitrous acid upon amines.

Spongy platinum boiled with ammonium sulphate and sulphuric acid gives SO_2 and N_2 (Delépine, Compt. rend. 1905, 141, 886), probably in accordance with the following equations—

(1) $4H_2SO_4+Pt=Pt(SO_4)_2+2SO_2+4H_2O.$
(2) $3Pt(SO_4)_2+2(NH_4)_2SO_4=2N_2+3Pt+8H_2SO_4.$

This explains the loss of nitrogen when platinichlorides of organic bases are estimated by the Kjeldahl method.

Properties.—Nitrogen is a colourless, inodorous, tasteless, neutral gas. Its density has been determined by many observers (*v.* Ramsay, Chem. News, 1899, 79, 13), and the discrepancy between the densities of atmospheric and chemically prepared nitrogen led to the discovery by Rayleigh and Ramsay of argon.

The density (air=1) and weight of 1 litre at N.T.P. are respectively 0·96737 and 1·25092 (Rayleigh, Proc. Roy. Soc. 1898, 62, 209), 0·96717 and 1·25070 (Leduc, Compt. rend. 1898, 126, 413), these giving for H=1 the values 14·002 and 14·004 respectively (Leduc, *ibid.* 1908, 146, 399).

The density of atmospheric nitrogen (containing the inert gases) is 0·97209 (Rayleigh *l.c.*).

Rayleigh's later determinations (Proc. Roy. Soc. 1904, 73, 153) give the densities (H = 1) at atmospheric and at very low pressures as 14·003 and 14·009 respectively. B.p. —195·0° (Dewar, *ibid.* 1902, 69, 360); —195·9 (Grunmach, Sitzungsber. K. Akad. Wiss. Berlin, 1906, 679); —195·55 (Alt, Ann. Physik. 1906, [iv.] 19, 739).

Olzewski (Compt. rend. 1884, 99, 133) gives the b.ps. at high pressures as follows—

P. in atm.	35	31	17
°C.	—146	—148·2	—160·5

See also Baly (Phil. Mag. 1900, [v.] 49, 517) and Fischer and Alt (Sitzungsber. K. Akad. München, 1902, 113).

	Baly	Dewar	Fischer and Alt.
M.p.	—210·52	—210·5	—210·48

Critical pressure 32·29 atm., critical temperature —146·25° (Wroblewski, Compt. rend. 1885, 100, 979). Critical volume 42·6 c.c.; critical density 0·0235 (Dewar, Proc. Roy. Soc. 1904, 73, 251).

Sp.gr. of liquid nitrogen.

°C.	Sp.gr.	Observer
—193·93	0·8084	Inglis and Coates.
	0·8010	Baly and Donnan.
—195·5	0·8042	Dewar.
—198·3	0·8297	Inglis and Coates.
	0·8218	Baly and Donnan.

Sp.gr. of solid nitrogen.

—210·5	0·8792	Dewar.
—252·5	1·0265	Dewar.

Molecular volume at 0° abs. (calc.)=25·49 (Dewar, Proc. Roy. Soc. 1904, 73, 251). Specific volume at m.p. 221·3 c.c. (*ibid.* 1902, 69, 360). Sp.ht. of liquid nitrogen for temperature range of —196° to —208° is 0·430±0·008 (Alt, Ann.

Physik. 1904, [iv.] 13, 1010). Sp.ht. of gaseous nitrogen 0·2348 between 0° and 200° (Regnault); 0·2419 from 20° to 440°; 0·2464 from 20° to 630°; 0·2492 from 20° to 800° (Holborn and Austin, Sitzungsber. K. Akad. Wiss. Berlin, 1905, 175), and has a mean value $0{\cdot}2350+0{\cdot}000019\theta$ between 0° and θ° (Holborn and Henning, Ann. Physik. 1907, [iv.] 23, 809).

Latent heat of vaporisation at b.p. 50·4 cal. (Dewar, Proc. Roy. Soc. 1905, A, 76, 325): at b.p. 47·65, at −202°, 49·42, at −210°, 51·61 (Alt, Ann. Physik. 1906, [iv.] 19, 739).

Vapour pressure at m.p. 93·5 mm.; from Fischer and Alt's values of the vapour pressures near the m.p. the m.p. calculated by Ramsay and Young's method is −210·24°. For atmospheric nitrogen the vapour pressure at the m.p. is 90·2 mm., and the calculated m.p. is −210·47°. The lowering of 0·23° is brought about by argon (1·70 gram per 100 grams N) from which the molecular depression is calculated as 5·39 and from this the latent heat of fusion is 14·49 cal. (Estreicher, Bull. Acad. Sci. Cracow, 1903, 831).

Surface tension 8·514±0·02 dynes/cm. (Grunmach, Sitzungsber. K. Akad. Wiss. Berlin, 1906, 679). Tables showing variation of surface tension and density of liquid nitrogen with temperature are given by Baly and Donnan (Chem. Soc. Trans. 1902, 907).

The available pressure, volume, and thermal data for nitrogen at low temperatures have been collected and analysed by Plank (Physikal. Zeitsch. 1910, 11, 633).

Coefficient of expansion of liquid nitrogen varies from 0·002996 at 11°–132° abs. under 6 mm. to 0·003674 at 100° abs. under 1000 mm. (Erdmann, Ber. 1906, 39, 1207), and that of gaseous nitrogen 0·003643 from 0° to 1067° (Jacquerod and Perrot, Compt. rend. 1904, 138, 1032). The compressibility of gaseous nitrogen has been studied by Regnault, Natterer, Cailletet, Amagat (Ann. Chim. Phys. 1893, [vi.] 29, 68, 505), and Rayleigh (Proc. Roy. Soc. 1905, 74, 446). For the data the original papers must be consulted.

For viscosity constants of pure and atmospheric nitrogen, *v.* Markowski (Ann. Physik. 1904, 14, 742).

The inversion temperature of the Joule-Kelvin phenomenon for atmospheric nitrogen is 243° at 159 atm. and 163° at 30 atm. (Olzewski, Bull. Acad. Sci. Cracow, 1906, 792; *v.* also Porter, Phil. Mag. 1910, [vi.] 19, 888). Refractive index of gaseous nitrogen 1·000297 (Ramsay and Travers. Zeitsch. physikal. Chem. 1898, 100, 25), and of liquid nitrogen 1·2053 (Liveing and Dewar, Phil. Mag. 1893, [v.] 36, 328; *v.* also Cuthbertson, Proc. Roy. Soc. 1910, 83, A, 151). Electromagnetic rotation 0·000127 (Kundt and Röntgen, Wied. Ann. 1880, 10, 257).

Solubility.—Liquid oxygen at −195·5° dissolves 458 times its volume, or 50·7 p.c. of its weight of gaseous nitrogen (Erdmann and Bedford, Ber. 1904, 37, 1184). The solution obeys Henry's law, and liquid nitrogen therefore has the normal molecular weight, although oxygen dissolved in nitrogen is associated (Inglis and Coates, Chem. Soc. Trans. 1906, 886). Grunmach, however, from its surface tension calculates its molecular weight in the liquid state to be 37·3 (Sitzungsber. K. Akad. Wiss. Berlin, 1906, 679).

Solubility in water.

Temp.	0°	10°	20°	30°	40°	50°
cc. per litre	23·00	18·54	15·54	13·55	12·15	11·02

(Fox, Trans. Faraday Soc. 1909, 5, 68; *see* also Winckler, Zeitsch. physikal. Chem. 1892, 9, 171). For solubility in alcohol see Carius, Annalen, 1855, 94, 136; in petroleum see Gniewosz and Walfisz, Zeitsch. physikal. Chem. 1887, 1, 70; in glycerol and *iso*butyric acid see Drucker and Moles, *ibid.* 1910, 75, 405; in solutions of organic substances see Hûfner, *ibid.* 1907, 57, 611.

Wood charcoal absorbs ten times as much nitrogen at −185° as at 0° (Dewar, Compt. rend. 1904, 139, 261).

Chemical properties.—Nitrogen is not combustible, and does not support combustion, and in the free state is remarkable for its inactivity. It may, however, be made to unite directly with boron, silicon, magnesium, titanium, tantalum, and tungsten. It is absorbed by a mixture of magnesium powder and lime, and, under certain conditions, combines with hydrogen, oxygen, and carbon, as, *e.g.*, when a series of electric sparks is passed through oxygen and nitrogen gases standing over a solution of caustic alkali, when a nitrate of the metal is produced. Traces of nitric acid and ammonium nitrate are produced by burning hydrogen gas mixed with nitrogen in an atmosphere of air or oxygen. Nitrogen can unite with hydrogen to form ammonia when the gases are in the nascent state. Carbon and nitrogen unite directly when nitrogen gas or atmospheric air is passed over an ignited mixture of charcoal and potash, or charcoal and baryta.

Nitrogen reacts slightly with steam at 2000°: $N_2+2H_2O=2NO+H_2$ (Tower, Ber. 1905, 38, 2945).

If, however, the pure gas is subjected to the action of the electric discharge from a Leyden jar it undergoes a remarkable change in physical and chemical properties. The gas glows for some time after the discharge has been discontinued, exhibiting a characteristic band spectrum, with green, yellow, and red bands of about equal intensity. If passed through a glass tube moderately heated at one point the glow disappears locally. If strongly heated, the glow is permanently extinguished. Its brilliancy is increased during cooling by liquid air, but at the coolest part it is finally extinguished. Yellow phosphorus combines violently, iodine gives a magnificent blue flame, and sulphur and arsenic give faint blue and green flames respectively on being heated in the gas so treated. It combines with sodium and mercury on warming, forming with the latter an explosive compound, line spectra of the elements being developed, as is the case with cadmium, magnesium, potassium, zinc, and lead. When compound substances are volatilised in the gas, their band spectra are produced. It also reacts with organic halogen compounds, and with acetylene, with formation of a brilliant cyanogen spectrum. With nitric oxide nitrogen peroxide is produced, probably as represented by the equation $2NO+N=NO_2+N_2$ (Strutt, Proc. Roy. Soc. 1911, 85, A, 219).

A detailed account of the spectrum is given by Fowler and Strutt (*ibid.* 1911, 85, A, 377). For the spectrum of nitrogen, *v.* also Deslandres (Compt. rend. 1902, 134, 747), Mosengeil (Ann. Physik. 1906, [iv.] 20, 833), Walter (*ibid.* 1906, [iv.] 20, 327), Nasini and Anderlini (at 3000°, Gazz. chim. ital. 1906, 36, ii. 561), Purvis (in strong magnetic field, Proc. Camb. Phil. Soc. 1906, 13, 354), Angerer (at low temperatures, Ann. Physik. 1910, [iv.] 32, 549), Helm (long-waved portion, Zeitsch. wiss. Photochem. 1910, 8, 405), Wien (canal rays, Physikal. Zeitsch. 1910, 11,377), Croze (infra red, Compt. rend. 1910, 150, 860).

Nitrogen is an essential constituent of many of the most potent and valuable medicines, as well as of some of the most powerful poisons, *e.g.* quinine, morphine, prussic acid, and strychnine. The slight affinity existing between nitrogen and other elements gives a peculiar character to its compounds, many of which are extremely prone to decomposition. Many nitrogen compounds, especially those which contain the oxygenated radicle *nitryl* (NO_2), are highly explosive, as in the case of the picrates, certain azo compounds, gun-cotton, the fulminates of silver and mercury, nitroglycerine, &c.

HALIDES OF NITROGEN.

Nitrogen fluoride was supposed by Warren (Chem. News, 55, 289) to be formed when a saturated aqueous solution of ammonium fluoride was electrolysed, oily drops being noticed at the negative pole, which exploded violently when connected with the positive pole or in contact with organic matter, glass, or silica. Ruff and Geisel (Ber. 1903, 36, 2677) find, however, that nitrogen fluorides do not exist; that electrolysis of ammonium fluoride gives only pure fluorine, and that Warren's substance was probably nitrogen chloride produced from ammonium chloride present as an impurity.

Nitrogen chloride NCl_3. First prepared by Dulong in 1812 by the action of chlorine on an aqueous solution of ammonium chloride

$$NH_4Cl+3Cl_2=NCl_3+4HCl.$$

The reaction has been studied by Noyes and Lyon (Amer. Chem. J. 1900, 23, 460). Balard (Ann. Chim. Phys. 1834, [ii.] 57, 225) prepared it by the action of hypochlorous acid, and Hentschel (Ber. 1897, 30, 1434, 1792) by that of sodium hypochlorite on ammonium chloride.

It is also formed in the electrolysis of a concentrated ammonium chloride solution (Kolbe, J. pr. Chem. 1847, 41, 137), this being the method best suited for lecture experiments (*v.* Meyer, Ber. 1886, 21, 26; Hofer, Chem. Zeit. 1896, 20, 470).

By adding a calcium hypochlorite solution saturated with hydrochloric acid to ammonium chloride solution, and shaking with benzene the NCl_3 formed is dissolved in the benzene (Hentschel, Ber. 1897, 30, 2642).

By covering 150 c.c. of carbon tetrachloride with a concentrated aqueous solution of ammonium chloride, and passing in chlorine gas with vigorous shaking, and then washing with water, a bright yellow solution of the substance is obtained.

It is a yellowish volatile very pungent smelling oil, the vapour of which strongly attacks the eyes and mucous membrane; sp.gr. 1·653, b.p. 71°. It detonates on being heated to 93°, or when brought into contact with organic matter, phosphorus, arsenic, ozone, and alkalis. Metals, and strong acids, resins, and sugar do not cause its explosion, which is, however, brought about by exposure to strong light.

It dissolves in benzene, ether, chloroform, carbon tetrachloride, and carbon disulphide, giving highly refracting sulphur-yellow solutions, stable in the dark, but slowly decomposing in light. Its benzene solution has been used for chlorinating organic substances (Hentschel, *l.c.*; *ibid.* 1898, 31, 246). Heat of formation −38,477 cal. (Troost, Compt. rend. 1868, 69, 204).

The formula NCl_3 was assigned to it by Dulong (Schweigger's J. Chem. Pharm. 1812, 8, 32), Bineau (Ann. Chim. Phys. 1845, [iii.] 15, 82), and Deville and Hautefeuille (Compt. rend. 1869, 69, 152). Davy (Phil. Trans. 1813, 103, 1, 242) found the chlorine to be in excess of that required for this formula. Porret, Wilson and Kirk (Gilb. Ann. 1814, 47, 56, 59), and Gladstone (Chem. Soc. Trans. 1854, 7, 51) concluded that hydrogen was present (the latter giving the formula as N_2HCl_5), but the methods of analysis were not accurate. Gattermann determined the chlorine directly by decomposing a weighed quantity of the carefully purified and dried substance with concentrated ammonia, thus forming ammonium chloride, in which the chlorine was estimated as silver chloride, the result closely agreeing with the formula NCl_3 (Ber. 1888, 21, 755; *v.* also Hentschel, *l.c.*). This formula was confirmed by Chapman and Vodden (Chem. Soc. Trans. 1909, 141), who determined the ratio of nitrogen to chlorine, and also proved the absence of hydrogen.

Seliwanoff (Ber. 1894, 27, 1012) represents its hydrolysis with water as follows—

$$NCl_3+3H_2O \rightleftarrows NH_3+3HClO.$$

This explains the easy reduction to ammonia, and the apparently greater solubility in hydrochloric acid than in sulphuric acid or water, since hydrochloric acid destroys hypochlorous acid. This is confirmed by Chapman and Vodden by shaking the CCl_4 solution with moderately concentrated HCl, removing any NCl_3 from the aqueous solution, and distilling with KOH, when ammonia is obtained in quantity—

$$\begin{gathered} NCl_3+3H_2O \rightleftarrows NH_3+3HClO \\ HClO+HCl \rightleftarrows Cl_2+H_2O \\ NH_3+HCl \rightleftarrows NH_4Cl. \end{gathered}$$

Nitrogen bromide is said to be formed as a dark red highly explosive volatile oil by adding potassium bromide to nitrogen chloride under water, and is possibly formed in a manner similar to the chloride, but no definite compound has been isolated.

Nitrogen iodide was first prepared by Courtois, and has since been obtained in a variety of ways, viz. by digesting aqueous ammonia with powdered iodine (Stas) or alcoholic iodine solution (Serullas, Ann. Chim. Phys. 1829, [ii.] 42, 200), or a solution of iodine in *aqua regia*, or directly with iodine chloride in potassium iodide solution (Schönbein; Guyard, Compt. rend. 1883, 97, 526); from alcoholic ammonia and iodine solutions (Bunsen), and from ammonium iodide and bleaching powder (Gladstone, Chem. Soc. Trans. 1855, 51).

It forms copper-coloured crystals, light red by transmitted light, sp.gr. 3·5, very readily exploded by shock, warming, or exposure to strong light. It is never obtained free from hydrogen, and at low temperatures gives molecular compounds with varying quantities of ammonia, viz. $NI_3{\cdot}NH_3$, $NI_3{\cdot}2NH_3$, $NI_3{\cdot}3NH_3$, $NI_3{\cdot}12NH_3$ (Hugot, Ann. Chim. Phys. 1900, [vii.] 21, 5; Ruff, Ber. 1900, 33, 3025). The compound $NI_3{\cdot}NH_3$ is usually isolated, this formula representing its structure (Chattaway and Orton, Amer. Chem. J. 1900, 24, 331; Silberrad, Chem. Soc. Trans. 1905, 55).

Silberrad finds it to react with zinc ethyl as follows—

$$(1)\ NH_3{\cdot}NI_3+3Zn(C_2H_5)_2 \\ =3ZnC_2H_5I+NH_3+N(C_2H_5)_3$$

$$(2)\ 2NH_3+Zn(C_2H_5)_2=Zn(NH_2)_2+2C_2H_6$$

According to Seliwanoff (Ber. 1894, 27, 1012) its hydrolysis with water is as follows—

$$NH_3{\cdot}NI_3+3H_2O \rightleftarrows 2NH_4IO+HIO.$$

It is reduced by H_2S, SO_2, As_2O_3, similarly to NCl_3. Hydriodic acid liberates iodine, hydrochloric acid forms iodine chloride, hydrocyanic acid iodine cyanide, and alkalis a mixture of iodide and iodate. It reacts with organic iodides (Silberrad and Smart, Chem. Soc. Trans. 1906, 172).

NITROGEN AND SULPHUR.

Nitrogen sulphide was first prepared by Fordos and Gélis (Compt. rend. 1850, 31, 702), who assigned to it the formula SN.

It is obtained by passing dry ammonia gas into a solution of sulphur dichloride in carbon disulphide or benzene solution.

According to Francis and Davis (Chem. Soc. Trans. 1904, 259), it is best prepared from a 10–15 p.c. solution of S_2Cl_2 in benzene, into which a rapid current of dry ammonia is passed until red fumes appear, after which the liquid is cooled and the current continued for a short time longer. The ammonium chloride is filtered off, and on evaporation of the filtrate, orange-red prisms are obtained which, recrystallised from boiling benzene, toluene, or carbon disulphide, melt at 185°. It is more stable than previous observers have stated, its supposedly greater tendency to explode probably being due to impurities present, as indicated by the lower melting-points given by them (*cf.* Schenck, Annalen, 1896, 290, 171). It may be sublimed under reduced pressure. Crystallographic constants (Artini, Chem. Zentr. 1906, i. 1774)

$$[a:b:c=0{\cdot}8806:1:0{\cdot}8430\ ;\ \beta=89°\ 20']$$

Its formation is usually represented by the equation—

$$8NH_3+3S_2Cl_2=6NH_4Cl+2NS+S_4$$

but according to Ruff and Geisel (Ber. 1904, 37, 1573), the relation of the yield to the composition of the sulphur chloride employed indicates SCl_4 to be concerned in the reaction—

$$12SCl_4+16NH_3=3S_4N_4+48HCl+2N_2.$$

Its molecular formula is S_4N_4 (Schenck, *l.c.*; Muthmann, Ber. 1896, 29, 340; Francis and Davis, *l.c.*).

With chlorine in chloroform solution, the *tetrachloride* $N_4S_4Cl_4$ is formed, which crystallises on cooling in magnificent yellow crystals which decompose on heating—

$$N_4S_4Cl_4=2N_2+2S_2Cl_2.$$

It is excessively unstable, giving a black tarry mass on exposure to moist air (Demarçay, Compt. rend. 91, 854; Muthmann and Seiter, Ber. 1897, 30, 627).

Demarçay also describes the compound $(SN)_3Cl$, as produced by adding the requisite proportion of nitrogen sulphide to the tetrachloride in chloroform solution. This is probably *thio-trithioazylchloride* N_3S_4Cl, obtained by the action of N_4S_4 upon S_2Cl_2 in chloroform solution, or by heating N_4S_4 with acetyl chloride. It is an intensely yellow crystalline powder, which explodes a few minutes after becoming dry. It readily absorbs ammonia.

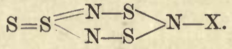
Muthmann and Seiter (*l.c.*) also describe the following derivatives—

Thio-trithioazylnitrate $N_3S_4NO_3$, obtained as sulphur yellow prisms when the chloride is dissolved in concentrated nitric acid and evaporated *in vacuô*. Its solution in water darkens after a few minutes, giving a black deposit. When dry it is very explosive.

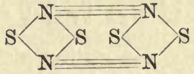
Thio-trithioazylbromide N_3S_4Br is formed by the action of N_4S_4 on S_2Br_2 in CS_2 solution, or of bromine on the chloride in CS_2 solution, or by exposing the tetrabromide of nitrogen sulphide (prepared similarly to the chloride) to moist air. It is stable in air.

Thio-trithioazyliodide N_3S_4I is prepared from solutions of the chloride and potassium iodide in ice cold water. It is very unstable.

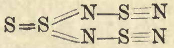
Thio-trithioazylthiocyanate N_3S_4CNS, from ice-cold solutions of the chloride or nitrate and potassium thiocyanate, forms lustrous bronze leaflets, fairly soluble in benzene and chloroform which resist the action of the air. These compounds have the constitution—



Schenck assigns to N_4S_4 the constitutional formula—

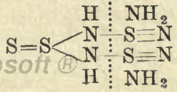


but Ruff and Geisel (*l.c.*) regard the divalence of the sulphur atoms as improbable, and suggest the formula—



which is supported by its reaction with metallic iodides in anhydrous liquid ammonia. Lead iodide gives olive green prisms of the dithio-di-imide, $Pb{\cdot}N_2S_2{\cdot}2NH_3$, and mercury iodide bright yellow crystals of the thio-di-imide, $Hg{\cdot}N_2S{\cdot}NH_3$, but in neither case is precipitation complete, and the mother liquor from the lead salt gives the mercury compound with mercury iodide, whilst that from the mercury salt gives the lead compound with lead iodide. These facts are accounted for by the supposition that in ammonia solution dissociation of the above molecule takes place into the ions—

$$N{\equiv}S{\cdot}NH_2 \text{ and } S{=}S(NH)_2$$



Nitrogen sulphide reacts with a number of metallic chlorides giving additive compounds (Wölbing, Zeitsch. anorg. Chem. 1908, 57, 281); with amines (Schenck, *l.c.*); with acetic acid and its halogen derivatives (Francis, Chem. Soc. Trans. 1905, 1836); with aromatic aldehydes (Davis, *ibid.* 1831); with hydrofluoric acid (Ruff and Thiel, Ber. 1905, 38, 549).

Stannous chloride does not combine, but on warming in benzene solution the N_4S_4 is reduced with formation of yellow lustrous leaflets, m.p. 152°, of the empirical formula NSH. It is not combustible or explosive. NH_3 is evolved on heating with KOH (Wölbing, *l.c.*).

According to Moissan (Compt. rend. 132, 510), the reaction $10S+4NH_3 \rightleftarrows 6H_2S+N_4S_4$ is reversible; nitrogen sulphide can be obtained from sulphur and ammonia in presence of silver iodide.

Dry HCl reacts as follows—

$$N_4S_4+12HCl=4NH_3+4\underbrace{S+12Cl}$$

showing that sulphur is united to nitrogen by 12 valencies, and hence, in agreement with Ruff and Geisel's formula, no N atoms are linked. Ht. of formation of $N_4S_4-81{,}900$ cal. (Berthelot and Vieille, Ann. Chim. Phys. 1882, [v.] 28, 202).

A blue modification of the yellow sulphide N_4S_4 is described by Burt (Chem. Soc. Trans. 1910, 1171) as obtained by subliming the latter over silver gauze. It is much less volatile, and evidently formed from an unstable intermediate reduction product which loses nitrogen.

A liquid sulphide N_2S_5 is obtained when N_4S_4 and CS_2 are heated together at 100° for two hours under 5 atm. pressure (Muthmann and Clever, Zeitsch. anorg. Chem. 1897, 13, 200).

Oxides and Oxyacids of Nitrogen.

Nitrous oxide. *Laughing gas*, N_2O. First obtained by Priestley in 1772, by the action of easily oxidisable substances, such as potassium sulphide or sulphite, on nitric oxide. NO is also reduced to N_2O by iron or zinc filings, or stannous chloride.

Nitrous acid and nitrites yield N_2O when reduced by platinum black, and by sodium amalgam.

Nitric acid and nitrates give N_2O among their reduction products with various reducing agents, especially from zinc and dilute nitric acid or a mixture of equal parts of nitric and sulphuric acids diluted with eight to ten parts of water.

It is usually supposed not to be formed by direct union, *v.*, however, method (6), *infra.* Warburg and Leithäuser (Sitzungsber. K. Akad. Wiss. Berlin, 1908, 148) find that Siemen's ozoniser gives N_2O and N_2O_5, and that the spark between platinum electrodes gives NO_2 and N_2O, the alternating arc at high potential in dry air giving only NO_2.

No combination between nitrogen and oxygen is effected under the influence of ultraviolet light (Berthelot and Gaudechon, Compt. rend. 1910, 150, 1517).

The best methods in practice are—

(1) Campari's method (Chem. Zentr. 1888, 1569), by heating to boiling a mixture of 5 parts stannous chloride, 10 parts hydrochloric acid of sp.gr. 1·21 and 0·9 parts of nitric acid of sp.gr. 1·38. These proportions should be adhered to, or the gas is liable to be evolved with explosive irregularity (*v.* also Gay Lussac, Ann. Chim. Phys. 1847, [iii.] 23, 229).

(2) By reduction of nitrous acid with hydrazine—

$$N_2H_4+HNO_2=NH_3+N_2O+H_2O$$

(Francke, Ber. 1905, 38, 4102).

(3) By decomposition of ammonium nitrate by heat; $NH_4NO_3=N_2O+2H_2O$. The decomposition begins at about 170°, and becomes explosive unless carefully regulated. Organic impurities must be absent, and also ammonium chloride, otherwise CO_2 and Cl_2 respectively are formed (Soubeiran, J. Pharm. Chim. 1826, 13, 332).

Lidoff (J. Russ. Phys. Chem. Soc. 1903, 35, 59) recommends mixing the nitrate with sand, and washing the gas with ferrous sulphate solution, afterwards drying it with an emulsion of ferrous sulphate in concentrated sulphuric acid.

(4) By Thilo's method (Chem. Zeit. 1894, 18, 532), patented in 1894. An equimolecular mixture of ammonium sulphate and sodium nitrate is heated at 240°. A regular and quiet evolution of nitrous oxide results.

(5) By the reaction between sodium nitrite and hydroxylamine hydrochloride solutions, NO being removed ferrous sulphate solution—

$$NH_2OH+HNO_2=N_2O+2H_2O$$

(Meyer, Pollak's modification, Annalen, 1875, 175, 141).

(6) Pictet (Fr. Pat. 415594, April 19, 1910) and Södermann (*ibid.* 411785, Jan. 21, 1910) obtain it from the nitrogen-oxygen flame, produced electrically or by other means, under suitable conditions. At a definite part of the flame, ascertained spectroscopically or in other ways, the chief product is N_2O, and by rapid and efficient cooling at this point the gas may be obtained in 25 p.c. yield.

Properties.—Nitrous oxide is a colourless gas with pleasant odour and sweetish taste. Density (air=1) 1·5301 (Leduc, Compt. rend. 1905, 140, 642), 1·5297 (Rayleigh, Proc. Roy. Soc. 1905, 74, 181). Weight of one litre 1·9774 grams (Guye and Pintza, Compt. rend. 1905, 141, 51), 1·9777 (Rayleigh), 1·9780 (Leduc).

Coeff. of expansion 0·0037067 (Jolly). For its volume-pressure relations, *v.* Rayleigh (Proc. Roy. Soc. 1905, 74, 406).

Viscosity coeff. 0·0001353 at 0°; 0·0001815 at 100° (Wüllner, Wied. Ann. 1876, 4, 321).

Refractive index for sodium light 1·00516. Magnetic rotation 16·02 (Becquerel, Compt. rend. 1880, 90, 1407; *v.* also Dufour, *ibid.* 1908, 147, 1471). Sp.ht. at const. vol. 0·15130 at 0°; 0·17384 at 100° (Wüllner, *l.c.*). Sp.ht. at const. press. 0·1983 at 0°; 0·2212 at 100° (Wiedermann, Pogg. Ann. 1875, 157, 1).

Cp./Cv.=1·31 at 0°; 1·2724 at 100°.

Heat conductivity 0·0000350 at 0°; 0·0000506 at 100°.

It is easily liquefied, and was first obtained in liquid form by Faraday (Phil. Trans. 1823, 189). It is colourless, mobile, and has a low refractive index (1·193 at 16°, according to Bleikrode, 1·3305 at 90°, according to Liveing and Dewar); b.p. −89·8° (Ramsay and Shields, Chem. News, 1893, 67, 190; −89·4° (Grunmach, Sitzungsber.

K. Akad. Wiss. Berlin. 1904, 1198); m.p. −102·3° (Ramsay and Shields, *l.c.*). Critical temp. and press. 36·4°, 73·07 atm. (Cailletet and Matthias); 35·4° and 75·0 atm. (Dewar, Phil. Mag. 1884, [v.] 18, 210).

Density at b.p. 1·2257 (Grunmach). Surface tension at 89·3°, 26·323 dynes/cm. Calculated molecular weights using the critical values given above are 43·26 and 43·78 respectively, hence N_2O has the same molecular weight in both states (Grunmach). The vapour pressures are tabulated by Regnault (J. 1863, 70) and Villard (Ann. Chim. Phys. 1897, [vii.] 10, 387).

For densities of liquid N_2O and its saturated vapour, *v.* Cailletet and Mathias (Compt. rend. 1886, 102, 1202 ; Villard (*ibid.* 1894, 118, 1096). Mol. heat of volatilisation 2900 cal. (−20°), 2600 (0°), 400 (35°) (Cailletet and Mathias, Ann. Chim. Phys. 1890, [vi.] 21, 69). Heat of formation −21,700 cal.

Solubility in water at	5°	10°	15°	20°	25°
	1·048	0·8778	0·7377	0·6294	0·5443

(Geffcken, Zeitsch. physikal. Chem. 1904, 49, 257).

Findlay and Creighton (Chem. Soc. Trans. 1910, 549) show that it obeys Henry's Law.

$$\text{At } 25^\circ \quad \frac{\text{Conc. liquid phase}}{\text{Conc. gaseous phase}}=0·592.$$

For its solubility in alcohol, *v.* Carius (Annalen, 1855, 94, 139).

Nitrous oxide is decomposed into its elements on strongly heating. This is shown by its power to support the combustion of phosphorus, carbon, sulphur, etc., when burning sufficiently vigorously to start the decomposition of the gas. At 500°, only about 1·5 p.c. is decomposed, but at 900° decomposition is practically complete. Hunter (Zeitsch. physikal. Chem. 1905, 53, 441) finds its decomposition to be mainly bi-molecular, $2N_2O=2N_2+O_2$, and gives the velocity coefficients at various temperatures. It also decomposes slightly under pressure. At 600 atm. and 420°, slight decomposition occurs with increase in volume (Briner and Wroczynski, Compt. rend. 1910, 150, 1324).

Mixed with oxygen and submitted to the action of ultra violet light it gives nitrogen and higher oxidation products (Berthelot and Gaudechon, Compt. rend. 1910, 150, 1517).

It is readily reduced by hydrogen on passing the mixed gases through a red-hot tube, or over platinum or palladium sponge. It is analysed by explosion with hydrogen (Hempel, Zeitsch. Elektrochem. 1906, 12, 600). The velocity of explosion is 2305 metres per sec. (Dixon, Chem. News, 1891, 64, 70). It oxidises a large number of metals and lower oxides, and reduced nickel brings about its reduction with hydrogen to water and nitrogen (Sabatier and Senderens, Compt. rend. 1902, 135, 278) Potassium and sodium, when slightly heated in the gas, form the peroxides, but when strongly heated produce the nitrates.

Nitrous oxide is a valuable anæsthetic for short operations. Prolonged inhalation causes death. Mixed with about one-fourth its volume of oxygen it produces an exhilarating and intoxicating effect. For a discussion of its preparation and requisite purity for use as an anæsthetic, *v.* Baskerville and Stevenson (J. Ind. Eng. Chem. 1911, 3, 579).

Hyponitrites may be regarded as salts of this oxide, though the acid is not formed by its solution in water. At low temperatures a solid hydrate $N_2O·6H_2O$ is formed (Villard, Ann. Chim. Phys. 1897, [vii.] 11, 289).

Nitric oxide NO differs from the other oxides in being neither an acid anhydride as N_2O,N_2O_3, and N_2O_5, nor a mixed anhydride, as N_2O_4. It was the first oxide of nitrogen investigated (Priestley, 1772).

It is usually said to be the first oxidation product of elementary nitrogen (*v.* however *Nitrous Oxide*) and is formed by direct union by a number of methods. It is produced together with ozone in the silent electric discharge, and has an inhibiting effect upon the formation of ozone (Manchot, Ber. 1908, 41, 471).

It is produced (also along with ozone) when air is slowly led over a glowing Nernst filament (Fischer and Marx, Ber. 1906, 39, 3631), and in various flames, *e.g.* C_2H_4, CO, and H_2, as well as in the electric arc, electric spark, and at white-hot solid surfaces (Haber and Coates, Zeitsch. physikal. Chem. 1909, 69, 337).

In the combustion of hydrogen in air at ordinary pressures, practically no nitric oxide is formed, but at 20 atm., 0·3 molecules of NO are produced for every 100 of water. With equal mixtures of N_2 and O_2, the yield though small at low pressures is as much as 3 mols. per 100 of water at 15 atm. (Wolokitin, Zeitsch. Elektrochem. 1910, 16, 814).

The conditions under which the union is most efficient have been studied by Haber and his co-workers (*v.* Haber and others, Zeitsch. Elektrochem, 1910, 16, 810, and earlier papers), Nernst and others. Briefly, a high temperature favours a rapid rate of formation, and a high yield of NO, but also favours dissociation. Hence rapid cooling is necessary at the moment of formation, which is realised by sweeping the gases out of the region of the arc, or by forming and interrupting the arc successively several thousand times a second, or by playing the arc in different regions of the space. The gases passing out of the chamber contain 1–2 p.c. of NO by volume. For practical details, *v.* NITROGEN, ATMOSPHERIC, UTILISATION OF.

Nitric oxide is also produced by the action of a variety of reducing agents upon nitric and nitrous acids and the higher oxides.

The most convenient methods are—

(1) Nitric acid of sp.gr. 1·2 on metallic copper.

$$3Cu+8HNO_3=3Cu(NO_3)_2+4H_2O+2NO$$
$$(3Cu+N_2O_5=3CuO+2NO)$$

(*v.* Kämmerer, Ber. 1885, 18, 3064).

(2) An alkaline nitrate on a solution of ferrous chloride in hydrochloric acid.

$$6FeCl_2+2NaNO_3+8HCl$$
$$=6FeCl_3+2NaCl+4H_2O+2NO$$

(Pelouze; Gay Lussac, Ann. Chim. Phys. 1847, [iii.] 23, 203).

(3) Deventer's method (Ber. 1893, 26, 589) of dropping a mixture of potassium nitrite and ferrocyanide into dilute acetic acid.

$$K_4Fe(CN)_6+HNO_2+CH_3COOH$$
$$=K_3Fe(CN)_6+H_2O+CH_3COOK+NO$$

(4) Aqueous ferric chloride on sodium nitrite.

$$FeCl_3+3NaNO_2=Fe(NO_2)_3+3NaCl$$

$$2Fe(NO_2)_3+3H_2O=2Fe(OH)_3+3NO_2+3NO.$$

If the $NaNO_2$ is placed under carbon disulphide and hydrated $FeCl_3$ in carbon disulphide suspension added, the NO_2 remains dissolved in the carbon disulphide (Matuschek, Chem. Zeit. 1905, 29, 31).

(5) SO_2 into warm HNO_3 of sp.gr. 1·15.

$$3SO_2+2HNO_3+2H_2O=2H_2SO_4+2NO$$

(Weber, Pogg. Ann. 1867, 130, 277).

Moser (Zeitsch. anal. Chem. 1911, 50, 401) considers the best methods are—

(*a*) Reduction of HNO_2 in H_2SO_4 with Hg.

(*b*) Reduction of HNO_2 with HI.

The gas is purified by absorption in concentrated ferrous sulphate solution, from which it is expelled again on gently heating. It is also absorbed by potassium permanganate or dichromate.

Properties.—Nitric oxide is a colourless gas, of density 1·0387 (Leduc, Compt. rend. 1893, 116, 322). Wt. of one litre at N.T.P. 1·3402 (Gray, Chem. Soc. Proc. 1903, 66; Guye and Davila, Compt. rend. 1905, 141, 826). Cp. 0·23175 (Regnault), Cp./Cv. 1·40. Coeff. of expansion (mean) between −140° and 0°, 0·0037074 (Adventowski, Bull. Acad. Sci. Cracow, 1909, 742). Viscosity coeff. 0·000168 (Meyer and Springmühl, Pogg. Ann. 1873, 148, 526).

Refractive index for white light 1·000303 (Dulong); for sodium light 1·000297 (Mascart, Zeitsch. physikal. Chem. 1891, 7, 25), 1·0002939 (Cuthbertson and Metcalfe, Proc. Roy. Soc. 1908, A, 80, 406).

Nitric oxide shows very little divergence from Boyle's law (Jacquerod and Schener, Compt. rend. 1905, 140, 1384). It is with difficulty condensed to a colourless liquid.

B.p.	M.p.	Crit. temp.	Crit. press.	Observer
−153·6°	−167·0°	−93·5°	71·2 atm.	Olzewski[1]
−150·2°	−160·6°	−92·9°	64·4 atm.	Adventowski

For b.pts. at pressures other than atmospheric, *v.* Olzewski (*l.c.*). V.p. at m.p. 168 mm.

The vapour pressure curve of the liquid would appear to indicate that polymerisation of the molecules takes place at very low temperatures. This is borne out by the high sp.gr. of the liquid at its b.p. (1·269) (Adventowski, *l.c.*).

Heat of formation of NO −21,575 cal. (Thomsen), −21,600 cal. (Berthelot, Compt. rend. 1874, 78, 162).

SOLUBILITY IN WATER.

°C.	Absorption coeff.	°C.	Absorption coeff.
0	0·07381	40	0·03507
5	0·06461	50	0·03152
10	0·05709	60	0·02954
15	0·05147	70	0·02810
20	0·04706	80	0·02700
25	0·04323	90	0·02648
30	0·04004	100	0·02628

(Winkler, Ber. 1901, 34, 1408; *v.* also Zeitsch. physikal. Chem. 1892, 9, 171).

It is more soluble (0·316 at 0°) in alcohol (Carius, Annalen, 1885, 94, 138). For its solubility in H_2SO_4, *v.* Lunge (Ber. 1885, 18, 1391); Tower (Zeitsch. anorg. Chem. 1906, 50, 382).

Nitric oxide is the most stable oxide of nitrogen. At 700° only 0·5 p.c. is dissociated into nitrogen and oxygen, and at 1000° only 3–4 p.c. The dynamics of the equilibrium have been studied by Muthmann and Hofer (Ber. 1903, 36, 438); Nernst (Zeitsch. anorg. Chem. 1906, 49, 213); Jellinek (*ibid.* 1906, 49, 229), and Brode (Zeitsch. Elektrochem, 1905, 11, 752).

At ordinary temperatures it combines with oxygen with production of ruddy fumes (*v.* Emich, Monatsh. 13, 86) characteristic of the peroxide, but at the temperature of liquid air the product is always nitrogen tetroxide, whatever the proportions taken, even if both the oxygen and nitrogen are in the gaseous state provided the temperature be below −110°. N_2O_3 is transformed by oxygen to N_2O_4 only above −100°, and N_2O_4 is reduced by NO to N_2O_3 at temperatures below −150° (Francesconi and Sciacca, Gazz. chim. ital. 1904, 34, i. 447). Nitric oxide may be reduced in a variety of ways, giving nitrogen, ammonia, and in a few instances nitrous oxide. Hydrogen sulphide and alkaline sulphides, sulphurous acid, and phosphine give N_2O largely. Metals reduced in hydrogen are readily oxidised at a low temperature with formation of nitrogen. Passed with hydrogen over nickel, ammonia and some nitrogen are produced (Sabatier and Senderens, Compt. rend. 1902, 135, 278). The reaction commences at 300° and then proceeds at 120°, the production of ammonia being almost quantitative (Neogi and Adhicány, Zeitsch. anorg. Chem. 1910, 69, 209).

With hydriodic acid, ammonia is produced. Stannous chloride gives hydroxylamine and ammonia (Chesnau, Compt. rend. 1899, 129, 100) and in alkaline solution hyponitrite as well. Chromous salts give ammonia in neutral solution, hydroxylamine in acid solution (Kohlschütter, Ber. 1904, 37, 3053). Alkaline pyrogallol reduces it to nitrous oxide (Oppenheimer, *ibid.* 1903, 36, 1744).

It also reacts with oxidising agents. H_2O_2 gives nitrous and nitric acids; PbO_2, Pb_3O_4, MnO_2, Ag_2O in water give nitrite; $KMnO_4$ gives nitrate; iodine nitric acid (Schönbein), ClO_2 gives N_2O_4, and hypochlorous acid nitric acid (Balard).

In the dry state it acts on many oxidising agents, forming nitrite and nitrate (Auden and Fowler, Chem. News, 1895, 72, 163). It gives N_2O_3 with N_2O_4 at low temperatures (*v.* under *Nitric trioxide*).

It is slowly decomposed by potash, forming KNO_2 and N_2 (*v.* also Emich, Monatsh. 1892, 13, 90), and according to Moser (Zeitsch. anal. Chem. 1911, 50, 401) it cannot be preserved unchanged over water, partly owing to dissolved oxygen, and partly to hydrions of the water

$$4NO+2H_2O=2HNO_2+H_2N_2O_2$$

(*cf.* Zimmermann, Monatsh. 1905, 26, 1277).

The latter gives N_2O, and also ammonium nitrite, $3H_2N_2O_2=2N_2O_3+2NH_3$ (*cf.* Hantzsch and Kauffmann, Annalen, 1896, 292, 317), which further breaks down giving nitrogen in increasing quantity with the length of time the

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[1] Compt. rend. 1885, 100, 940.

gas remains over water. The moist gas can, however, be preserved unchanged over mercury.

Fluorine gives NO_2F (*q.v.*); iodine does not react; chlorine and bromine give the corresponding halide (*v.* under *Nitrous acid*).

If allowed to remain at high pressures in a sealed tube it becomes bluish green, and drops of blue liquid appear, first noticed at about 28 atms. If hydrochloric acid be also present, NOCl is formed, the change being probably represented by

$$6NO = 2N_2O_3 + N_2$$
$$N_2O_3 + 2HCl = 2NOCl + H_2O$$

(Briner and Wroczynski, Compt. rend. 1909, 149, 1372).

It is absorbed by a number of acids and salts, forming compounds of whose constitution little is known, which break down again on dilution with water, or gently heating.

H_2SO_4 in presence of oxygen yields

$$NO{\cdot}OSO_3H$$

(Lunge, Ber. 1885, 18, 1384).

It reacts with nitric acid (*v.* Saposhnikoff, J. Russ. Phys. Chem. Soc. 1901, 33, 506, and under HNO_3) and is absorbed by phosphoric acid (Reinsch, J. pr. Chem. 1843, 28, 385), arsenic, and some organic acids, and by many halides, such as those of B, Si, Bi, Fe, Cu (for example $BiCl_3{\cdot}NO$; $2FeCl_3{\cdot}NO$) (Besson, Compt. rend. 1889, 108, 1012; Thomas, Ann. Chim. Phys. 1898, [vii.] 13, 145). $FeSO_4$ gives the compound $FeSO_4{\cdot}NO$ (Manchot and Zechentmayer, Annalen, 1906, 350, 368; *v.* Hûfner, Zeitsch. physikal. Chem. 1907, 59, 416; Asher, *ibid.* 1908, 62, 622) which has been isolated in red leaflets (Manchot and Huttner, Annalen, 1910, 372, 153). Conductivity of NO in $FeSO_4$ solutions (Zimmermann, Monatsh. 1905, 26, 1277). It combines with Ni, Co and Mn sulphates (*v.* Hûfner, *l.c.*; Asher, *l.c.*).

$Fe_2(SO_4)_3{\cdot}NO$ is formed from ferric sulphate in 90 p.c. H_2SO_4 solution (Manchot, Zeitsch. physikal. Chem. 1910, 372, 179).

The violet colouration produced by NO in solutions of $CuSO_4$ in concentrated H_2SO_4 is due to the formation of an easily dissociated compound $CuSO_4{\cdot}NO$ (Manchot, Annalen, 1900, 375, 308).

A number of other iron-nitric oxide-sulphur derivatives of uncertain constitution are described by Hofmann and Wrede (Zeitsch. anorg. Chem. 1896, 11, 288, and previous references), Marie and Marquis (Compt. rend. 1896, 122, 137), Bellucci and Venditori (Atti. R. Accad. Lincei. 1905, [v.] 14, i. 98), Manchot (Zeitsch. angew. Chem. 1911, 24, 13) and Raschig (*ibid.* 160).

Complex cyanogen compounds are described by Miolatti (Zeitsch. anorg. Chem. 1900, 25, 318); complex nitrates and chlorides of the type $Co(NH_3)_5(NO)X_2$ by Sand and Singer (Annalen, 1903, 329, 190) and other complex amines containing NO by Werner.

Nitrogen trioxide, *Nitrous anhydride*, N_2O_3. When nitric oxide and nitrogen peroxide are mixed, or when half the corresponding atomic proportion of oxygen is added to nitric oxide a gas of the composition N_2O_3 is obtained which condenses to a liquid and solid of the same composition. In the two latter states it behaves as a homogeneous body N_2O_3, and chemically as such at higher temperatures, but physically as an equimolecular mixture of NO and N_2O_4, the third component N_2O_3 being present only in minimum quantity.

Preparation.—(1) By reduction of nitric acid of suitable concentration by a reducing agent, usually starch or As_4O_6. According to Lunge (Ber. 1878, 11, 1229), acid of sp.gr. 1·20 gives NO, acid of sp.gr. 1·35 N_2O_3, and sp.gr. 1·5 practically all NO_2. As, however, the product varies with the concentration, obviously a pure compound cannot be obtained, as the concentration is changing throughout the experiment, and Ramsay and Cundall (Chem. Soc. Trans. 1885, 187) recommend acid of initial concentration 1·5 as the most suitable. The arsenious oxide and nitric acid are carefully heated on the water bath in a large retort or distilling flask. The action is apt to become very violent. The gas is dried over solid calcium chloride and liquefied by ice and salt. If N_2O_4 is in excess a bluish-green liquid results, which, on volatilising in a current of NO and recondensing, yields an indigo blue liquid at −10°. Its ready dissociation into NO and N_2O_4, the former of which is only liquid at −165°, the latter easily condensable, renders the removal of the last traces of N_2O_4 exceedingly difficult.

(2) By oxidation of nitric oxide with oxygen. At temperatures below −100° the product from any proportions of these gases is always N_2O_3 (*v.* under *Nitric oxide*).

(3) By oxidation of liquid nitrogen bypassing electric discharges through liquid air. So formed it remains suspended in the liquid air as a flocculent green substance, strongly resembling precipitated chromic hydroxide, but on evaporation of the excess of air is left as a slightly blue amorphous powder, which melts at −111°, and then assumes a deep blue colour which persists after resolidification in liquid air (Helbig, Atti. R. Accad. Lincei. 1903, [v.] 12, i. 166; Fischer and Braemar, Ber. 1906, 39, 940). According to Scarpa (Gazz. chim. ital. 1907, 37, ii. 185), NO is formed in the region of the arc, and in the boiling air combines further with oxygen, giving N_2O_3, which under favourable conditions may be complete, since N_2O_3 is solid at temperatures lower than the critical dissociation temperature. The best form of apparatus is described.

(4) By reduction of N_2O_4 by NO (Péligot, Ann. Chim. Phys. 1841, [iii.] 2, 58; Porschnew, Zeitsch. anorg. Chem. 1894, 7, 214). On saturating liquid N_2O_4 with NO and subsequently cooling dark blue crystals of N_2O_3 separate, m.p. −103°, no other compound being formed. The eutectic mixture (63·6 N_2O_4, 36·4 NO), melts at −112° (Wittorff, J. Russ. Phys. Chem. Soc. 1904, 36, 857).

N_2O_3 is also produced by action of water on lead chamber crystals, and on nitrogen peroxide.

Properties.—N_2O_3, at ordinary temperatures, gives a brown gas which has a density corresponding to a mixture of NO and NO_2, allowing for polymerisation of the latter (Ramsay and Cundall, Chem. Soc. Trans. 1890, 37, 590; Porschnew, *l.c.*), borne out by the fact that the spectra of NO_2 and gaseous N_2O_3 are identical (Moser, Wied. Ann. 1877, 2, 139), while the blue liquid has no definite b.p. At −21°, however, its composition is very closely N_2O_3 (Francesconi and Sciacca, Gazz. chim. ital. 1904, 34, 1, 447).

M.p. −103° (Wittorff), −111° (Helbig); sp.gr. at 0° 1·4490 (Geuther, Annalen, 1888, 245, 96).

The discovery that dissociation of ammonium chloride and other substances does not take place in complete absence of moisture led to a similar investigation of N_2O_3 (Baker and Baker, Chem. Soc. Trans. 1907, 1862). Bulbs containing known weights of the carefully prepared and dried liquid were broken in a Lunge nitrometer over dry mercury (which is practically unaffected), and the densities so found varied from 43·2–48·6, that of undissociated N_2O_3 being 38. On admitting concentrated H_2SO_4 absorption took place so rapidly that the impact of the mercury endangered the tube, whereas a mixture of NO and N_2O_4 is only comparatively slowly absorbed. Further determinations with a special V. Meyer apparatus (*ibid.* 1900, 647) varied from 38·1 to 62·2, the samples being taken from several preparations which had been condensed at different temperatures and dried for varying lengths of time, and containing varying proportions of the polymeric N_4O_6, which, however, was not obtained in the pure condition.

In the hope that in solution at low temperatures the higher polymeride would be present in greater amount, molecular weight determinations were made in benzene solution, but the values obtained were 83, 83·2, and 95, showing this not to be the case. N_2O_3 is without action on benzene.

As usually prepared it mixes with water, giving a blue-green liquid which above 0°, by further concentration, evolves NO, and on dilution gives nitrous acid; but according to Baker it is practically insoluble in water and sinks, forming NO and N_2O_4, the latter dissolving in the water.

With concentrated H_2SO_4, *nitrosylsulphuric acid* (*q.v.*) is formed.

Oxygen is without action below −110°. Above −100° it is converted into N_2O_4 (*v.* under NO). As an oxidising agent on metals it behaves as a mixture of NO and NO_2, NO being formed at low temperatures, and N_2 at higher temperatures. Like N_2O_4 it is absorbed by alkalis, but more rapidly, and it is supposed that it is the N_2O_3 in the equilibrium

$$NO+NO_2 \rightleftarrows N_2O_3$$

which is absorbed (*cf.* le Blanc, Zeitsch. Elektrochem. 1906, 12, 544). This is borne out by the fact that liquid N_2O_3 at −22° is instantly absorbed by NaOH, whereas liquid N_2O_4 reacts only slowly (Foerster and Blich, Zeitsch. angew. Chem. 1910, 23, 2017).

Its solution in carbon tetrachloride reacts with one of SO_3 precipitating *sulphonitrous anhydride* $(SO_3)_3(N_2O_3)_2$ in needles, m.p. 190°–200°; b.p. 302°–305°/728 mm. Hence Provostaye's *nitrosyl sulphate* (Ann. Chim. Phys. 1840, [ii.] 73, 362), m.p. 217°–230°; b.p. 360° is therefore of greater complexity than $(SO_3)_2N_2O_3$, probably $(SO_3)_6(N_2O_3)_3$. The *tetrasulphate* is also known (Pictet and Karl, Bull. Soc. chim. 1908, [iv.] 3, 1114).

Nitrosyl perchlorate $NO{\cdot}OClO_3{\cdot}H_2O$ separates in leaflets when N_2O_3 is passed into concentrated perchloric acid (Hofmann and Ledtwitz, Ber. 1909, 42, 2031). With unsaturated carbon compounds it forms additive compounds.

Nitrogen peroxide, or **tetroxide** ("hyponitric acid"). This oxide is only capable of existing as NO_2 in a pure condition within narrow limits of temperature. At low temperatures the polymerised product N_2O_4 is the stable form, which dissociates on rise of temperature into NO_2, but this in turn is easily dissociated on further rise of temperature into NO and oxygen.

Preparation.—It is produced by oxidation of nitric oxide with oxygen, as first shown by Gay Lussac, and thus results on oxidation of nitrogen with excess of oxygen under ordinary conditions. NO and O_2 in the proportion 2 : 1, dried and well mixed by passing through a tube filled with glass or porcelain fragments, condense at −20° to a colourless crystalline mass of N_2O_4 (Dulong, Ann. Chim. Phys. 1816, [ii.] 2, 317; Péligot, *ibid.* 1841, [iii.] 2, 58). Similarly the gas resulting from the action of concentrated nitric acid on arsenious oxide is converted by excess of oxygen into N_2O_4.

Mandl and Russ (Zeitsch. angew. Chem. 1908, 21, 486) state that the rate and extent of union of NO and O_2 is affected by the character of the oxygen; for example, electrolytic oxygen is more active after passing over heated palladium, and ozonisation retards the action. According to Holwech (*ibid.* 2131), however, this is not the case, union being practically complete in each instance, and the velocity of reaction the same with oxygen from all sources.

A good yield of NO_2 is said to be obtained by passing air and steam through a thin-walled porous porcelain tube at 1600°, the diffusion of the hydrogen formed being increased by raising the inside pressure and lowering that outside the tube (Westdeutsche Thomasphosphatwerke, D. R. P. 182297).

It is also obtained by passing nitric acid vapour through a hot tube, and by heating metallic nitrates,

$$Pb(NO_3)_2=PbO+O+2NO_2.$$

Those of the alkalis evolve NO_2 when electrolysed in the fused condition (Bogorodski, J. Russ. Phys. Chem. Soc. 1905, 37, 703). It is formed by union of N_2O_3 and N_2O_5. Also by treating with fuming sulphuric acid a homogeneous mixture of alkali nitrate and nitrite, made by fusing the salts together or pouring the fused mixture into carbon tetrachloride.

$$NaNO_2+NaNO_3+H_2S_2O_7=2NaHSO_4+2NO_2.$$

Sufficient $NaHSO_4$ from a previous preparation is added to fix any free SO_3 present—

$$2NaHSO_4+SO_3=Na_2S_2O_7+H_2SO_4$$

(Winans, D. R. P. 193696).

It is evolved on warming chamber crystals with KNO_3, thus:

$$NO_2{\cdot}SO_3H+KNO_3=2NO_2+KHSO_4,$$

and by the action of nitric acid on nitrous acid or a nitrite—

$$HNO_3+R{\cdot}NO_2=R{\cdot}OH+2N_2O_2$$

(Girard and Pabst, Bull. Soc. chim. 1878, [ii.] 30, 531).

Properties.—At ordinary temperatures an orange-coloured corrosive gas of peculiar and unpleasant odour. At higher temperatures it becomes much darker in colour, turning lighter again on further rise, and finally colourless when dissociation into NO and oxygen is complete. It condenses to an orange-yellow liquid, b.p. 25°–26° (Hasenbach; Bruni and Berti, Atti. R. Accad. Lincei, 1900, [v.] 9, i. 321). At 10° it is pale yellow, and when solid colourless. M.p. −10·1° (Ramsay, Zeitsch. physikal. Chem. 1890, 5, 221), −10·95° (Bruni and Berti, *l.c.*). Critical temperature 171·2°; critical pressure 0·66 atmospheres.

In the solid state it probably exists entirely as N_2O_4, and almost entirely so in the liquid state, though not ascertained by experiment. In the gaseous state and in solution, however, its behaviour is accurately known from its vapour density measurements, which are in accord with the conclusions drawn from other physical properties, such as absorption of light, conductivity for heat, and specific heat.

The liquid is not polymerised further than N_2O_4 nor is the gas, as shown by its molecular weight in acetic acid (Ramsay and Shields, *ibid.* 1893, 12, 433; Ramsay, Chem. Soc. Trans. 1888, 53, 621).

Its further dissociation into nitric oxide and oxygen is accurately known from its density.

	−5°	−2°	0°	5°	10°	15°
Sp.gr.	1·5035	1·5020	1·4935	1·4880	1·4770	1·4740

(Geuther, Annalen, 1888, 245, 96). At +1°, 1·4903; at 21·6°, 1·4396 (Thorpe, Chem. Soc. Trans. 1880, 37, 141).

Thorpe finds the expansion of liquid N_2O_4 to be very regular, 1 vol. at 0° becoming at

5°	10°	15°	20°
1·00789	1·01573	1·02370	1·03196

The vapour densities found by various observers have been collected by Schreber (Zeitsch. physikal. Chem. 1897, 24, 651), and the dissociation constants calculated. The following values of $K=[N_2O_4]^{\frac{1}{2}}/[NO_2]$ are given—

$t°$	K
0·0	8·060
18·3	3·710
49·9	1·116
73·6	0·544
99·8	0·273

At 64° one-half of the N_2O_4 mols. are dissociated, and at 150° they are wholly dissociated (*v.* also Bodenstein and Katayama, Zeitsch. Elektrochem. 1909, 15, 244). Above 150° decomposition into NO and oxygen takes place, and at 620° is practically complete. At 184°, 5 p.c. is dissociated, and at 494° 56·5 p.c. (Richardson, Chem. Soc. Trans. 1887, 51, 397). Sp.ht. of liquid 0·477° (Ramsay, Zeitsch. physikal. Chem. 1890, 5, 221).

Apparently anomalous values, obtained by Berthelot and Ogier (Ann. Chim. Phys. 1883, 30, 382) for the sp.ht. of the gas, are explainable by its dissociation (Swart, Zeitsch. physikal. Chem. 1891, 7, 120).

Heat of formation $2N+4O=N_2O_4$ −3900 cal. (Thomsen) (9 p.c. NO_2, 91 p.c. N_2O_4). Heat of dissociation about −13,000 cal., and calculated heat of formation of undissociated N_2O_4 −2650, and of NO_2 −8125 cal. Heat of formation of liquid −2200 and −2500 cal. (for NO_2 = 46 gr.) (Berthelot, Ann. Chim. Phys. 1875, [v.] 6, 145); heat of vaporisation at 180° −4300 cal. Latent heat of fusion −32·2 to −37·2 cal.; calculated from freezing-point lowering, −33·7 (Ramsay, *l.c.*).

The heat conductivity values also reveal its dissociation (Feliciani, Chem. Zentr. 1905, i. 331). At 150°, the conductivity of NO_2 is 0·0033.

Refraction equivalent of liquid 11·8, dispersion equivalent 0·82 (Gladstone, Chem. News, 1887, 55, 300). Refractive index of vapour at 36°, 1·000503 (Dulong; *v.* Zeitsch. physikal. Chem. 1901, 36, 332). For the spectra of nitrogen peroxide, *v.* Bell (Amer. Chem. J. 1885, 7, 32). The vapour does not conduct electricity, and the liquid only slightly.

Dielectric constant (*v.* Bädeker, Zeitsch. physikal. Chem. 1901, 36, 305).

Chemical properties.—It is reduced to ammonia if passed with hydrogen over platinum black (Kuhlmann, Annalen, 1839, 29, 272), or over reduced nickel or copper (Sabatier and Senderens, Compt. rend. 1902, 135, 278). Carbon, sulphur and phosphorus burn in the gas, carbon monoxide burns to CO_2, and hydrogen sulphide to sulphur, with formation of NO.

Potassium burns with a red flame, and sodium, though not igniting, decomposes the gas at the ordinary temperature, while many metals and lower oxides are oxidised on heating to 500°, and some metals form additive compounds ("nitro metals") with the liquid N_2O_4 (Cu_2NO_2,Ni_4NO_2) similar to the carbonyl compounds (Sabatier and Senderens, Ann. Chim. Phys. 1896, [vii.] 7, 348). Other metals, such as K, Na, Hg, Pb, form the nitrate with production of NO. It also forms additive compounds with many metallic salts ($FeCl_3{\cdot}NO_2$, $SnCl_4{\cdot}NO_2$, etc.) (Thomas, *ibid.* 1898, [vii.] 13, 145) and with unsaturated organic compounds (nitrosates).

With water N_2O_4 exhibits its mixed anhydride character. With small quantities of water, however, the reaction

$$2N_2O_4+H_2O=N_2O_3+2HNO_3$$

takes place at low temperatures, two layers being formed, the lower, deep blue N_2O_3. Further dilution converts the nitrous anhydride to nitrous acid, which on rise of temperature is decomposed with evolution of NO (Schönhein, Pogg. Ann. 1848, 73, 326).

With aqueous alkalis, a mixture of nitrite and nitrate is formed (*v.* also under N_2O_3). Metallic oxides under pressure form the nitrate only, evolving NO. BaO, however, according to Dulong, forms a mixture of nitrite and nitrate at 200° (Annalen, 1862, 122, 18).

Liquid ammonia reacts explosively with solid N_2O_4 at −80°, but a current of gaseous NH_3 led over the solid at −20° reacts less vigorously, and the products are N_2, NO, H_2O, NH_4NO_3 and a trace of NH_4NO_2 (Besson and Rosset, Compt. rend. 1906, 142, 633). Dry oxygen does not oxidise it, but ozone converts it to the pentoxide. In presence of water, oxygen and oxidising agents convert it into nitric acid. It is absorbed by dilute and concentrated HNO_3 (*v.* Weber, Pogg. Ann. 1867, 130, 277; Lunge, Ber. 1879, 12, 1058). With SO_2 and SO_3 it gives various substances of not very clearly defined character (Weber, *l.c.*; Hasenbach, J. pr. Chem. 1871, [ii.] 4, 4; Friedburg, Chem.

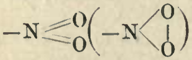
News, 1883, 47, 52). With sulphuric acid it forms *nitrosyl-sulphuric* and *nitric acids.*

$$H_2SO_4+N_2O_4=NO_2{\cdot}SO_3H+HNO_3$$

Lunge (Ber. 12, 357).

It has been used as a solvent for cryoscopic measurements. Molecular raising of b.p. 13·7°, molecular lowering of freezing point 41° (Ramsay, Zeitsch. physikal. Chem. 1890, 5, 221; Frankland and Farmer, Chem. Soc. Trans. 1901, 79, 1356; Bruni and Berti, Gazz. chim. ital. 1900, 30, ii. 151). The liquid has been used in explosives (Settlick, Chem. Zentr. 1888, 461).

Constitution.—The formula of the dioxide may be written—



$$-N{<}^{O}_{O}\left(-N{<}^{O}_{O}\right)\text{ and }-O-N=O$$

and that of the tetroxide—

$O_2{\equiv}N{-}N{\equiv}O_2$, $O_2{\equiv}N{-}O{-}N{=}O$, $O{=}N{-}O{-}N{=}O$. The reaction with water favours the second of these. Piloty and Schwerin (Ber. 1901, 34, 1884 and 2354) suggest $O{=}N{=}O$ as the formula for the dioxide; but Divers (Chem. Soc. Trans. 1904, 110) prefers the formula $O{-}N{=}O$ for the dioxide, and for N_2O_4 advances reasons in favour of the formula $(NO)_2O_2$, "di-nitric peroxide."

iso-Nitrogen tetroxide.—According to Raschig (Chem. Zeit. 1907, 31, 359), the red vapours formed from nitric oxide and air are of different composition from that usually accepted, the first product being *iso*-nitrogen tetroxide (*a*) distinguished from the ordinary tetroxide (*b*) by its reaction with sodium hydroxide—

(*a*) $N_2O_4+2NaOH=2NaNO_2+H_2O+O$

(*b*) $N_2O_4+2NaOH=NaNO_2+NaNO_3+H_2O$.

With larger excess of oxygen the *iso-pentoxide* and a *hexoxide* and *heptoxide* are said to be formed—

$N_2O_5+2NaOH=NaNO_2+NaNO_3+H_2O+O$.
$N_2O_6+2NaOH=2NaNO_2+H_2O+3O$.
$N_2O_7+2NaOH=NaNO_2+NaNO_3+H_2O+3O$.

Nitrogen pentoxide, *nitric anhydride* N_2O_5, may be prepared as follows:—

(1) By oxidation of nitrogen peroxide with ozone (Helbig, Atti. R. Accad. Lincei, 1903, [v.] 12, i. 211; Zeitsch. Elektrochem. 1906, 12, 550).

(2) As first prepared by Deville (Ann. Chim. Phys. 1849, [iii.] 28, 241) by action of dry chlorine on silver nitrate warmed to 50°–60°.

$$4AgNO_3+2Cl_2=4AgCl+O_2+2N_2O_5,$$

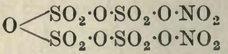
the gaseous product being condensed in a freezing mixture.

(3) Most conveniently, as first obtained by Weber, by dehydration of pure nitric acid with phosphorus pentoxide, with constant cooling (Meyer, Ber. 1889, 22, 23).

The syrupy liquid produced is poured into a dry retort and distilled into a receiver surrounded by a freezing mixture. The orange-red distillate separates into two layers, the upper of which is poured into a separating funnel and cooled in ice. The crystals formed are drained, again melted and crystallised and drained from the mother liquor.

After recrystallisation it is obtained in white glistening rhombic crystals, sp.gr. 1·63, m.p. 29·5 (Berthelot, Bull. Soc. chim. 1874, [ii.] 21, 53). It boils with decomposition into N_2O_4 and oxygen at about 45°. It darkens in colour on rise of temperature, the crystals becoming yellow some time before melting, at which point it is orange coloured, further turning dark-brown as the temperature rises. Calculated molecular heat of fusion −8280 cal., and heat of evaporation −4840 cal. Heat of formation of solid N_2O_5 13,100 cal. (Berthelot, Ann. Chim. Phys. 1875, [v.] 6, 202). Hence heat of formation of gaseous N_2O_5 is practically nil. Heat evolved with one molecule of water, 2300 cal. Heat of solution in excess of water 16,200 cal. (Berthelot, *l.c.*).

N_2O_5 dissolves in water giving nitric acid. It has no action on carbon or metals. It is useful as a nitrating agent. For this purpose, Gibson (Proc. Roy. Soc. Edin. 1908, 28, 705) gives details for making large quantities. It dissolves in freshly distilled and fused sulphur trioxide, giving a practically pure product in almost theoretical yield, b.p. 218°–220°; m.p. 124°–128°, which is also obtained as a crystalline precipitate on mixing carbon tetrachloride solutions. Its formula is $(SO_3)_4{\cdot}N_2O_5$, and its probable constitution—



$$O{<}^{SO_2\cdot O\cdot SO_2\cdot O\cdot NO_2}_{SO_2\cdot O\cdot SO_2\cdot O\cdot NO_2}$$

(Pictet and Karl, Compt. rend. 1907, 145, 238).

Nitrogen hexoxide.—Hautefeuille and Chappuis observed a characteristic absorption spectrum during the passage of a silent electric discharge in air (Compt. rend. 92, 80; 94, 946, 1306). Warburg and Leithäuser (Sitzungsber. Akad. Wiss. Berlin, 1907, 229) observed the same from ozone and N_2O_5 at 0°–18°. It exists only in presence of ozone. It is suggested that is due to a higher oxide, probably N_2O_6.

Nitrous acid HNO_2. Nitrous anhydride dissolves in excess of ice-cold water with production of this acid. The solution, however, is extremely unstable, and the acid itself has never been isolated, but its metallic and ethereal salts are comparatively stable.

Nitrites are found to some extent in nature, and occur in the juices of certain plants. Their universal presence in air has been shown by Schönbein (Chem. News, 1862, 241), Warington (Chem. Soc. Trans. 1881, 220), and Hayhurst and Pring (*v.* under NITROGEN).

All nitrites are soluble in water, and the majority dissolve in alcohol.

Preparation.—Alkali and alkaline earth hydroxides and carbonates absorb N_2O_4 and N_2O_3, in the first case, giving a mixture of nitrite and nitrate, and in the second case, if NO be present in slight excess practically pure nitrite (Divers, Chem. Soc. Trans. 1899, 75, 85). On the commercial scale, the nitrous fumes electrically produced from the air are kept at 300° until absorbed, whereby oxidation of the NO only proceeds as far as N_2O_3 and on absorption (in strong nitrite solutions, which have low vapour tensions), pure nitrite is produced (Badische Anilin u. Soda Fabrik, D. R. P. 188188).

Nitrites are obtained by reduction of nitrates, and also by oxidation of nitrogen compounds richer in hydrogen.

Many nitrates are reduced to nitrites by fusing with lead, copper, carbon (Fischer, Pogg. Ann. 1848, 74, 115), sulphites (Etard, Bull. Soc. chim. 1877, [ii.] 27, 434), sulphides (Roy, Compt. rend. 1889, 108, 1251), and in solution by reduction with Na, K, Ca and other metals (Schönbein, J. pr. Chem. 1868, 105, 206), and further by electrolytic reduction, the conditions for which have been worked out by Müller and Weber (Zeitsch. Elektrochem. 1903, 9, 955, 978) and Müller and Spitzer (*ibid.* 1905, 11, 917). Silver is found to be the best cathode, reduction to nitrite being almost complete before further reduction to ammonia takes place. Using a copper anode the yield is almost quantitative.

Nitrites are also produced by oxidation of ammonia with hydrogen peroxide (Weith and Weber, Ber. 1874, 7, 1745; Hoppe-Seyler, *ibid.* 1883, 16, 1917).

Schönbein has shown that copper is oxidised when immersed in aqueous ammonia in contact with air, whilst the ammonia is at the same time oxidised to nitrite, and Traube and Biltz (Ber. 1904, 37, 3130; 1906, 39, 166) have studied the electrolytic oxidation of aqueous NaOH containing ammonia, in presence of copper hydroxide as catalyser. With a current strength of 5–15 amperes and platinum or iron electrodes, practically the whole of the anode oxygen is used up in converting the ammonia present into nitrite. The final product is nitrate.

Properties.—Though very unstable in solution it is chemically a fairly strong acid, about 20 times as strong as acetic acid. It is slowly displaced from solutions of its salts by carbon dioxide (Moore, J. Amer. Chem. Soc. 1904, 26, 959).

Conductivities at dilutions of 512, 1024, and 1536, are 150·7, 189, and 217·0 respectively (Schumann, Ber. 1900, 33, 527). Calculated velocity of nitrite ion 64·5 (Pick finds 63 from $AgNO_2$, and Vogel (Zeitsch, anorg. Chem. 1903, 35, 385) 61·7 from $Ba(NO_2)_2$), and dissociation constant 0·00045. Bauer (Zeitsch. physikal. Chem. 1902, 41, 681) finds 0·00064.

Heat of neutralisation (with baryta) 10,600 cal. (with ammonia) 9100 cal. (Berthelot, Ann. Chim. Phys. 1875, [v.] 6, 145).

Heat of formation

$$N+O_2+H+Aq=HNO_2+30,770 \text{ cal.}$$

The aqueous solution on warming evolves NO leaving nitric acid

$$3HNO_2=HNO_3+2NO+H_2O,$$

this decomposition proceeding in the cold in presence of rough surfaces (sand, glass fragments, &c.). For the dynamics of the equilibrium, *v.* Saposhnikoff (J. Russ. Phys. Chem. Soc. 1901, 33, 506), Lewis and Edgar (J. Amer. Chem. Soc. 1911, 33, 292), and of the decomposition of silver nitrite, Abegg and Pick (Zeitsch. anorg. Chem. 1906, 51, 1).

It is completely oxidised to nitric acid by the usual oxidising agents. Its oxidation by hydrogen peroxide and subsequent precipitation with 'nitron' acetate is recommended by Busch (Ber. 1906, 39, 1401) as a good method of estimation. (For its detection and estimation, *v.* under ANALYSIS.)

It also behaves as an oxidising agent, being itself reduced to NO, $H_2N_2O_4$, N_2O, NH_2OH, or even further to N_2 and NH_3 by reducing agents such as stannous chloride, hydrogen sulphide, sodium amalgam (Divers, Chem. Soc. Trans. 1899, 75, 87), and by electrolytic reduction (Tanatar, Ber. 1896, 29, 1039).

The primary reduction product appears to be the radical NOM′, which gives hyponitrite by condensation, and hydroxylamine and ammonia by reduction (*v.* under *Hyponitrous Acid*).

With hydrazine the following quantitative reaction takes place—

$$N_2H_4+HNO_2=N_2O+NH_3+H_2O.$$

There is no evolution of nitrogen as Girard and Saporta (Bull. Soc. chim. 1904, [iii.] 31, 905) state (Francke, Ber. 1905, 38, 4102).

Constitution.—The molecular weight from cryoscopic measurements in aqueous solution is in accordance with the formula HNO_2 (Saposhnikoff, J. Russ. Phys. Chem. Soc. 1909, 41, 1704).

In most of its reactions its behaviour indicates the constitution $O{=}N{\cdot}OH$, but it may have the constitution $O_2{\equiv}N{\cdot}H$. The fact that many nitrites readily evolve NO_2 on heating, and give nitroparaffins with alkyl iodides, would suggest the latter to be correct (Divers, Chem. Soc. Trans. 1885, 47, 205; Kieseritzky, Zeitsch. physikal. Chem. 1899, 28, 421). As, however, alkyl nitrite is also produced in yield which varies with the alkyl iodide used, this latter reaction affords no definite clue to its constitution.

Ley, on the other hand, shows that mercurous nitrite exists in solution as an oxy salt (Ber. 1899, 32, 1357), and the reduction of nitrous acid to hyponitrous acid also points to an oxy-structure.

ACID HALIDES OF NITROUS ACID.

Nitrosyl fluoride NOF is prepared by the action of nitrosyl chloride on silver fluoride. A small flask containing NOCl cooled to −5° is attached to one end of a long platinum tube containing the silver fluoride, and kept at 200°–250°, and the NOCl slowly distilled through. The product is condensed in a small platinum flask cooled in liquid air, and on fractionation gives a colourless gas, b.p. −56°, m.p. −134°. In the cold, silicon, boron, red phosphorus, and sodium take fire in the gas, and antimony is at once acted on, the fluoride and nitric oxide being formed. Lead, aluminium, bismuth, and copper are slowly attacked, but iodine, sulphur and carbon do not react even on heating. Brown fumes are produced in moist air and with water, hydrofluoric and nitrous acids being formed. Its analysis and vapour density (1·683 air=1) are in agreement with the formula NOF. It closely resembles *nitryl fluoride* NO_2F (*q.v.*) in chemical and physical properties, but differs from it in its behaviour towards water and iodine. It gives additive compounds with arsenic and antimony pentafluorides (Ruff and Stäuber, Zeitsch. anorg. Chem. 1905, 47, 190; Ruff, Stäuber, and Graf, *ibid.* 1908, 58, 325).

Nitrosyl chloride NOCl is obtained—

(1) By direct union of NO and chlorine (Gay Lussac, Ann. Chim. Phys. 1848, [iii.] 23, 203).

The best procedure is to pass a mixture of the dried gases in the proportion 2 : 1 over finely granulated animal charcoal at 40°–50°, under slight pressure (Francesconi and Bresciani, Atti. R. Accad. Lincei, 1903, [v.] 12, 1175).

Its formation at low temperatures has been studied by Boubnoff and Guye (J. Chim. Phys. 1911, 9, 290). After removing excess of NO at −160° to −150°, an excess of chlorine (3·4 p.e.) above that required for the formula NOCl always remains, but is expelled at −80°. Tilden and others have shown that no higher oxychloride exists, and this is confirmed by the liquidus curve, which, however, denotes the existence of a highly dissociative additive compound, probably $NOCl{\cdot}Cl_2$, at about −109°.

(2) By distillation of *aqua regia*.

(3) By distillation of potassium nitrite with phosphorus pentachloride.

(4) By heating nitrosyl sulphuric acid with sodium chloride.

$$NO_2{\cdot}SO_3H+NaCl=NOCl+NaHSO_4$$

(Tilden, Chem. Soc. Trans. 1874, 630, 852; Girard and Pabst, Bull. Soc. chim. 1878, [ii.] 30, 531).

(5) By action of nitrosamines on hydrochloric acid (Lachmann, Ber. 1900, 33, 1035).

(6) By action of hydrochloric acid on N_2O_4 (Müller, Annalen, 1862, 122, 1), and on N_2O_3 (*v.* Briner and Wroczynski, under *Nitric Oxide*).

(7) By action of NO on $FeCl_3$ (Thomas, Compt. rend. 1895, 120, 447).

Nitrosyl chloride is a ruby-red mobile liquid, b.p. −5·6°/751 mm., giving lemon-yellow crystals, m.p. −61° to −60°. Critical temperature 163°–164° (Francesconi and Bresciani, *l.c.*). Vapour density (2·29–2·32 at 10°) is in agreement with the formula NOCl. Sp.gr. of liquid 1·4165 at −12°; 1·4250 at −15°; 1·4330 at −18° (Geuther, Annalen, 1888, 245, 96).

It is fairly stable towards heat, dissociation being first measurable at 700° (Sudborough and Miller, Chem. News, 1890, 62, 1307).

With water it at once gives nitrous and hydrochloric acids, and with metallic oxides forms the nitrite and chloride of the metal (Sudborough, Chem. Soc. Trans. 1891, 59, 655).

It forms double compounds with many metallic chlorides, some of which decompose on heating, evolving NO

$$CuCl{\cdot}NOCl \rightarrow CuCl_2+NO$$

while others are stable and may be sublimed *e.g.* —$AuCl_2{\cdot}NOCl$— and with unsaturated organic compounds forms addition products like N_2O_3 and N_2O_4.

With amines nitrogen is evolved and the chloride formed

$$R{\cdot}NH_2+NOCl=RCl+N_2+H_2O$$

(Solonina, J. Russ. Phys. Chem. Soc. 1898, 30, 431). For its action on mercaptans, *v.* Tasker and Jones (Chem. Soc. Trans. 1909, 1910).

Absorption spectrum (*v.* Magnanini, Zeitsch. physikal. Chem. 1889, 4, 427).

Sulphur trioxide forms *nitrosyl sulphonic chloride* $NO_2{\cdot}SO_2Cl$.

Nitrosyl bromide NOBr is obtained as a dark-brown liquid (1) by direct union of NO and bromine at −7° to −15° (Laudolt, Annalen, 1861, 116, 177); (2) by action of NaBr on $NO_2{\cdot}SO_3H$ (Girard and Pabet, *l.c.*).

It boils at −2° with dissociation, thus differing from the chloride, which it resembles in its chemical properties.

Landolt's *dibromide* $NOBr_2$ and Muir's *tribromide* $NOBr_3$ are mixtures of the monobromide with bromine (Frölich, Annalen, 1884, 224, 270).

The corresponding iodine compound has not been isolated.

Reaction of Nitrous and Sulphurous Acids.

The following equations represent the changes which occur—

(1) $HNO_2+H_2SO_3=[NO{\cdot}SO_3H]$ nitrosulphonic acid (1);

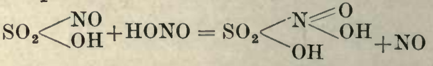
(2) $HNO_2+2H_2SO_3=HO{\cdot}N(SO_3H)_2$ hydroxylamine disulphonic acid (2);

(3) $HNO_2+3H_2SO_3=N(SO_3H)_3$ nitrilo sulphonic acid (3).

The existence of (1) was postulated by Raschig, but has never been isolated, a mixture of equivalent quantities of the two acids giving a very unstable liquid, which by further action of nitrous acid gives—

Nitrosisulphonic acid $HO_2N{\cdot}SO_3H$, also obtained by Sabatier (Compt. rend. 1896, 123, 255) by reduction of nitrosylsulphuric acid.

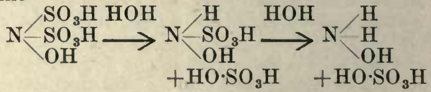
According to Raschig (Zeitsch. angew. Chem. 1905, 18, 1281) its formation and constitution are represented as follows—



$$SO_2\begin{array}{l}\diagup NO\\ \diagdown OH\end{array}+HONO=SO_2\begin{array}{l}\diagup N\begin{array}{l}\diagup\!\!\diagup O\\ \diagdown OH\end{array}\\ \diagdown OH\end{array}+NO$$

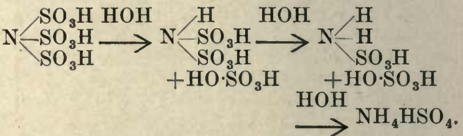
v. also Lunge and Berl (*ibid.* 1906, 19, 808, 857, and 881). The solution of the free acid, and of the copper salt, is blue. The iron salt is red.

Acid hydrolysis of (2) produces successively hydroxylamine sulphonic acid and hydroxylamine—



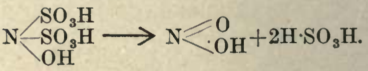
$$N\begin{array}{l}\diagup SO_3H\\ -SO_3H\\ \diagdown OH\end{array}\xrightarrow{HOH}N\begin{array}{l}\diagup H\\ -SO_3H\\ \diagdown OH\end{array}\xrightarrow{HOH}N\begin{array}{l}\diagup H\\ -H\\ \diagdown OH\end{array}$$
$$+HO{\cdot}SO_3H \qquad +HO{\cdot}SO_3H$$

Acid hydrolysis of (3) produces successively imino sulphonic acid, amino sulphonic acid, and ammonia—



$$N\begin{array}{l}\diagup SO_3H\\ -SO_3H\\ \diagdown SO_3H\end{array}\xrightarrow{HOH}N\begin{array}{l}\diagup H\\ -SO_3H\\ \diagdown SO_3H\end{array}\xrightarrow{HOH}N\begin{array}{l}\diagup H\\ -H\\ \diagdown SO_3H\end{array}$$
$$+HO{\cdot}SO_3H \qquad +HO{\cdot}SO_3H$$
$$\xrightarrow{HOH}NH_4HSO_4.$$

Hydrolysis by alkalis usually regenerates the sulphite and nitrite—



$$N\begin{array}{l}\diagup SO_3H\\ -SO_3H\\ \diagdown OH\end{array}\longrightarrow N\begin{array}{l}\diagup\!\!\diagup O\\ \diagdown OH\end{array}+2H{\cdot}SO_3H.$$

For further details, and conditions under which these compounds are formed *v.* Hydroxylamine.

Hyponitrous acid $H_2N_2O_2$. The sodium salt of this acid was obtained by Divers (Proc. Roy. Soc. 1871, 19, 425) by reduction of the nitrate (*v.* also Maumené, Compt. rend. 1870, 70, 146), but though its metallic salts and diethyl ester have been known for some time the free acid has only recently been isolated in the solid state. It is prepared—

(1) By condensation of nitrous acid with hydroxylamine, usually the sodium or silver salt with the sulphate or hydrochloride, in aqueous solution (Wislicenus, Ber. 1893, 26, 771; Paal, *ibid.* 1026) or free hydroxylamine and N_2O_3 in methyl alcoholic solution (Kauffmann, Annalen, 1898, 299, 98).

(2) By oxidation of hydroxylamine—

(*a*) With metallic oxides, as CuO, HgO, Ag_2O (Hantzsch and Kauffmann, *ibid.* 1892, 292, 317);

(*b*) With sodium hypobromite (Kolotow, J. Russ. Phys. Chem. Soc. 1891, 23, 1, 3),

(3) By reduction of NO, HNO_3, and, still better, HNO_2. A dilute sodium amalgam is used, and the temperature kept low. The hyponitrite is most stable in excess of alkali. After reduction any hydroxylamine formed is destroyed by HgO, and the liquid, after neutralising with HNO_3, precipitated with $AgNO_3$, or the hydroxylamine may be further reduced by sodium amalgam, and the ammonia removed by evaporation *in vacuô* over sulphuric acid.

(4) By alkaline hydrolysis of certain oxy-amino- compounds, $OH{\cdot}NH{\cdot}SO_3H$ (Divers and Haga, Chem. Soc. Trans. 1899, 77),

$$OH{\cdot}NH{\cdot}SO_2C_6H_5$$

(Piloty, Ber. 1896, 29, 1559); $OH{\cdot}N{=}NO_2H$ (*q.v.*) behave in this way.

The most convenient procedure is to treat the sodium salt of hydroxylamine disulphonic acid (easily obtained by the action of sulphurous acid on sodium nitrite) with concentrated or fused alkali, when it is obtained by precipitation with $AgNO_3$ as the silver salt in 60 p.c. yield (Kirschner, Zeitsch. anorg. Chem. 1897, 16, 424; *v.* also Hantzsch and Sauer, Annalen, 1898, 299, 89; Wieland, *ibid.* 1903, 329, 225). The methods described for the reduction of nitrites by aluminium amalgam, iron hydroxide, and fusion with iron filings are useless.

The free acid may be isolated by decomposing the silver salt with an ethereal solution of hydrochloric acid, and evaporating the filtrate in a desiccator. It is thus obtained in white, crystalline leaflets, very explosive, decomposing on friction, contact with solid KOH or acid vapours, and often spontaneously.

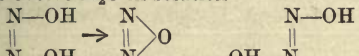
It dissolves very readily in water, readily in alcohol, and is fairly soluble in most organic solvents.

Its decomposition into N_2O and H_2O is not reversible. Small amounts of nitric and nitrous acids are formed at the same time (*v.* further Ray and Ganguli, Chem. Soc. Trans. 1907, 1886; Divers, Chem. Soc. Proc. 1908, 16). Heat of formation $2N+O+Aq.=H_2N_2O_2Aq.-57{,}400$ cal. (Berthelot, Ann. Chim. Phys. 1889 [vi.] 18, 571). It can be oxidised to nitric acid by bromine and by $KMnO_4$. It is not reduced by sodium amalgam (Divers), but yields hydrazine with sodium bisulphite (*v.* Brackel, Ber. 1900, 33, 2115).

It forms neutral and acid salts, the latter very unstable, only the acid ammonium salt being known in the pure state. The neutral salts are mostly insoluble in water, and can be obtained by precipitation. Esters of hyponitrous acid are obtained by action of the iodide on silver hyponitrite.

The *ethyl ester* is a yellow oil (Zorn, Ber. 1878, 11, 1630), and the *benzyl ester* a low-melting solid (Hantzsch and Kauffmann, *l.c.*).

Constitution.—The molecular weight determined by the cryoscopic method corresponds with the formula $H_2N_2O_2$, which, with its modes of formation and acid properties points to its being *diazodihydroxide.* Hantzsch considers it to be the anti-form, assigning the syn-structure to the isomeric *nitramide* (*q.v.*) owing to the great ease with which even salts of the latter evolve N_2O in solution—



Nitramide. Hyponitrous acid.

Nitric acid HNO_3. This is, with the exception of ammonia, the earliest compound of nitrogen investigated, its preparation being known to the Egyptians. In the ninth century Geber obtained it by distilling nitre with blue vitriol and alum, and it was known under various names, such as *aqua fortis, spiritus nitri acidus,* and *spiritus nitri fumans Glauberi.* Its composition was investigated by Lavoisier (1776) and by Lavoisier and Priestley (1784–1786).

Occurrence.—It is found in nature in combination with NH_4, Na, K, Ca, Mg, and in smaller quantities with Al and Fe. It is produced by atmospheric electrical discharges, and by oxidation of nitrogenous organic matter through the medium of nitrifying bacteria, subsequently combining with ammonia in the air, and with the various bases present in the soil, and occurs in largest quantity as Chile saltpetre ($NaNO_3$) and Bengal saltpetre (KNO_3).

Preparation.—Being the highest oxidation product of nitrogen it is produced by the action of suitable oxidising agents upon all the less oxygenated compounds.

Ammonia is oxidised to nitric acid by atmospheric oxygen in presence of catalytic agents such as $Cu(OH)_2$, Cu, Fe, Ni, Pt (Kuhlmann, Annalen, 1839, 29, 281; Schönbein, J. pr. Chem. 1859, 70, 129; Kraut, Annalen, 1856, 136, 69). Lead manganate and permanganate, sodium manganate and lead chromate also bring about this oxidation (Motay, Ber. 1871, 4, 891; Schwarz, Dingl. poly. J. 1875, 218, 219) upon which principle the patents of Ostwald (Eng. Pat. 698) and Bayer and Co. (D. R. P. 168272) depend.

According to Schmidt and Böcker (Ber. 1906, 39, 1366) the primary oxidation product is NO (*v.* further Smith, Chem. Soc. Trans. 1906, 473).

Ammonia gas is oxidised by heated MnO_2 and Fe_2O_3 to ammonium nitrate, and its solution by ozone, H_2O_2, H_2CrO_4, $KMnO_4$, and by electrolytic and biochemical oxidation.

Nitrous acid is similarly oxidised to nitric acid. Nitrogen and its lower oxides are only oxidised by oxygen to N_2O_4, unless water is present, when nitric acid is formed (*v.* also NITRIC ACID, MANUFACTURE OF; ATMOSPHERIC, NITROGEN, UTILISATION OF).

Properties.—By distillation in a current of CO_2, 98 p.c. acid can be obtained. Fractional crystallisation gives a product with maximum purity of 99·4±0·1 p.c. Absolute nitric acid only exists in the form of snow-white crystals, m.p. −41°. On melting, a yellow liquid results which is a solution of nitric anhydride and water in nitric acid (Küster and Munch, Zeitsch. anorg. Chem. 1905, 43, 350).

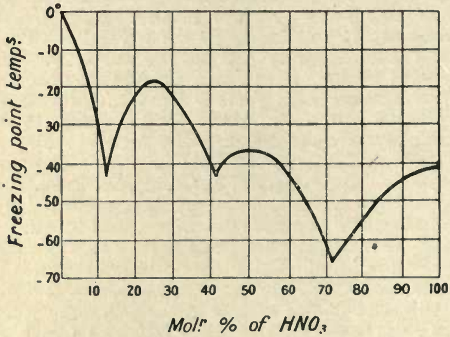
The physical properties show discontinuities which point to the existence of various hydrates. The freezing-point curve (p. 692), constructed from the values of Pickering (Chem. Soc. Trans. 1893, 63, 436) and Küster and Kremann (Zeitsch. anorg. Chem. 1905, 41, 1), shows two maxima, at −18·5° and −38°, corresponding to

$$HNO_3,3H_2O$$

and HNO_3,H_2O respectively; and three minima, corresponding to the cryohydrates (1) ice $+HNO_3,3H_2O$ (m.p. −43°); (2)

$$HNO_3,3H_2O+HNO_3,H_2O$$

(m.p. −42°); and (3) HNO_3,H_2O+HNO_3 (m.p. −66°).



According to Erdmann (Zeitsch. anorg. Chem. 1902, 32, 431; Zeitsch. angew. Chem. 1903, 16, 1001) orthonitric acid $N(OH)_5$, crystallises in needles, stable below −15°, m.p. −35°, b.p. 40°–40·5°/13 mm. Octobasic nitric acid $O[N(OH)_4]_2$, m.p. −39°, tribasic nitric acid $O{=}N(OH)_3$, m.p. −34°, and tetrabasic nitric acid $O[NO(OH)_2]_2$, m.p. −65·2°, are also described. Independent evidence for the existence of the ortho-acid is obtained from the refractive index curves (Veley and Manley, Proc. Roy. Soc. 1901, 69, 86; Chem. Soc. Trans. 1903, 1015), and from the absorption spectra (Hartley, Proc. Roy. Soc. Dublin, 1905, [ii.] 10, 373), but the existence of the polybasic acids is disputed (Küster and Kremann, Zeitsch. anorg. Chem. 1904, 41, 1; Küster, Zeitsch. angew. Chem. 1903, 16, 1079).

The freezing-points of dilute solutions and the corresponding dissociation values are given by Jones (Zeitsch. physikal. Chem. 1893, 12, 630) and Jones and Getman (Amer. Chem. J. 1902, 27, 433). The change in the value of the molecular lowering with concentration is indicated by the following selected values—

Gram mols. HNO_3 per litre	Molecular lowering
0·001054	3·7951°
0·01153	3·7294°
0·1059	3·5269°
0·25	3·501°
0·5	3·621°
1·0	3·796°
2·0	4·174°
3·0	4·603°

The densities, and the changes in density with temperature, of nitric acid solutions of different concentrations have been determined by Lunge and Rey (Zeitsch. angew. Chem. 1891, 165) and Veley and Manley (*l.c.*), and afford further evidence of the existence of hydrates (Veley and Manley).

The following table is constructed from Lunge and Rey's values—

$d_4^{15°}$	p.c. HNO_3	$d_4^{15°}$	p.c. HNO_3
1·00	0·10	1·30	47·49
1·05	8·99	1·35	55·79
1·10	17·11	1·40	65·30
1·15	24·84	1·45	77·28
1·20	32·36	1·50	94·09
1·25	39·82	1·52	99·67

Density of normal HNO_3 solution (63·13 grams per litre) = 1·0318 at 18·6° (Kohlrausch, Wied. Ann. 1865, 26, 161), 1·0324 at 18° (Loomis, *ibid.* 1897, 60, 532).

The expansion of dilute solutions with temperature has been studied by Forch (Wied. Ann. 1895, 55, 100) and Ostwald (J. pr. Chem. 1877, [ii.] 16, 385), and that of concentrated solutions by Küster and Kremann, who find two breaks in the otherwise continuous concentration, at 54·0 p.c. HNO_3 and 77·77 p.c. HNO_3, corresponding to $HNO_3,3H_2O$, and HNO_3,H_2O respectively.

For the conductivity of nitric acid solutions, *v.* Kohlrausch (Wied. Ann. 1885, 26, 161), Arrhenius (Zeitsch. physikal. Chem. 1889, 4, 96), Loomis (Wied. Ann. 1897, 60, 547), Veley and Manley (Proc. Roy. Soc. 1897, 62, 223), and Küster and Kremann (*l.c.*). The existence of the above hydrates is again indicated; two irregularities in the conductivity curve occurring at 25 and 50 mols. p.c. HNO_3, corresponding to the compounds $HNO_3,3H_2O$ and HNO_3,H_2O respectively, and a third at 96–100 p.c. HNO_3, at which concentration irregularities also occur in the density and freezing-point curves, pointing to the commencement of anhydride formation previously mentioned.

Nitrates dissolved in concentrated nitric acid increase its conductivity in proportion to the amount dissolved (Bouty, Compt. rend. 1888, 106, 595, and 654).

The viscosity of nitric acid has been determined by Graham (Phil. Trans. 1861, 153, 373), Reyher (Zeitsch. physikal. Chem. 1888, 2, 744), Paggliani and Oddone (Wied. Ann. Beibl. 11, 415), and Küster and Kreman (*l.c.*). The last-named give the following values $\eta = 1$ for water at 0°—

p.c. HNO_3	98·5	82·0	70·0	65·0	50·0	30·0	10·0	0·0
η (+15°)	0·548	1·036	1·277	1·300	1·144	0·822	0·655	0·667
η (−15°)	0·833	2·241	3·268	3·304	2·369	1·635	—	—

The maximum at about 65 p.c. corresponds to the constant boiling mixture $2HNO_3,3H_2O$ first investigated by Dalton. It is not a compound, its composition varying with the pressure. At 735 mm. it contains 68·0 p.c. HNO_3 (b.p. 120·5°) and at 1220 mm. 68·6 p.c. HNO_3 (Roscoe, Annalen, 1860, 116, 203), while, by passing indifferent gases through the acid at ordinary temperatures residues differing still more widely in composition are obtained.

The vapour tensions of nitric acid solution have been determined by Saposhnikoff (Zeitsch. physikal. Chem. 1905, 53, 225). For the higher concentrations they are as follows—

d_4	p.c. HNO_3	p.c. H_2O	p (mm. at 15°)	p.c. N in vapour
1·400	65·30	34·70	1·90	19·32
1·453	78·10	21·90	9·40	22·52
1·462	82·10	17·90	16·64	22·65
1·487	88·65	11·35	29·70	23·05
1·497	92·93	7·07	42·60	23·50
1·510	98·00	2·00	46·20	23·75

As HNO_3 contains only 22·22 p.c. N, oxides are also present in the vapour.

With mixtures of nitric and sulphuric acids, however, the vapour tension rises and then falls with increasing percentages of HNO_3. The maximum for HNO_3 of sp.gr. 1·40 occurs at 45 p.c. HNO_3 (23·5 mm.), and for HNO_3 of sp.gr. 1·48 at 67 p.c. HNO_3 (34 mm.). With the pure acids the value rises steadily to 41 mm. at 80 p.c. HNO_3, remains constant up to 92 p.c. and rises subsequently to 46 mm. with pure HNO_3 (Saposhnikoff, *ibid.* 1904, 49, 697; 1905, 51, 609). The purest obtainable nitric acid boils at 86° with partial decomposition. Under 24 mm. it boils at 21·5° (Erdmann, Zeitsch. anorg. Chem. 1902, 32, 431).

Refractive index.

$d_4^{20°}$	D line	Mol. dispn.
1·50999	1·39584	0·338
1·50875	1·36870	0·340

(Brühl, Zeitsch. physikal. Chem. 1897, 22, 373). The maximum value (1·4061 at 14·2°) is shown by 70 p.c. HNO_3, while the values for 50 p.c. and 99 p.c. acid are practically identical (Veley and Manley, Proc. Roy. Soc. 1901, 69, 86). For the absorption spectra, *v.* Hartley, Chem. Soc. Trans. 1903, 658.

Heat of formation.—

$$H+N+O_3+Aq.=HNO_3Aq.+49{,}090 \text{ cal.}$$

(Thomsen), 48,800 (Berthelot), which, by subtracting the heat of solution (7490, Thomsen; 7180, Berthelot) gives

$$H+N+O_3=HNO_3+41600 \text{ cal.}$$

Mol. heat of evaporation 7250 cal., mol. heat of fusion 600 cal. (Berthelot, Ann. Chim. Phys. 1877, [v.] 12, 530).

Specific heat.—

p.c. HNO_3	58·3	12·3	3·4	26	15	3·4
Sp.ht. .	0·6651	0·8752	0·9618	0·768	0·849	0·963

The first three are Marignac's values at 21°–52° (Annalen, 1872 (suppl.), 8, 335), the last three Thomsen's at 18°.

Chemical properties.—Nitric acid has been shown by the usual methods (rate of hydrolysis of methyl acetate, inversion of cane sugar, freezing-point lowering and conductivity) to be the strongest known acid. Accordingly it has a high value for its heat of neutralisation (with NaOH 13,680 cal.; with KOH 13,770 cal. Thomsen, Th.U. 1906, 40). Its heat of dissociation for $v=1·5–6$ is about 2800 cal. (Petersen, Zeitsch. physikal. Chem. 1893, 11, 174), for $v=10$ about 1362 cal. (Arrhenius, *l.c.*).

It dissolves readily in ether, and the ether-water partition coefficients have been determined by Bogdan, Zeitsch. Elektrochem. 1905, 11, 824; 1906, 12, 489; *v.* also Hantzsch and Sebaldt, Zeitsch. physikal. Chem. 1899, 30, 285). The molecular weight in ethereal solution is normal.

The nitrate ion is one of the most electronegative ions. Migration velocity 61·8 at 18° (Landolt-Börnstein, 1905, 237). All its salts are soluble, and there is little tendency to form complexes.

The chief characteristic of nitric acid is its remarkable oxidising power, being itself capable of reduction to HNO_2, NO_2, NO, N_2O, $H_2N_2O_2$, NH_2OH, N_2, and NH_3. Ostwald (Grundliss. d. allgem. Chemie, 1899, 440) explains the formation of these products on the supposition that nitric acid can so dissociate that it forms OH ions with the loss of positive charges—

$$\begin{array}{llll}
HNO_3 & \rightarrow NO_2^{\cdot}+OH' & \rightarrow & NO_2+OH'+\oplus \\
 & \nearrow NO_2H^{\cdot\cdot}+2OH' & \rightarrow & NO_2H+2OH'+2\oplus \\
NO(OH)_3 & & & \\
 & \rightarrow NO^{\cdot\cdot\cdot}+3OH' & \rightarrow & NO+3OH'+3\oplus \\
 & \nearrow NOH^{\cdot\cdot\cdot\cdot}+4OH' & \rightarrow & \frac{(NOH)_2}{2}+4OH'+4\oplus \\
NO(OH)_5 & & & \\
 & \searrow N^{\cdot\cdot\cdot\cdot\cdot}+5OH' & \rightarrow & \frac{N_2}{2}+5OH'+5\oplus
\end{array}$$

The oxidation potential (Ihle, Zeitsch. physikal. Chem. 1896, 19, 589) is lowered by the presence of nitrous acid, which, however, increases the rate of oxidation.

Nitric acid is not affected by hydrogen at ordinary temperatures or at 100° (Berthelot, Compt. rend. 1898, 127, 27), but is reduced by it to ammonia in presence of platinum sponge (Wagner, Dingl. poly. J. 1867, 183, 76). The concentrated acid oxidises boron on slightly warming to boric acid with evolution of NO and N_2, carbon to carbon dioxide, in the cold if finely divided, phosphorus to phosphorous, and finally to phosphoric acid (when, according to Montemartini, Gazz. chim. ital. 1898, 28, i. 397, ammonia is also produced). Sulphur is oxidised to H_2SO_4 with great readiness if finely divided, selenium to H_2SeO_3, and iodine to iodic acid with production of nitrous acid. Hydrides are also oxidised: PH_3 readily, H_2S only if NO_2 be present (acid of sp.gr. 1·18 free from NO_2 has no action: Kemper, Annalen, 1857, 102, 342), SeH_2 violently (Hofmann, Ber. 1870, 3, 660). HBr at 0° forms Br_2 and NO_2, HI yields I_2 and NO (HNO_2 in dilute solution, Eckstädt, Zeitsch. anorg. Chem. 1901, 29, 51) and HCl,NOCl (*q.v.*).

SO_2 reduces HNO_3 readily, some N_2O being formed. In presence of dilute sulphuric acid reduction is still more readily effected, with evolution of NO, and in presence of concentrated H_2SO_4 nitrosyl sulphuric acid (Weber, Pogg. Ann. 1867, 130, 277).

Ferrous salts yield NO, stannous salts NH_2OH and NH_3,$AsCl_3$ and As_4O_6 arsenic acid, and $SbCl_3$ antimonic acid.

Nitric acid attacks with more or less readiness according to their nature, and the concentration of the acid, all metals with the exception of Au, Rh, Ir, and Pt (the last-named when alloyed with other metals goes into solution, *e.g.* an alloy of 4·64 p.c. Pt and 95·35 Hg is entirely soluble (Tarugi, Gazz. chim. ital. 1903, 33, [ii.] 171) with formation of the nitrate except in the case of Sn, W, Mo, and As, when the anhydride of the corresponding acid is produced, the nitric acid itself being reduced to various stages. Sn forms stannic nitrate first, which breaks up yielding the dioxide. Sb is converted into Sb_2O_4. Briefly it may be stated that with the less reactive metals, such as Hg, Ag, Cu, Bi, reduction to the first stage only takes place, and is probably not due to the agency of nascent hydrogen, but to nitrous acid, the influence of which on the reactivity of nitric acid was first noticed by Millon (J. Pharm. Chim. 1842, [iii.] 2, 179). Thus, with copper—

(i.) $Cu+4HNO_2=Cu(NO_2)_2+2H_2O+2NO$;
(ii.) $Cu(NO_2)_2+2HNO_3=Cu(NO_3)_2+2HNO_2$;
(iii.) $HNO_3+2NO+H_2O=3HNO_2$.

The nitrous acid thus continuously produced at once decomposes—

$$3HNO_2=HNO_3+2NO+H_2O,$$

nitric oxide being evolved (Veley, Roy. Soc. Trans. 1891, 182, A, 279).

From the equilibrium

$$3NO_2+H_2O \rightleftarrows 2HNO_3+NO$$

it is evident that with concentrated acid the product is NO_2.

The most complete reduction (to N_2 and NH_3) takes place with the more electro-positive metals such as Sn, Co, Ni, Fe, Cd, Zn, Mn, Mg. Thus Zn and very dilute acid give ammonia, whilst with Sn reduction is less complete, hydroxylamine being one of the products. With more reactive metals, such as Mg, some hydrogen (which may be regarded as the primary product) escapes oxidation. The action is greatly affected by conditions, being slow at first, accelerating as the reduction products, which act catalytically, accumulate. Further, different concentrations yield different products, and hence as the concentration changes during the reaction, mixed products in varying proportions are usually obtained. With Zn, in intermediate concentrations, even nitrous oxide and nitrogen may be found in considerable quantities amongst the gaseous products. For further details, *v.* Acworth and Armstrong (Chem. Soc. Trans. 1877, 32. 54), Montemartini (Atti. R. Accad. Lincei, 1892, [v.] 1, i. 63), Walker (Chem. Soc. Trans. 1893, 63, 845), Higley (Amer. Chem. J. 1899, 21, 377), Stillmann (*ibid.* 1897, 19, 711), Bijlert (Zeitsch. physikal. Chem. 1899, 31, 131), Gladstone (Phil. Mag. 1900, [v.] 50, 231), Stausbie (J. Soc. Chem. Ind. 1908, 27, 365; 1909, 28, 274), Rennie (Chem. Soc. Trans. 1908, 1162), Dunstan and Hill, passivity in (Chem. Soc. Trans. 1911, 1853).

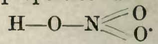
Electrolytic reduction, as shown by Schönbein and Brewster, yields first nitrous acid, and finally ammonia. The nature of the product depends on the temperature, current strength, material of cathode, and its potential, and upon whether the solution is acid or alkaline. With a mercury cathode only hyponitrite is formed (Zorn, Ber. 1879, 12, 1509), with a copper cathode, ammonia (Ulsch, Zeitsch. Elektrochem. 1897, 3, 546).

Nitric acid of 40 p.c. strength containing 1 p.c. of dissolved nitrous gases yields NO (99–100 p.c.) at the cathode on electrolysis (Meister, Lucius and Brüning, Eng. Pat. 10522, May 1, 1911; *v.* Müller and Weber, Zeitsch. Elektrochem. 1903, 9, 955; Müller, *ibid.* 978; Müller and Spitzer, *ibid.* 1905, 11, 509; Ber. 1905, 38, 1190; and Tafel, Zeitsch. anorg. Chem. 1902, 31, 289). The mechanism of the reaction is not clearly understood. Tafel finds that though nitric acid is reduced only to NH_2OH by mercury or well-amalgamated electrodes, copper reduces it to ammonia, and yet has no action on hydroxylamine itself.

Metallic nitrates are normal salts (in only a very few instances are acid or basic salts obtained, and then only under special conditions) which are readily soluble in water, and in many cases in alcohol, or acetone, stable in aqueous solution, and which usually crystallise in the anhydrous form.

Nitric acid forms nitro derivatives with many organic compounds, and with alcohols yields esters.

On contact with the skin substances of bright yellow colour (xantho-proteic acids) are produced. Its chemical properties are best represented by the formula



$H{-}O{-}N\begin{smallmatrix} \nearrow O \\ \searrow O \end{smallmatrix}$.

Estimation (*v.* ANALYSIS).—The most characteristic test is the red colour developed with brucine and concentrated H_2SO_4. Arbutin and berberine under similar conditions yield a deep yellow, and a dark brownish-red colour respectively (Reichard, Chem. Zeit. 1906, 30, 790).

Cinchonamine nitrate is nearly insoluble in water (Howard and Chick, J. Soc. Chem. Ind. 1909, 28, 53).

Di-9-10-monoxyphenanthrylamine dissolved in conc. sulphuric acid forms a delicate test for nitric acid in presence of other oxidising substances. As a reagent, 0·1 gram is dissolved in 1 litre of conc. sulphuric acid and 0·1 gr. of the substance to be tested is added to 2 c.c. of the reagent, when, if nitrates be present, the blue colour turns to a claret-red. Nitrous acid does not alter the colour unless it becomes oxidised to nitric acid (Schmidt and Lumpp, Ber. 1910, 43, 787 and 794).

Fuming nitric acid. A red, fuming liquid with powerful oxidising properties, produced by adding to concentrated HNO_3, nitrous acid, nitrogen trioxide, or nitric oxide, by distilling nitre with potassium acid sulphate, and also by adding kieselguhr saturated with formaldehyde to the concentrated acid (Vanino, Ber. 1899, 32, 1392).

As prepared by any of these methods it contains free NO_2 (Marchlewski, Zeitsch. anorg. Chem. 1892, 1, 363), and in the case where NO is used may be supposed to be formed either by direct union with oxygen, or as represented by the equation $2NO+HNO_3+H_2O \rightarrow 3HNO_2$, the latter then giving NO_2 with the excess of HNO_3. The intermediate production of nitrous acid is shown by addition of water, when it becomes green, blue, and finally colourless (*v.* further Marchlewski and Liljenstein, Zeitsch. anorg. Chem. 1892, 2, 18; 1894, 5, 288).

The specific gravities of the fuming acid of different NO_2 content are given by Lunge and Marchlewski (Zeitsch. angew. Chem. 1892, 1).

Fuming nitric acid oxidises organic compounds to carbon dioxide and water, any sulphur present being converted into H_2SO_4, and phosphorus into H_3PO_4 (Carius, Ber. 1870, 3, 697).

Aqua regia. First obtained by Geber in the eighth century by dissolving salammoniac in *aqua fortis.* Also formed by mixing HCl and HNO_3. The reaction is represented by

$$HNO_3+3HCl=2H_2O+NOCl+Cl_2$$

(*v.* Tilden, J. 1874, 214; Goldschmidt, Annalen, 1880, 205, 372). So named on account of its solvent action on the noble metals.

Pernitric acid HNO_5 is said to be obtained as the silver salt as a black crystalline mass on electrolysing $AgNO_3$ solution (Mulder and Heringa, Rec. trav. chim. 1898, 17, 129). Its existence is doubtful.

ACID HALIDES OF NITRIC ACID.

Nitryl fluoride NO_2F is formed by the action of excess of fluorine on nitric acid at the temperature of liquid air. It is a gas which attacks the mucous membrane, m.p. −139°, b.p. −63·5°; v.d. 2·17–2·31 (air=1) calculated for NO_2F

2·26. It does not combine with hydrogen, sulphur, or carbon, but attacks boron, silicon, phosphorus, arsenic, antimony, iodine, alkali, and alkaline earth metals, aluminium, iron and mercury. With water the quantitative reaction $NO_2F + H_2O = HF + HNO_3$ takes place. It reacts with many organic compounds (Moissan and Lebeau, Compt. rend. 1905, 140, 1573).

Nitryl chloride NO_2Cl (Müller, Annalen, 1862, 122, 1; Odet and Vignon, Compt. rend. 1870, 70, 96) and *nitryl bromide* NO_2Br (Hasenbach, J. pr. Chem. 1871, [ii.] 4, 1) are, according to Gutbier and Lohmann (J. pr. Chem. 1905, [ii.] 71, 182) non-existent.

NITRIC ACID, MANUFACTURE OF. At the present time the nitric acid of commerce is obtained by distilling nearly equal weights of 'oil of vitriol' and sodium nitrate in iron retorts. The residue consists of a fused mixture of sodium sulphate and disulphate ($Na_2S_2O_7$) which may also contain sodium hydrogen sulphate ($NaHSO_4$) if the heating has not been carried so far as to drive off the last traces of water. This fused residue is discharged into iron pans where it solidifies, or it may be run into the pan of a salt-cake furnace, mixed with salt and converted into salt cake. A part of the nitre cake now produced is also converted into sodium sulphide.

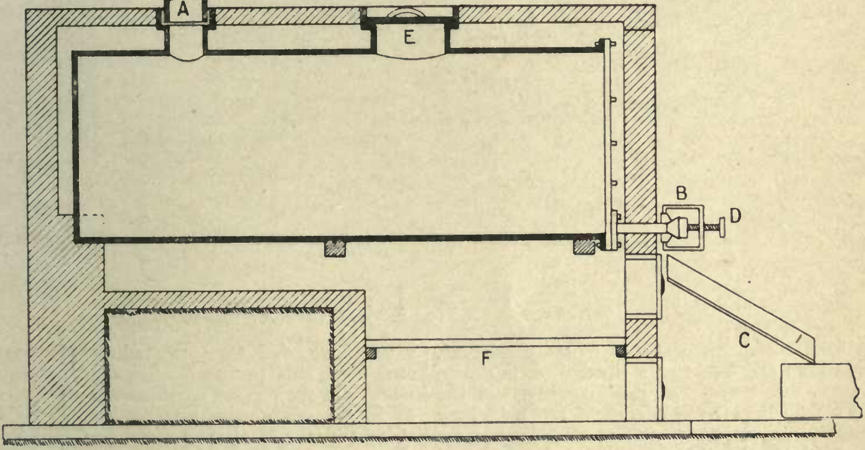


Fig. 1.

Since the specific heat of strong nitric acid is low, the fuel consumption need not be large, and for the same reason the vapour is easily condensed. When nitric acid boils, decomposition into water and nitric oxide takes place. The condensed nitric acid will, therefore, usually contain nitrous acid. This may be avoided by keeping the condensed distillate hot until it escapes from the cooling worm. If very strong sulphuric acid and previously melted sodium nitrate are used, the nitric acid obtained will be very strong. If water is present, the first distillate will be strongest and the last distillate nearly pure water. Formerly the mixture was such that sodium sulphate remained in the retort, but this is now considered poor practice since a longer time and more fuel are required and the sodium sulphate must be dug out of the retort. In most installations a horizontal cylindrical cast-iron retort is used, something like that shown in Fig. 1. Sodium nitrate and sulphuric acid are introduced at E and the nitric acid distils off through A. At the end of the distillation the retort is emptied by turning the screw stopper D, the fused residue falling into the trough C. Another form of retort devised by Hart is shown in cross-section in Fig. 2. The cylinder, of cast iron, is supported on trunnions and is inverted at the end of the distillation. The form of pot retort emptied by dipping out the liquid contents, frequently described, is quite inadmissible in good practice as the workmen are exposed to the fumes of nitric acid, and the operation is needlessly

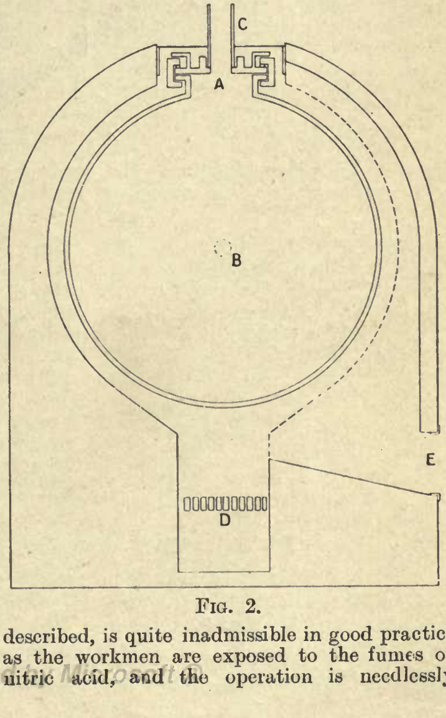


Fig. 2.

expensive. A workable pot retort used in the Valentiner system is shown in Fig. 8.

Condensers.—In the older installations air condensation was relied upon, and this answers well in cold climates, especially in winter, but in summer the surface exposed must be very large and the distillation slow, which results in high fuel and labour cost and small output so that cooling by water is commonly used in the larger plants.

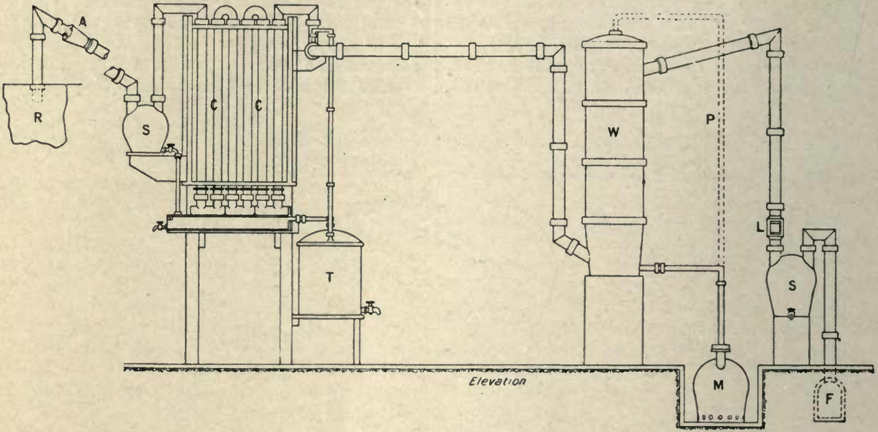


FIG. 3.

Guttmann's apparatus. This condenser, devised by the late Oscar Guttmann, is shown in Figs. 3 and 4. The gases coming from the still R pass into the enlargement A. Here they produce an injector action and suck in a quantity of air through the perforations in the socket pipe, this air causing oxidation of the nitrous to nitric acid. The nitric vapours are led to a preliminary receiver S, and from this to the water-cooled condensing battery of six vertical earthenware pipes. These fit into a connecting pipe below. From this, three pipes, not shown, carry the acid to the cooling trough made of earthenware with transverse pipes through which cooling water circulates. Samples may be taken and the trough emptied by means of a tap. The condensed acid overflows into the collecting vessel T. The apparatus is usually erected in pairs requiring only one cooling trough. Uncondensed gases pass into the tower W. This is filled with stoneware balls presenting a very large surface. The acid condensed here is pumped up repeatedly through the tower, and when

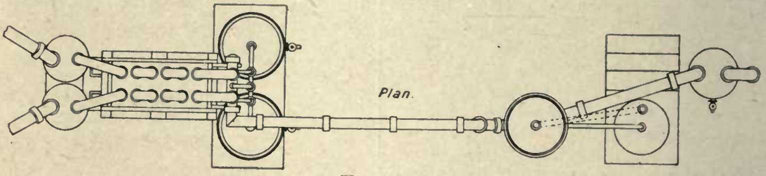


FIG. 4.

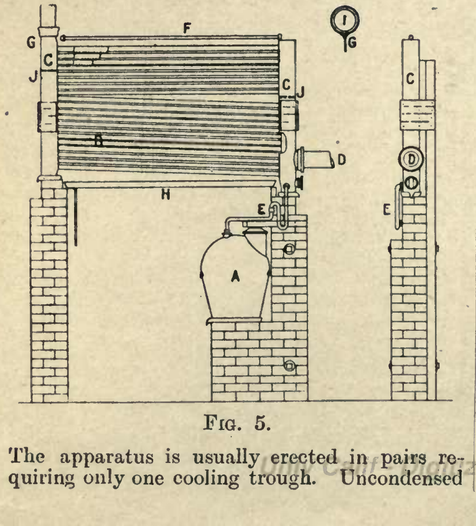


FIG. 5.

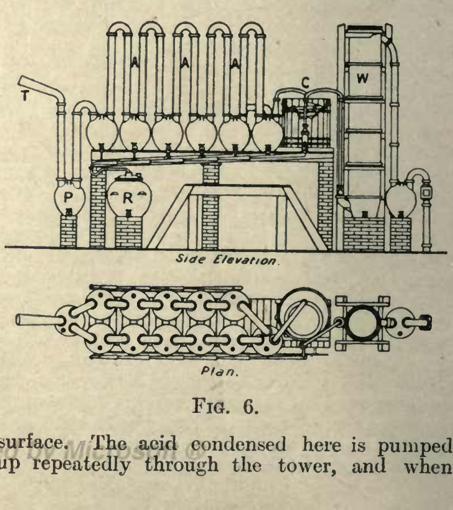


FIG. 6.

it has reached the strength 38°B. it is added to the next charge in the still. The loss of acid is claimed not to exceed 0·60 p.c. Ten hours are required to run off a charge of one ton nitrate, 2 hours for emptying and refilling. Two double batteries for 10,800 lbs. sodium nitrate require, with tower and automatic montejus, a space of 30×45×18 feet. The total cost for a double battery of four stills, including building and erection, is estimated at £1450. This will produce in 24 hours 9820 lbs. nitric acid of 96½ p.c. requiring four men and 15 cwt. coal.

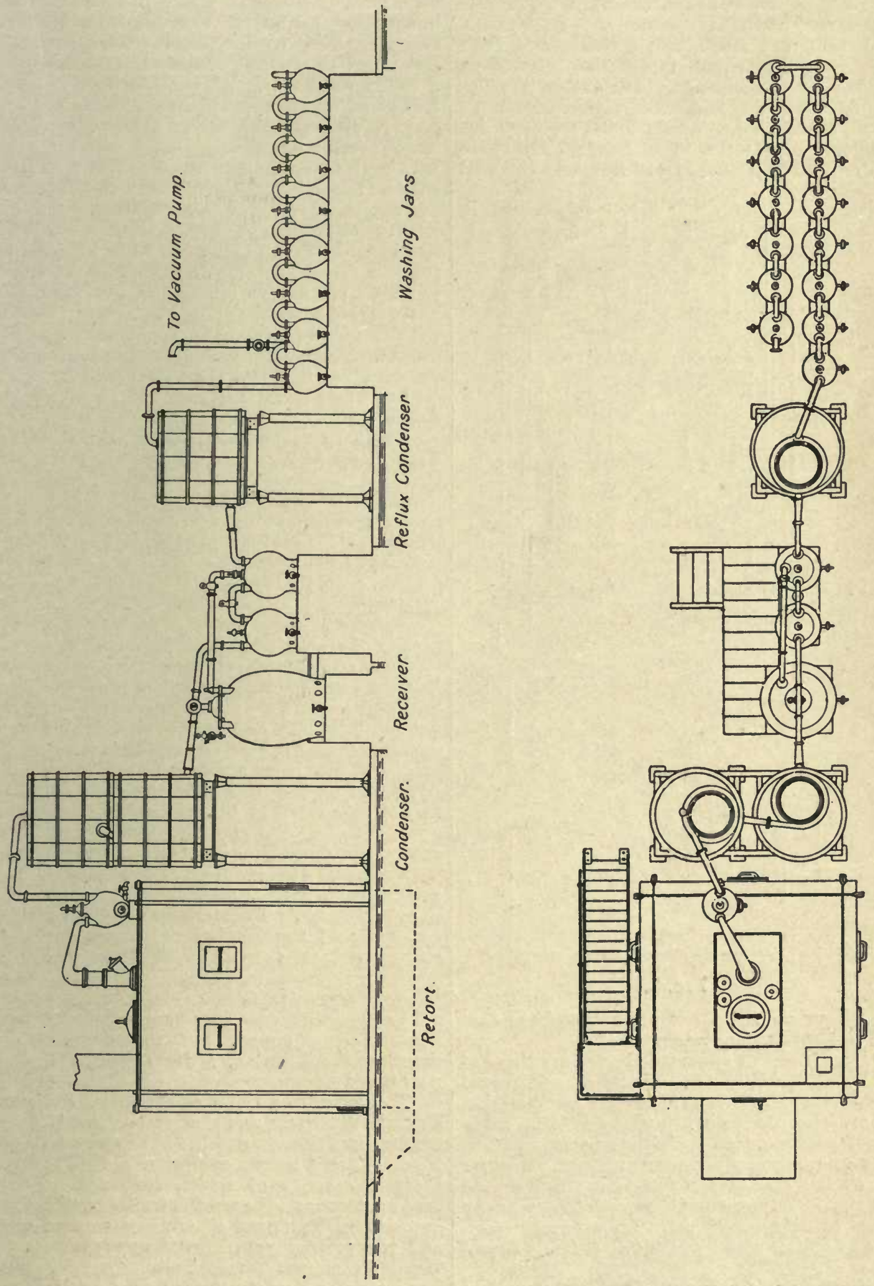


Fig. 7.

Hart's apparatus is shown in Fig. 5. Vapour from the retorts passing through the pipe D is divided, passing through the glass tubes B. These are two metres long, with a diameter of about 4½ centimetres. The cooling water is showered upon a cotton cloth surrounding the upper tube and then drops upon the next lower tube. Even distribution of the cooling water is effected by cutting the two selvedge edges into saw teeth as shown at G and on the upper left-hand corner of the elevation. The glass tubes, being thin, are much better conductors than stoneware pipes, and much less surface is required for condensation. The cost of installation is, therefore, less than with Guttmann's system amounting to about £1200 for 9820 lbs. nitric acid of 96½ p.c. in 24 hours. The space required is about 30×30×18 feet, and the coal and labour do not differ materially from that used in Guttmann's system.

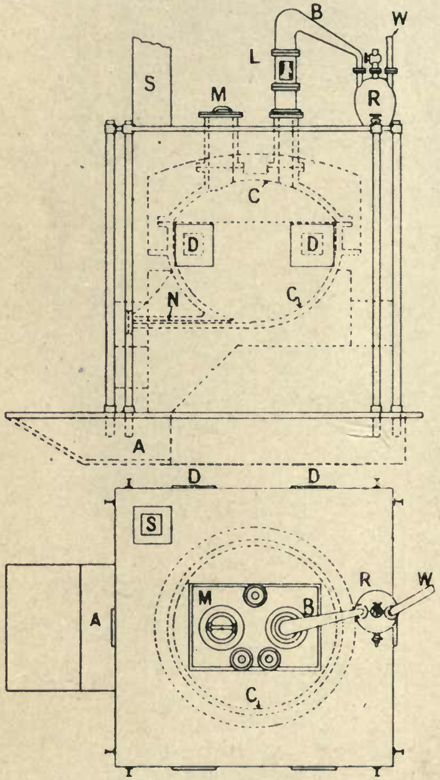


Fig. 8.

Other forms of apparatus in use are those of Dr. Uebel, the Griesheim apparatus, and that of Mr. James M. Thomson in use at Waltham Abbey. In Thomson's apparatus the nitric acid is condensed at a high temperature. The retort has an iron pipe passing through the cover and at the end of the distillation the melted bisulphate is blown out through this pipe by means of compressed air. An air-cooled condensing system sold by Doulton & Co. is shown in Fig. 6.

Distillation in vacuum. This is the method used in Valentiner's process, in which the outlet pipe from the still, Figs. 7 and 8, passes into a small tourill half filled with pumice stone, in which any acid or salt coming over as foam is collected. The vapours then pass through two large water-cooled stoneware coils in series. By a three-way cock the condensed acid at the beginning and end of the operation may be collected in one large receiver, and the 96 p.c. acid, forming about 80 p.c., coming over in the intervening period is collected in a separate receiver. The vapour then passes into the lower end of another stoneware coil acting as a reflux condenser. Then come eight tourills, half of which are half filled with water and half empty, placed alternately. Finally, there are seven tourills alternately empty and half filled with milk of lime. The last tourill is connected with a 12-inch vacuum pump with 16-inch stroke running at 60 revolutions per minute.

For the method of vacuum distillation, lower fuel consumption, purer acid, since less decomposition results, greater durability of the stoneware, no leakage to annoy the workmen, and hence larger yield are claimed. The first cost of the apparatus is, however, very heavy as compared with other systems. Recent improvements are described in U.S. Patent 920224.

Nitric acid from atmospheric air, *v.* Nitrogen, Atmospheric, utilisation of. E. H.

NITROGEN, ATMOSPHERIC, UTILISATION OF. Many nitrogenous substances, more particularly nitrates and ammonium salts, are largely used as plant manures, for though natural formation of nitrogenous bodies does take place, the amount so produced is not nearly sufficient to supply the want of the soil in this respect, more particularly in view of the wastage of combined nitrogen which is always taking place, from bacterial action and from the present system of sewage disposal.

The natural sources from which a soil obtains its supply of nitrogenous substances are electrical discharges in the atmosphere, causing the union of oxygen and nitrogen, with ultimate formation of nitrates and nitrites. By these means it has been estimated that every acre of ground in this part of the world is enriched to the extent of 11 lbs. of combined nitrogen annually. In the tropics, where thunderstorms are more frequent, the amount is larger.

Further, certain leguminous plants, *e.g.* peas, beans, vetch, and clover, possess root nodules, which, by the aid of certain bacteria, are able to fix atmospheric nitrogen, and consequently their growth enriches the soil with nitrogenous products. This discovery was made by Hellriegel in 1866.

Until recently one of the principal nitrogenous manures was guano, but the deposits are practically exhausted, Chile saltpetre having now taken its place.

The supply of Chile saltpetre is, however, limited. The raw material or 'caliche' is not pure sodium nitrate, and has to be recrystallised, which is not a simple operation in Chile, where there is scarcity of water, fuel, and labour. As a consequence, the most accessible and richest deposits in Tarapaca have been worked out, and the greater part of the new districts in Toco, Antofagasta, and Taltal contain, with few exceptions, raw material of much inferior quality to the old and richer deposits of Tarapaca. No trustworthy estimates of the amount of caliche in Chile are obtainable, and whilst it is sometimes stated that the supply will outlast the demand, it seems probable that the actual amount varies from 50,000,000 to 120,000,000 tons, the latter figure corresponding, at the present rate of increased annual consumption, to 42 years' supply, and the former to 21 years' supply.

A third substance used for supplying the soil with nitrogen in the combined form is ammonium sulphate, resulting as a by-product in the manufacture of coal gas, during which process only a small percentage of the nitrogen contained in coal is recovered as ammonia.

The nitrogen contained in ammonia is said to be only nine-tenths as valuable as the nitrogen of saltpetre when used as a manure, and even less when used in large quantities; and, further, in the event of the Chile saltpetre beds becoming exhausted, coal cannot supply all the combined nitrogen which is necessary for the cultivation of the soil, unless more rational methods are employed for the recovery of ammonia.

Moreover, ammonia and nitric acid are not solely used as manures. Numerous colouring matters, explosives such as dynamite and guncotton, or the smokeless powders, *e.g.* melinite, &c., all contain nitrogen, and nitric acid is required for the preparation of these substances and also largely in inorganic technical chemistry. Ammonia is used for manufacturing purposes, *e.g.* the ammonia soda process for the preparation of sodium bicarbonate; also in the laboratory and in the liquid state for ice machines. In addition, there are other important nitrogenous products, such as the cyanides, used for electroplating and in the extraction of gold from its ores. It is not, therefore, a matter for surprise, that many attempts have been made to manufacture nitrogenous products from the practically inexhaustible supply of nitrogen around us in the atmosphere, which is calculated to contain 4000 billion (4,041,200,000,000,000) tons; or, in other words, the air over every acre of ground contains 31,000 tons of nitrogen, or over every 11 acres 354,000 tons, *i.e.* approximately the amount contained in the Chile saltpetre exported in 1909.

Formation of Ammonia.

In considering the methods which may be employed for the fixation of atmospheric nitrogen, mention may be first made of the direct formation of ammonia from its elements nitrogen and hydrogen, for which purpose both these gases have to be isolated. The results of the work done up to the present in this direction have not been of a very hopeful nature, even when the reaction is carried out in the presence of catalysers, because it is reversible, so that at temperatures sufficiently high to cause the formation of ammonia an equilibrium mixture is obtained, containing only a fraction of a p.c. of ammonia.

The Badische Anilin und Soda Fabrik have recently taken up and are experimenting on a method of manufacturing ammonia directly from nitrogen and hydrogen which may prove to be of great importance, though no information from the technical point of view is at present forthcoming.

The process, which is due to Haber (Zeitsch. Elektrochem. 1910, 16, 244), consists in compressing a mixture of 1 part of nitrogen and 3 parts of hydrogen, in presence of a catalyst, the best being osmium, when at a pressure of 175 atmospheres and a temperature near 550°, about 8 p.c. by volume of ammonia is formed. The gases pass from the compression cylinder through a cooling arrangement, where the ammonia liquefies and may be drawn off, whilst the uncombined gases are returned to the compression chamber. Use is made of the heat generated during the reaction to raise the temperature of fresh quantities of gases before they are admitted to the pressure vessel.

Owing to the comparative rarity of osmium, and to the increasing demand for the element in connection with the manufacture of metallic filament lamps, another catalyst has been sought, and crude uranium, resulting when a mixture of uranium oxide and carbon is heated to incandescence between the poles of an electric arc, is now employed, as at a pressure of 175–200 atmospheres it falls to a fine powder, which possesses very high catalytic power.

The necessary nitrogen can be obtained from the atmosphere by using a Linde apparatus, and the hydrogen is produced at a relatively low cost from coal or coke, or by passing steam over heated iron.

The main technical difficulty would appear to be the construction of apparatus of any size capable of withstanding a pressure of 175–200 atmospheres.

Another type of method for the preparation of ammonia is exemplified by passing nitrogen over a heated mixture of magnesium and lime, when the gas is readily absorbed, and the product evolves quantities of ammonia when acted on by water. Methods based on this principle would not, however, appear to have any technical future before them.

There is a very different story to unfold as a result of the observation of Dawes in 1835 that the salt-like substances formed in the preparation of iron in blast furnaces were cyanides. The researches of Bunsen and Playfair about 1840 showed that these cyanides are formed by the union of atmospheric nitrogen with the potassium and carbon compounds in the blast furnace, and as a result a works was started in Grenelle for the manufacture of potassium cyanide by passing nitrogen over a white-hot mixture of coal and potashes or potassium hydroxide. In the next year a factory was built at Newcastle-on-Tyne with twenty-four ovens, but was given up in 1847 owing to the cost of production.

In 1862 Marguerite and de Sourdeval made the important discovery that the absorption of nitrogen took place more readily by using barium hydroxide or carbonate instead of potassium hydroxide, and from the barium cyanide so formed ammonia could be obtained by suitable treatment, whilst at the same time barium hydroxide was regenerated, and could be used over again. Many further modifications of this process were tried, in all of which a mixture as alkali or alkaline earth compounds with coal—*i.e.* a carbide forming mixture—was employed; and if they did not result in complete success, they, at all events, very considerably furthered the solution of the problem of the fixation of atmospheric nitrogen.

In 1869 Berthelot showed that acetylene

and nitrogen interacted to form hydrogen cyanide or prussic acid, and expressed the opinion that cyanides would ultimately be formed by the action of nitrogen at high temperatures on carbides. It was not, however, until 1894, when Moissan and Wilson found that calcium and barium carbides could be prepared in large quantities by heating together barium or calcium oxides with coke in an electric furnace, that the possibility of realising Berthelot's idea became a practical certainty, as proved by the researches of Frank and Caro in 1895–1897.

Moissan demonstrated that the pure carbides would not absorb nitrogen, whereas Frank and Caro proved that impure carbides absorbed large amounts of nitrogen, giving either barium cyanide or a mixture of barium cyanamide and carbon, according to the following equations—

$$BaC_2+N_2=Ba(CN)_2$$
$$BaC_2+N_2=BaNCN+C,$$

and both products formed sodium cyanide on fusion with sodium carbonate

$$Ba(CN)_2+Na_2CO_3=BaCO_3+2NaCN$$
$$BaNCN+C+Na_2CO_3=BaCO_3+2NaCN.$$

As a result a cyanide company was formed by Siemens and Halske, the Deutsche Bank, and the Frankfurt Gold and Silberscheideanstalt, and the whole process was modified as a result of the discovery that when calcium carbide is used instead of barium carbide no cyanide, but only cyanamide, is obtained—

$$CaC_2+N_2=CaNCN+C,$$

and, again, the mixture of calcium cyanamide and carbon can be converted into cyanide by fusion with alkali carbonates and chlorides—

$$CaNCN+C+Na_2CO_3=CaCO_3+2NaCN.$$

The crude mixture of calcium cyanamide and carbon is now known as 'Kalkstickstoff,' 'Stickstoffkalk,' or 'Nitrolim,' and works for the manufacture of this substance to the extent of 165,000 tons per annum have been completed in Norway, Germany, Austria-Hungary, Italy, France, Switzerland, the United States of America, the Central Provinces of India, and Japan, and are projected in South Africa and Canada. Great Britain is at present the notable exception.

The largest of these works is that of the North-Western Cyanamide Company, situated at Odda, on the Hardanger Fjord, Norway. It was constructed with British capital, and organised to manufacture a special acetylene plant designed for a dry process. Owing to the uncertainty of the supply of carbide, several undertakings, including the Alby Works in Sweden, combined for the construction of new factories, and at the present time there are at Odda a hydro-electric power installation, producing 23,000 electrical horse-power; the Alby Carbide Works, with an annual output of 32,000 tons of carbide; and the North-Western Cyanamide Works with an output of 20,000 tons of nitrolim annually.

The electric power for driving the works is derived from the river Tysse, with its source in the Ringedalsvand, which has a summer water level 1430 feet above the sea. The water passes by subterranean tunnel to the lower Vetlevand and thence again by tunnel to a basin constructed at the top of the precipitous slope of ground around the Hardanger Fjord. Then it falls through iron pipes 1350 feet directly on to the turbines in the power house, which is constructed close to the water level of the fjord, and contains six turbines of the Pelton wheel type and dynamos which work on the three-phase alternating system, with a tension of 12,000 volts and a frequency of 25 per second. They run 375 revolutions per minute, developing 4600 horse-power, and the output of the each generator~~s~~ is 4400 electric horse-power. Each turbine is coupled directly to its corresponding generator, and five sets run synchronously to produce at the present time 20,000 horse-power at the terminals of the switch-board at Odda, 3¾ miles distant, though the supply of water is ample to produce 80,000 horse-power when required.

Manufacture of Carbide. The calcium carbide used for making nitrolim is manufactured by the Alby Carbide Company by fusing together lime (as free as possible from magnesia and alumina) with anthracite coal brought from Wales. There are five lime-kilns, each of a capacity of 30 tons, and four of these supply the lime necessary for twelve electric carbide furnaces, each of 1400 kilowatts capacity, worked at 2800°–3000°, and capable of yielding 7–8 tons of carbide per 24 hours.

Preparation of Nitrogen. At Odda the necessary nitrogen is obtained from the atmosphere by using a Linde apparatus, which is run by a 200 horse-power electric motor, and is the largest yet made, being capable of producing 13,000 cubic feet of nitrogen per hour.

Air drawn through two towers, A, A, containing sodium hydroxide liquor to free it from carbon dioxide, is compressed (compressors, B,B,B,B) to about 4 atmospheres, cooled by passage through a water tower, C, and then a reversing air cooler, DD (cooled by cold oxygen or nitrogen from other parts of the apparatus), where the water contained in the air is condensed, and ice forms. This is got rid of by periodically reversing the direction of the flow of gas. The air next passes to an ammonia cooler, E, where the temperature is reduced to −20° or −25°, when practically all moisture is removed, and almost pure and dry air passes to a separator and rectifying column, F, where it is further cooled by an oppositely flowing current of nitrogen or oxygen evaporating from the liquid state. The air passes from this still at a very low temperature, and is led into a coil immersed in a tank of liquid oxygen, where it liquefies, being at a pressure of 4 atmospheres. From this coil it is allowed to expand through a throttle valve, with the result that a large portion is obtained in the liquid state, and at approximately atmospheric pressure. The liquid air is then led to a point near the top of the rectifying column, filled with glass marbles, over which it trickles. On its way down it meets an ascending current of gas evaporating from the liquid below, which gas is rich in oxygen (about 54 p.c.), and as the oxygen has a higher temperature of liquefaction than the liquid air which it meets in the rectifier, it is condensed by an equivalent proportion of nitrogen being distilled off from the descending liquid (at atmospheric pressure oxygen boils at −183° and nitrogen at −196°). The latter enters a tank at the bottom of the tower enriched in oxygen, while the gas passing off is nearly pure nitrogen, which is rendered quite pure by further rectification. As it is not possible to free air altogether from moisture and carbon dioxide before its admission to the rectifying column, these impurities are reduced to the solid state, and can be removed, but gradually choke the apparatus, every part of which is therefore in duplicate, and the working period of one part is from 6 to 10 days (*v.* NITROGEN).

At Westeregeln the method employed for preparing nitrogen is to pass air over heated copper, and subsequently to reduce the copper oxide formed with generator gas.

Caro's method consists in passing producer gas over a mixture of copper and copper oxide; all oxygen and carbon monoxide are got rid of, and there results a mixture of carbon dioxide and nitrogen, from which the carbon dioxide is absorbed by sodium bicarbonate.

Manufacture of nitrolim. In the preparation of nitrolim it is of the greatest importance that the nitrogen used should be pure, as the presence of (*a*) water would cause the decomposition of the carbide yielding acetylene—

$$CaC_2+2H_2O=Ca(OH)_2+C_2H_2;$$

(*b*) oxygen would increase the proportion of carbonate of lime at the expense of the cyanamide, and thus reduce the percentage of nitrogen; (*c*) carbon monoxide and carbon dioxide both act on calcium carbide, liberating carbon in the form of graphite—

$$CaC_2+CO=CaO+3C$$
$$2CaC_2+CO_2=2CaO+5C.$$

Moreover, when carbon dioxide acts on nitrolim at the temperature of the absorption process, nitrogenous compounds are decomposed with separation of carbon. Thus Caro (Chem. Trade Journ. 1909, 44, 621) has shown that a specimen of nitrolim containing 19·67 p.c. of nitrogen and 11·89 p.c. of carbon, when treated with carbon dioxide at 800°, gave a product containing 6·93 p.c. of nitrogen and 17·34 p.c. of carbon, whilst at 1000° the product contained 22·78 p.c. of carbon and only 1·82 p.c. of nitrogen.

Absorption process.—The absorption of nitrogen depends on the physical condition of the carbide, on the proportion of lime, sulphides, phosphides, carbon and carbides present, and as to whether the carbide is freshly treated or after prolonged storage. The reaction

$$CaC_2+N_2 \rightleftarrows CaNCN+C$$

(in which the carbon is liberated in the form of graphite) is exothermic and reversible, this latter at a temperature of 1360° for a certain specimen of carbide examined by Caro. For this reason the glowing carbide, as it comes from the electric furnaces (worked at a temperature of 2800°–3000°) cannot be directly treated with nitrogen. But on cooling, the carbide sets to a rock-like mass which is not permeable to nitrogen, it must therefore be crushed, an operation carried out in an air-tight apparatus in order to prevent access of moisture, which would, as already mentioned, decompose the carbide.

The furnaces are of two types, those heated internally and those heated externally. The latter, which are in use at Piano d'Orte, are similar in design to the well-known retorts used in the manufacture of coal gas, but they are

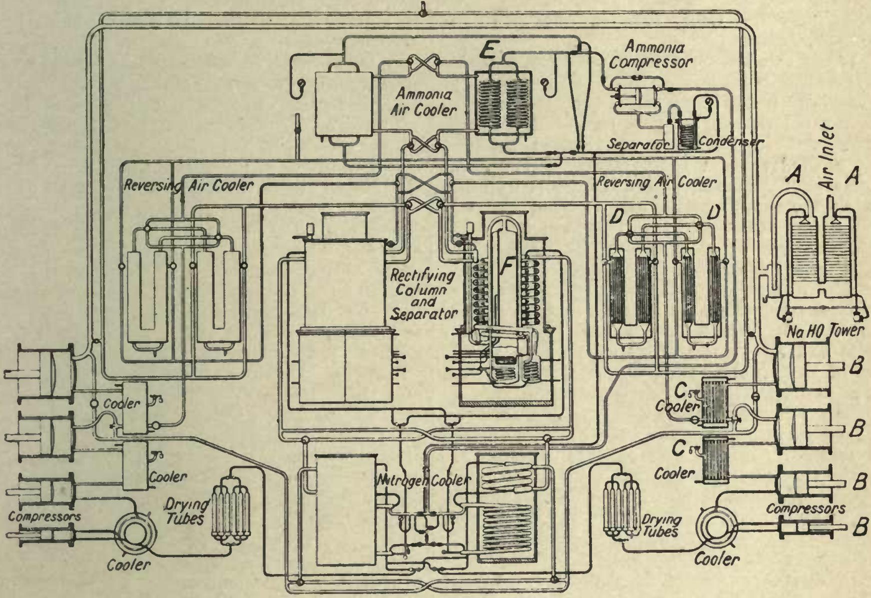


FIG. 1.

Diagram of the Linde Plant used at Odda.

open to several serious objections. The exothermic nature of the reaction causes overheating of the furnace walls and consequent rapid wear; the reaction may easily reach the point at which it becomes reversible, and the product, which has a considerably less bulk than the starting material, sets to a rock-hard mass on the outer walls of the furnace, from which it has to be removed by force. A good deal of work has been done in the direction of obviating these difficulties by lowering the reaction temperature by the addition of small amounts of certain salts, *e.g.* calcium chloride or calcium fluoride (Bredig, Zeitsch. Elektrochem. 1907, 13, 605, 610, 612; Foerster and Jacoby, *ibid.* 1909, 15, 820; Caro, Zeitsch. angew. Chem. 1910, 23, 2405).

When calcium chloride is used the reaction temperature is lowered to 700°–800°, cyanamide formation increasing with the amount of calcium chloride for a given time and temperature; but in the case of calcium fluoride, where the reaction temperature is 900°, the capacity of saturation of nitrogen is approximately the same, whether using 1, 2, 5, or 10 p.c. of calcium fluoride, the best results being obtained with 2 p.c.

If the limitation of absorption of pure carbide at temperatures under 1000° is due to the cyanamide forming a protecting layer over the carbide, which at higher temperatures melts and allows the entry of nitrogen to the rest of the carbide, then the action of calcium chloride or calcium fluoride is simply a lowering of the softening-point of this layer. There can be no doubt that the different influences exerted by calcium chloride and calcium fluoride are due to the differences in the melting-points of the salts (calcium fluoride, 1330°; calcium chloride, 780°), and these melting-points are further influenced (lowered) by admixture with carbide and cyanamide.

Calcium cyanamide, as already mentioned, passes readily into calcium cyanide when fused with certain salts, and the question naturally arises whether the use of calcium fluoride or chloride in the preparation of cyanamide would not tend to increase the amount of cyanide in the resulting product. Calcium cyanamide contains normally less than 0·1 p.c. of cyanide, and Foerster and Jacoby have proved that the amount is not influenced by the use of calcium salts in its preparation, though it is increased considerably when chlorides of the alkali metals are employed.

The work just alluded to is not only of theoretical interest, but has a practical bearing, for the process, due to Polzeniusz, and employed by the Gesellschaft für Stickstoffdünger at Westeregeln consists in treating a mixture of calcium carbide and calcium chloride (up to 10 p.c.) with nitrogen, the reaction temperature being about 700°. The resulting substance is known as 'Stickstoffkalk,' and has the approximate composition N=20; Ca=45·0; C=19·5; Cl=6·5; impurities=9 p.c. The technical importance of the process is shown by the fact that the Westeregeln company has built another large works at Knapsack, in the neighbourhood of Cologne, where 8000–10,000 tons of 'Stickstoffkalk' can be produced annually.

The above-mentioned objections to the externally heated furnace do not hold good when electric furnaces are employed, as by the North Western Cyanamide Company at Odda, in which the heating is effected within the mass and with very different results. The electric retorts proper are made of fireproof material, lined with sheet iron, and are transported between the charging hopper and the furnace by an overhead electric trolley. These retorts are placed in broad, not very high, thermally insulated drums, which do not come in contact with the heated mass. Each furnace has suitable regulating valves and small control meters. The nitrogen is delivered under pressure into the retorts, which are then heated to 800° by the passage of an electric current through a finger-thick pencil of carbon placed in the axis of the retort. Under each furnace a transformer is located converting a voltage of 11,100–50, giving 28,000 amperes. The absorption of nitrogen is allowed to proceed for from 30 to 40 hours, and saturation is made apparent by the controlling gas meter coming to a standstill. The reaction is not so strongly exothermic that when once started it will go on to completion, but it does so if the current is stopped, when a certain relation exists between the cyanamide formed and the unacted on substance, and since the heat generated is then used for the continuation of the reaction there can be no superheating, and therefore no reversal of the process. Moreover, as the reaction takes place from inside outwards, the shrinkage of material tends inwards, consequently there is a minimum wear of furnace material, and the product can be easily removed from the retort. During the process the carbide is converted into a hard mass, not unlike coke, which is removed from the furnace, after cooling by a current of air for 8–12 hours, ground to a fine powder in an air-tight plant, and then forms the 'nitrolim' of commerce.

This substance contains 57–63 p.c. of calcium cyanamide, corresponding to a total nitrogen content of 20–22 p.c.; 20 p.c. of lime; 7–8 p.c. of silicic acid, iron oxide, and alumina; 14 p.c. of carbon in the form of graphite, also very small amounts of urea, calcium carbamate, and guanidine, but the amounts of these latter substances increase when the nitrolim has been stored or exposed to the action of water vapour.

In the furnace house at Odda there are 196 electric furnaces, seven in a row, each capable of taking 300 kilogram charges and of producing about 1 ton of nitrolim per week.

Uses of nitrolim. The primary use of nitrolim, at the present time, is as a nitrogenous manure, and a considerable number of field experiments have been made on various crops in the United Kingdom. Accounts of the experiments carried out by Dr. Voelcker at Woburn for the Royal Agricultural Society are described in the Journals of that Society for the years 1908, 1909, and 1910, and the results of experiments made at Rothamsted under the direction of Mr. A. D. Hall are detailed in the annual reports issued by the Lawes Agricultural Trust for 1909 and 1910. Abstracts of numerous reports issued by various agricultural colleges and institutions will be found in the monthly summaries of agricultural experiments in Vol. XVI. and XVII. of the Journal of the Board of

Agriculture (*see* also this Journal, Vol. XIV. 652: Vol. XVI. 1006).

Nitrolim is converted by superheated steam into calcium carbonate and ammonia, but its decomposition in the soil is certainly not of such a simple nature. On exposure to moist air it spontaneously disengages small quantities of ammonia, but cyanamide is also formed,

$$CaNCN+CO_2+H_2O=CaCO_3+H_2NCN,$$

which may then be transformed into urea—

$$H_2NCN+H_2O=CO(NH_2)_2,$$

this latter substance yielding ammonium carbonate by the process of ammonic fermentation—

$$CO(NH_2)_2+2H_2O=(NH_4)_2CO_3.$$

Ammonium carbonate can be directly or indirectly assimilated by plants, indirectly after first being converted into nitric acid by the nitrifying bacteria. According to the conditions of the soil, other substances may be formed, *e.g.* basic calcium cyanamide, dicyandiamide, which latter substance, according to the opinion originally expressed by Immendorff, is toxic to plant life. It does not kill them when applied in proper quantity, but in excess it causes a considerable diminution in the crop. Analytical methods for the determination of the amounts of cyanamide and dicyandiamide have been suggested by Brioux (Ann. Chim. anal. 1910, 15, 341; *see* also Caro, Zeitsch. angew. Chem. 1910, 23, 2405).

Ammonium sulphate from nitrolim. When nitrolim is treated with superheated steam all its nitrogen is given off in the form of ammonia,

$$[C+CaNCN]+3H_2O=CaCO_3+2NH_3+C$$

and at Spandau, near Berlin, at Piano d'Orte, and at Odda plants have been constructed for the preparation of considerable quantities of ammonium sulphate by this method, in which all the lime and one-third of the necessary carbon are regained in a form suitable for the preparation of carbide.

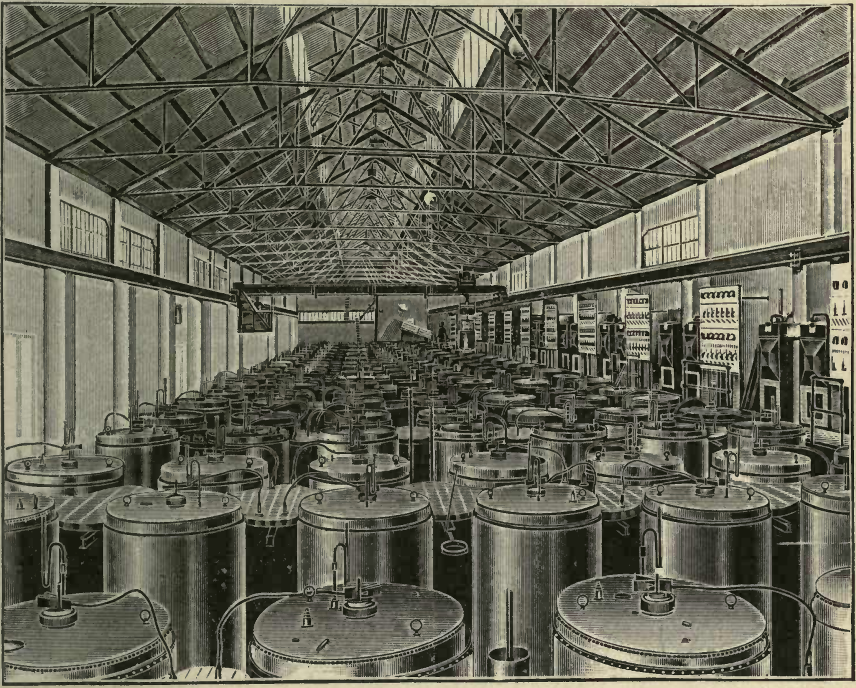


FIG. 2.

Odda Furnace House.

Nitric acid from nitrolim. The fact that ammonia can be converted into nitric acid by oxidation in presence of a catalytic agent has been known for a long time, but the desirability of making this a manufacturing process has not been given much attention until recent years; partly on account of the comparative scarcity of ammonia, and also because the action does not take place wholly in accordance with the equation $NH_3+2O_2=HNO_3+H_2O$; but other products, including elementary nitrogen, may be formed, $2NH_3+3O_2=2N_2+6H_2O$. The process has now been perfected by Ostwald, so that nitric acid is the sole product, being produced in 85–90 p.c. of the theoretical amount and of a purity rendering it suitable for use in the manufacture of explosives.

A plant has been in constant operation for some time at the works of the Lothringen Colliery Company at Gerthe, near Bochum, which is producing upwards of 1800 tons of nitric acid or 1200 tons of ammonium nitrate annually.

Carefully purified ammonia is mixed with air and passed through enamelled iron tubes to a chamber containing a special platinum catalyser, where the amount of nitric acid formed is largely influenced by the rate at which the mixture of gases is passed over the contact agent. The product passes through aluminium tubes to a condensing plant, consisting of six towers packed with broken earthenware over which nitric acid trickles and circulates continually, thus exposing a large amount of cooling surface. The acid formed contains 55 p.c. HNO_3, but further condensing arrangements can be added, whereby acid of 66 or 92 p.c. HNO_3 can be produced. The acid is at once neutralised with ammonia, and the resulting ammonium nitrate sent out into commerce.

The world's rights, other than in Westphalia and Rhineland for the production of nitric acid by this method have been taken over by the Nitrate Products Company Limited, and works will shortly be erected either near the Thames, the Scheldt, or at Odda, where the necessary ammonia will be produced directly from nitrolim.

Frank and Caro have suggested instead of platinum a mixture of thoria and ceria, and state that, though this method of making nitric acid is not the shortest, it is technically the most economical, and therefore specially applicable where power is scarce or expensive.

Cyanides from nitrolim. Cyanides are now manufactured from nitrolim by the Stickstoffwerke at Spandau, by a reaction represented by the following equation $C+CaNCN \rightleftarrows Ca(CN)_2$, and since the nitrolim contains the requisite amount of carbon it is only necessary to add some fusible material to effect this change. The raw fluxed substance is used for gold extraction, and is quite as good as pure potassium cyanide for this purpose.

It will be seen from the above equation that the process is a reversible one, and, moreover, the nitrolim $CaNCN+C \rightleftarrows CaC_2+N_2$ may form carbide at the temperature of the reaction, and this carbide would act on the cyanide as follows $Ca(CN)_2+CaC_2=2CaNCN+2C$. Exact details of the manufacture of cyanides at Spandau are not forthcoming, but 'by using appropriate furnaces, special appliances for melting and cooling the material,' the difficulties have been overcome, and cyanamide may be quantitatively converted into cyanide. Pure potassium cyanide is obtained from the resulting melt in the ordinary way, modified to suit the special conditions, and is put on the market in the form of briquettes.

Dicyandiamide, which is produced as a decomposition product of nitrolim by cold water $2CaNCN+4H_2O=2Ca(OH)_2+(H_2NCN)_2$, is used in the preparation of organic dyestuffs and in place of ammonium oxalate as a deterrent for reducing the temperature of combustion of explosives. In consequence of the high percentage of inert nitrogen (66·6 p.c.) in dicyandiamide, it evolves strong pressure in guns, but its decomposition produces little heat, unlike the other constituents of explosives, which contain more carbon and hydrogen. This is of importance with ordnance powders, *e.g.* cordite, which rapidly destroy rifling on account of the high temperature of combustion.

Various other substances may be produced by treating an aqueous solution of nitrolim with acids; among these are urea, guanidine, nitroguanidine, &c., which are manufactured at Spandau.

Ferrodur is a mixture of nitrolim and other materials used for case hardening and tempering iron and steel. It produces an extraordinary depth of hardened surface without deteriorating the material.

FORMATION OF NITRIC ACID.

Another and quite distinct type of method employed for the fixation of nitrogen involves the direct combination of nitrogen and oxygen.

The observation that the two gaseous elements, nitrogen and oxygen, are capable of direct combination was established by Priestley in 1784, who found that a slow union took place on passing electric sparks through the mixture. Cavendish confirmed and extended this observation in 1785, after having previously (1781) shown that the combustion of hydrogen in excess of air gave water containing nitric acid, and (1784) that the same result might be obtained when a mixture of hydrogen and air was exploded. But though patents were taken out by Newton and Le Febre in 1859 for the use of electricity in causing the union of nitrogen and oxygen, it was not till 1890 that the examination of the problem came into prominence.

In 1892 Sir William Crookes showed an experiment on the flame of burning nitrogen, in which air was caused to burn with the production of nitrous and nitric acids by the passage of a strong induction current, and in 1897 Lord Rayleigh published his Observations on the Oxidation of Nitrogen Gas, made in the course of the experiments which led him and Sir William Ramsay to the discovery of argon. In the actual experiment a glass vessel of 50 litres capacity contained a burning electric flame causing the combination of nitrogen and oxygen. The resulting oxides of nitrogen were absorbed by allowing a fountain of sodium hydroxide solution to play on the top of the vessel containing the arc, serving the double purpose of keeping the vessel cool and of presenting a large amount of absorbing surface. The practical result calculated from Lord Rayleigh's figures, was that 1 kilowatt hour would be required to form 50 grams of nitric acid. Lord Rayleigh pointed to the electrical difficulties of producing a steady high-tension flame for oxidising nitrogen, and though his apparatus could scarcely be made to apply to technical purposes, it is not too much to say that he was the first to show the possibility of fixing atmospheric nitrogen in an economical manner, proportionate to the electric energy expended.

It is interesting to note that an Englishman, McDougall (1899), in conjunction with Howles, was the first to establish a somewhat small, though complete, plant for the production of nitric acid from air, and, though the exploit had to be given up, the lessons learnt from it have been of the utmost importance for the solution of the problem. In 1902 Bradley and Lovejoy founded the Atmospheric Products Company (capital $1,000,000), which utilised the power of the Niagara Falls as the source of electricity; but owing to the comparative smallness of the yield (430 kilos. saltpetre per kilowatt year), coupled with the complexity of the apparatus, as well as the initial expense, the plant was closed down in 1904.

The method due to Kowalski and Moscicki resulted from the observation that the output of nitric oxide was increased by using a current of very high frequency and voltage; but it has apparently been abandoned, chiefly on account of the difficulties connected with the high voltage employed. A new form of furnace has been invented by Moscicki and is being experimented with at Fribourg, but no details of the process are at present forthcoming.

The first real practical success was attained by Birkeland, in Christiania (1903), when working in conjunction with Eyde, the Scandinavian French Company, founded by Birkeland and Eyde, established a factory at Notodden, in Norway, known as the Norsk Hydroelektrisk Kvaelstofaktieselskab. Work is carried on in the factory day and night, week-day and Sunday, some 300-400 people being employed in three shifts of 8 hours each. The electric power is derived from the Svaelgfoss, about 1½ miles up the valley, and it is interesting to note that the water falling over the Rjukanfoss, where 227,000 electric horse-power are to be developed, generates in its passage to the Hitterdal lake, 40,000 horse-power at the Svaelgfoss, 15,000 horse-power at the Lienfoss, and 20,000 horse-power at the Tinfoss, thus making a total of 75,000 horse-power at Notodden. It is calculated that the total available horse-power of Norway is 5-6,000,000, and of all Europe 50-60,000,000.

The problem of preparing nitric acid from air, has also been taken up in other countries than Norway, notably by the Badische Aniline and Soda Fabrik, who built an experimental works at Christiansand, in Norway, and in 1906, in conjunction with its two allied firms—the Farbenfabriken vorm. Fried. Bayer & Co. (Elberfeld) and the Actiengesellschaft für Anilinfabrikation in Berlin—an agreement was come to with the Scandinavian French Company, forces were united, and two new Norwegian companies were floated.

1. A power company (Kraft Aktieselskab), with a capital of 16,000,000 kronen, whose duty it is to develop and bring into harness further Norwegian waterfalls.
2. The Norsk Saltpeterverker, with a capital of 18,000,000 kronen, which is concerned in building and running Norwegian saltpetre factories making use of the power supplied by the first company.[1]

In addition to the Notodden factory belonging exclusively to the Norsk Hydroelektrisk Company, works are to be erected at Matre and Tyin falls, probably at the Vaunna Falls, and have been erected at the Rjukan Falls, near to Notodden (*cf.* Scott-Hansen, Faraday Society Lecture, May, 1911). These latter falls, where the total height for power purposes is over 1500 feet, will be harnessed in two stages, and are expected to yield 227,000 electric horse-power. The first power station is practically completed, as are the works at Saaheim, 3 miles lower down the valley. The produce of the works will be carried by a light railway, built for the purpose, from Saaheim to Rollag (18-19 miles) on Lake Tinn; thence the railway trucks are transported by steam ferry along the lake to Tinnosit (18-19 miles), where they again join the new railway to Notodden (9 miles). At present everything is taken by lighter from Notodden to Skien, where it is loaded into ocean-going vessels, but at no very far distant time the locks on the waterways and lakes between Skien and Notodden are to be increased to the necessary size to allow sea-going vessels to load up at Notodden.

Some theoretical considerations.—Sir William Crookes and Lord Rayleigh pointed out that in the union of nitrogen and oxygen electricity only works thermally, supplying the necessary energy in the form of heat, the primary product of the reaction—nitric oxide—being endothermic. But the reaction $N_2+O_2=2NO$ is incomplete, as it is reversible, and an equilibrium mixture is attained when a small but definite amount of nitric oxide is produced. Nitric oxide is not stable above 1200°, and the amount formed at this temperature is extremely small. Even at 1500° only one-tenth of a p.c. of the nitrogen in the air is converted into nitric oxide, and a very much higher temperature is necessary to bring about a reasonable degree of oxidation. Muthmann and Hofer, and especially Nernst (Zeitsch. anorg. Chem. 1906, 49, 213) and his pupils, have studied this question, and the following table gives an idea of the results obtained:—

Temperature. Absolute C	Volume per cent. NO observed	Volume per cent. NO calculated
1811	0·37	0·35
1877	0·42	0·43
2033	0·64	0·67
2195	0·97	0·98
2580	2·05	2·02
2675	2·23	2·35
3200	5·0 (about)	4·39

It is apparent that an essential of success must consist in heating the air to as high a temperature as possible, followed by very rapid cooling to a temperature at which the decomposition of the nitric oxide takes place so slowly as to be inappreciable—*i.e.* below 1000°. This rapid cooling can be more efficiently carried out on small scale experiments than on the large scale, and, consequently, the actual yields obtained in the manufacture of nitric oxide are always smaller than trial experiments would indicate. It must be remembered that every chemical change occupies a certain time, and that the equilibrium in this reaction does not occur instantaneously, so that the more rapid the cooling the more efficient the process becomes.

Further, as nitrogen and oxygen unite in the proportions $O_2:N_2$, the mixture of these gases in the atmosphere (21 p.c. oxygen, 78 p.c. nitrogen by volume) is not the most favourable for the formation of nitric oxide, and Haber and König have shown that when a mixture of equal volumes of nitrogen and oxygen are used the resulting gases contain as much as 14 p.c. of nitric oxide; but this is a point which at present

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[1] Since this article was written the Scandinavian French Company have bought all German interests in the manufacture of nitric acid from the atmosphere, which probably means that the Schönherr furnace and absorption system have not proved themselves to be better than those of Birkeland and Eyde.

would not appear to have much technical bearing, partly on account of the cost of production of the required oxygen, and partly because a very large proportion of the gases pass through the process unchanged and are lost.

It has been stated that the electric arc brings about the union of nitrogen and oxygen simply by the heat generated; but, on the other hand, many research workers have shown that nitric oxide is produced by the silent electric discharge, and Warburg (Zeitsch. Elektrochem. 1906, 12, 540; Ann. Physik. 1906, [iv.] 20, 743; 1907, 23, 203) has expressed the opinion that the kinetic energy of the gases produced by the electric discharge is directly used in the formation of nitric oxide, before the state of heat equilibrium is reached.

Holwech (Zeitsch. Elektrochem. 1910, 16, 369) has described experiments on the formation of nitric oxide by passing air through short electric arcs (0·8–4 mm.) with water-cooled anode, after the manner first proposed by Morden, whose results are confirmed. Generally speaking, the shorter the arc and the more slowly the air is supplied, the greater the concentration of nitric oxide, the maximum obtained being 9 p.c., and the yield of nitric acid 70–80 grams per kilowatt hour. As the temperature of the arc did not exceed 3000° (absolute), at which temperature the purely thermal equilibrium between oxygen, nitrogen, and nitric oxide corresponds with approximately 4 p.c. nitric oxide, the formation of the latter in these experiments must be due to collisions of ions, whereas in the low-tension arcs used industrially the phenomenon is probably purely thermal. Haber and Holwech (Zeitsch. Elektrochem. 1910, 16, 810) have also studied the formation of nitric oxide in the arc under pressure.

Many methods (*cf.* Haber and König, Zeitsch. Elektrochem. 1910, 16, 18) for causing the union of nitrogen and oxygen have been proposed in which the air is heated to a sufficiently high temperature by the combustion of certain substances, *e.g.* Haber's process, consisting in burning carbon monoxide with air under pressure, but they all suffer from the difficulty of obtaining a really high temperature, and from the fact that the oxides of nitrogen formed are mixed with enormous quantities of other gaseous products of combustion, especially water vapour (not the case in Haber's process), hence the difficulty of cooling the gases is greatly increased.

In the development of the technical problem of the oxidation of atmospheric nitrogen, only those processes have so far had any success which use electric energy as the means of bringing about the reaction, and of the various furnaces which have been proposed, those of Birkeland and Eyde, Schönherr and Pauling, may be quoted as typical examples.

The Birkeland and Eyde arc flame. In this type of furnace an electric arc is produced in a highly magnetic field.

When two pointed copper electrodes, attached to a high tension alternator, are placed horizontally between the poles of a powerful electromagnet in such a way that the terminals of the electrodes are in the middle of the magnetic field the electric arc flame assumes the form of a disc. Strictly speaking, the arc is blown into a half disc at every half period, but the impression on the eye is that of a quietly burning disc. When the length of the electric arc increases, the electric resistance becomes greater, until it becomes so great that a new electric arc starts from the points of the electrodes. The formation of these disc flames has been explained by Birkeland as follows (Faraday Society Lecture, 1906):—

‘At the terminals of the closely adjacent electrodes, a short arc is formed, thus establishing an easily movable and ductile current-conductor in a strong and extensive magnetic field, *i.e.* 4000–5000 lines of force per square centimetre in the centre. The arc thus formed then moves in the direction perpendicular to the lines of force, at first with an enormous velocity, which subsequently diminishes; and the extremities of the arc retire from the terminals of the electrodes. While the length of the arc increases, its electric resistance also increases, so that the tension is heightened until it becomes sufficient to create a new arc at the points of the electrodes. The resistance of this short arc is very small, and the tension of the electrodes, therefore, sinks suddenly, with the consequence that the outer long arc is extinguished. It is assumed that while this is taking place the strength of the current is regulated by an inductive resistance in series with the flame. In an alternating current all the arcs with a positive direction of current run one way, while all with a negative direction run the opposite way, presupposing the magnetising to be effected by direct currents. In this way a complete, luminous, circular disc is presented to the eye. When the flame is burning it emits a loud noise, from which alone an impression may be obtained

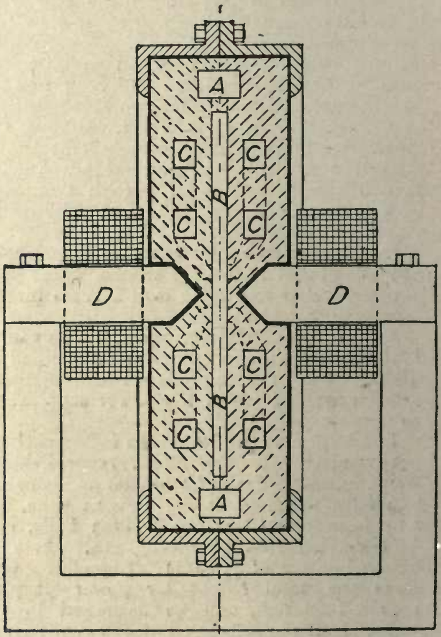


FIG. 3.

Original type of furnace.

of the number of arcs formed per second in the flame, a matter which may, however, be more minutely investigated by means of an oscillograph.'

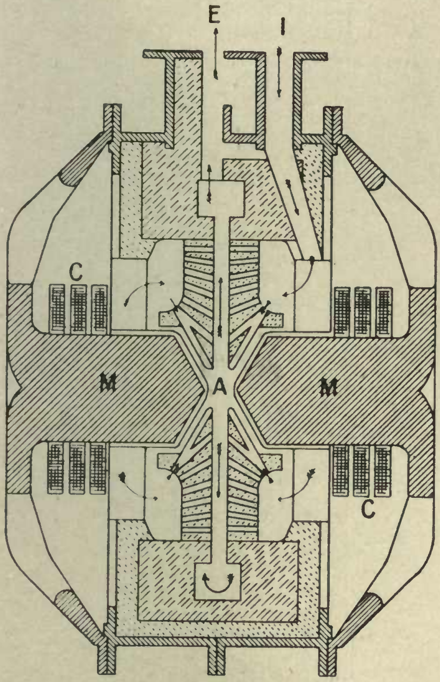


Fig. 4.
New type of furnace showing the passage of the gases.

For the purpose of utilising this alternating current disc flame (*cf.* Eyde, Journ. Royal Soc. Arts, 1909, 57, 568), it is enclosed in a special iron furnace, lined with fire-clay brick, and these linings are found to wear very well, for, in spite of the enormously high temperature of the disc flame, the temperature on the walls does not rise above 800° during normal working, owing to the cooling effect of the current of air.

The fire chamber of the furnace, B, Fig. 3, is from 5–15 cm. wide in the direction of the lines of force, and is made of perforated chamotte. It contains the electrodes, which are not shown in Fig. 3, but their position relative to the magnets D, D, may be seen in Fig. 5.

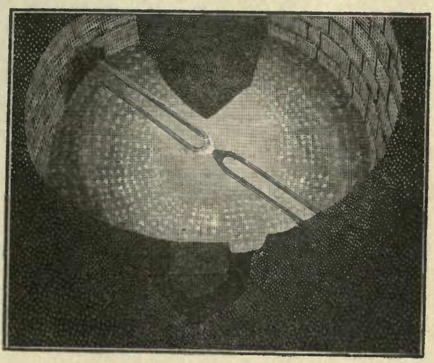


Fig. 5.
Birkeland and Eyde arc flame.

Air is driven by means of a Roots' blower to the flame along the channels marked C and through the chamotte lining of the fire chamber in an evenly distributed supply. After passing the flame in a radial direction it arrives at a peripheral channel A, whence it is conducted away to the oxidation towers. The passage of the gases through the furnace may be more easily followed by examining the section of a newer type of furnace shown in Fig. 4. The electrodes are made of 2·5 cm. thick copper tubing, through which water passes to cool

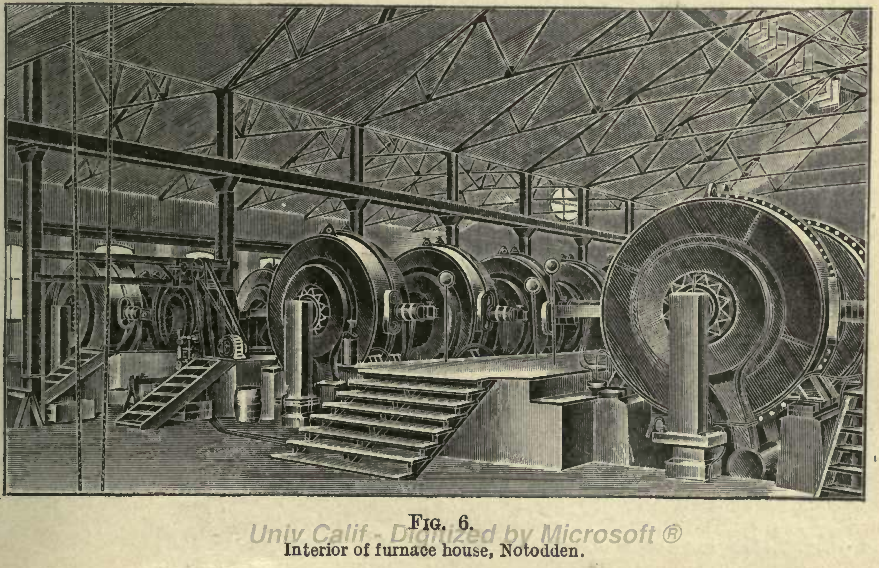


Fig. 6.
Interior of furnace house, Notodden.

them, and they are capable of taking up 1500 horse-power, giving a flame of 1·8 metres in diameter. They are exchanged and repaired after being in use for about 400–500 hours, the exchange itself taking about 15 minutes to accomplish. The temperature of the flame exceeds 3000° or, perhaps, 3500°, and the temperature of the escaping gases of which 26,000–28,000 litres pass every minute through each furnace, may vary between 800 and 1000°. In all thirty-six furnaces have been installed at Notodden, each employing 800 kilowatts, and with a working tension of 5000 volts.

Larger furnaces are being experimented with, one of 3000 kilowatts being in regular use, and it has been proved that the yield of nitric acid increases directly with increase in kilowatt power of the furnace.

The Schönherr arc flame. As already mentioned, the fixation of atmospheric nitrogen has occupied the attention of the Badische Anilin and Soda Fabrik, and as a result Schönherr, in conjunction with the engineer, Hessberger, has succeeded in bringing out an arc flame which, from the results obtained at the experimental works at Christiansand, is claimed to possess advantages over the Birkeland and Eyde flame. Whether this is so or not, has not been definitely decided, but extensive experiments are at present being carried out at Notodden to decide the point, and the new works at Rkujan will be fitted with the furnaces which, as a result of these experiments, are proved to have the greatest efficiency, when all the various manufacturing details have been fully worked out (*cf.* footnote, p. 705).

The Schönherr arc flame differs essentially from that of the Birkeland and Eyde, inasmuch as magnets and magnetic fields are done away with entirely, the arc being produced inside an iron tube of comparatively small diameter (Electrotechnische Zeit. 1909, 30, 365, 397).

The construction of the furnace is seen in Fig. 7. The iron tube A contains at its lower extremity the electrode insulated from the rest of the furnace. It consists of a strong copper body, B, pierced through its axis and cooled with water. Through the axis passes an iron bar, C, which can be pushed forward as required, and constitutes the actual electrode from which the arc starts at the point D. All the wear comes upon this bar, and at the intense heat of the arc becomes covered with a layer of melted ferric oxide, which slowly evaporates. As this proceeds the iron bar is gradually pushed forward, and its actual position can be observed through the peep-hole E. F is an igniting rod for starting the arc. The air enters the furnace as indicated, and at G passes into the iron tube through several series of tangential openings, situated one above the other, and regulated by means of the movable sleeve H. This device gives the entering air a rotary motion, which causes the arc once started from D, to travel up the tube A, and the air current is so regulated that the arc ends in the upper water-cooled portion of the iron tube, somewhere between K and M, which portion of the furnace can be observed through the peep-holes N and O. Under these circumstances the arc burns as steadily as a candle flame. The passage of the air through the furnace is indicated by the

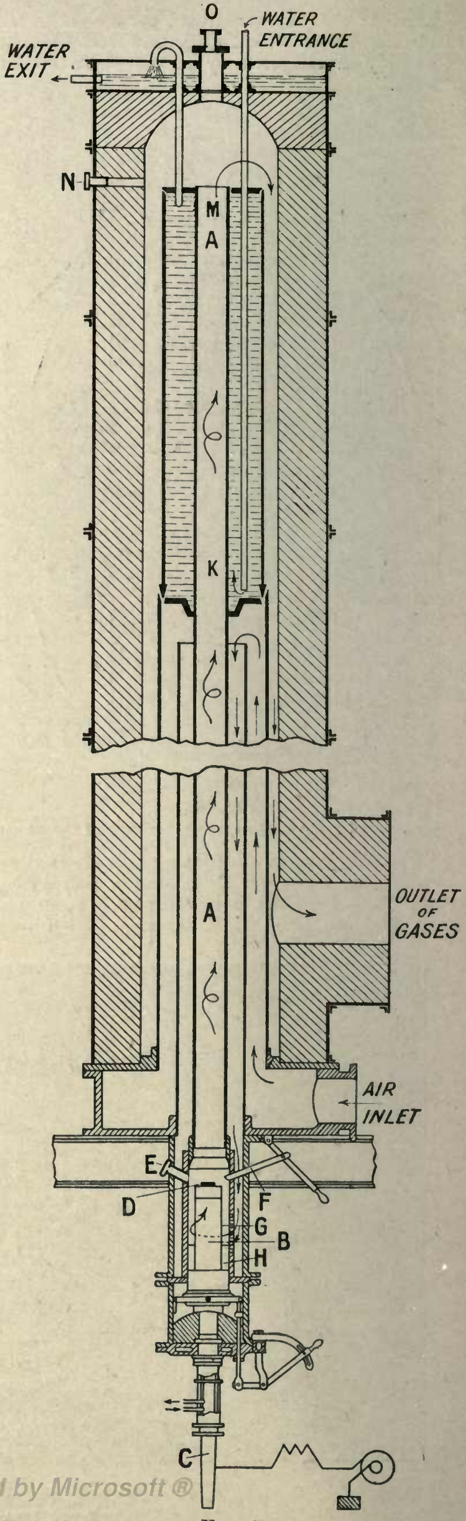


Fig. 7.

arrows, and it will be noticed that the incoming air is heated (to a temperature of about 500°) by the outgoing gases.

The furnace is connected electrically to earth, so that any part of the apparatus can be handled with impunity, except only the insulated electrode. The experimental furnaces at Christiansand are fed with about 600 horse-power at 4200 volts, and, although it appears possible to build furnaces which could consume 2000 horse-power, those regularly used will be built for 750 horse-power, and will require about 40,000 cubic feet of air every hour, and the arcs produced will be nearly 7 yards long. Though this arrangement departs from the principle of only allowing the gases to remain in contact with the arc flame for as short a time as possible (as it is obvious that the air will require a not inconsiderable time to travel from one end of the tube to the other), the gases leaving the tube contain about 2 p.c. of nitric oxide.

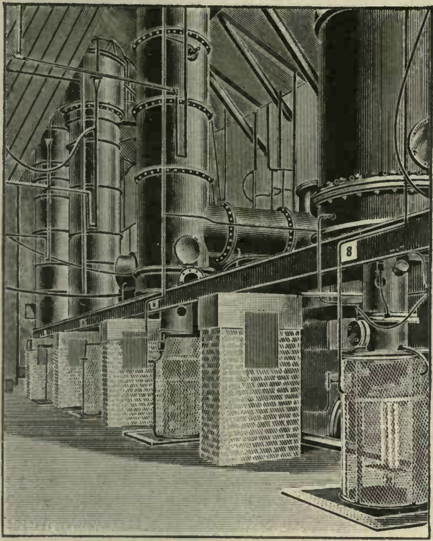


FIG. 8.
Experimental Furnaces at Christiansand Works.

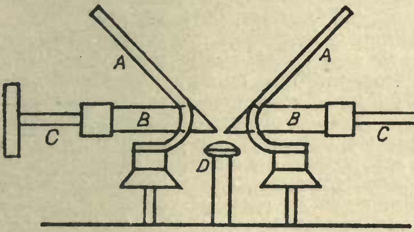


FIG 9.

The Pauling arc flame. In the production of this flame (Russ, Zeitsch. Elektrochem. 1909, 15, 544) the main electrodes AA, Fig. 9, are bent into the shape of a V, and at the lowest point of the V (40 mm. wide) they form a vertical slot, through which are introduced narrow 'lighting knives,' B, B, which can be brought together by an adjusting arrangement, CC, until only separated by a few millimetres.

The arc lighted at the narrowest portion of the spark gap, shows a tendency to rise, owing mainly to the upward pull of the hot gases, but it is interrupted at every half period of the alternating current, only to be reformed at the lowest and narrowest part of the electrodes. A high speed current of previously heated air is introduced into the V formed by the electrodes, through a nozzle, D, so shaped as to cause the air to diverge and surround the whole length of the electrodes. This device has the further effect of blowing out and broadening the arc, the flame so produced burning with remarkable steadiness from the electrical point of view, and in practice having a length of 1 metre.

The iron electrodes are cooled with water, and last approximately 200 working hours; whilst the lighting knives are very thin (so as not to interfere with the motion of the air), and consequently burn away quickly, hence the necessity for adjustment from time to time. The furnace gases are cooled by 'so-called circulation air,' which is introduced sideways into the upper portion of the flame, at a lower speed than the main air current, thus exerting a suction effect on the flame, causing it to be drawn out, and further broadened. The gases leave the furnace at a temperature of 700°–800°, and contain 1·5 p.c. of nitric oxide.

This flame is employed by the 'Salpetersäure Industrie Gesellschaft Gelsenkirchen' in their works at Patsch, near Innsbruck, where 15,000 horse-power are available. The present type of furnace (of which there are twenty-four at Patsch) takes 400 kilowatts at a tension of about 4000 volts, and 600 cubic metres of air per hour, but larger furnaces taking 1500–2000 kilowatts are being installed.

The success of this process has been sufficient to warrant the erection of a second works (10,000 horse-power) at Legnano, near Milan, and another factory (10,000 horse-power) under the auspices of 'La Société Nitrogene' at La Roche-de-Dame in the south of France, in both of which the Pauling flame is used.

A comparison of the efficiency of these three flames is given by Haber and Koenig (Zeitsch. Elektrochem. 1910, 16, 11) as follows—

	Yield. Grams HNO_3 per kilowatt-hour	Concentration p.c. NO
Pauling	60	1–1·5
Birkeland and Eyde	70	2·0
Schönherr	75	2·5

But the actual amount of nitric oxide produced is not the only factor which has to be taken into account industrially, and among many other points for consideration is whether the heat produced in the arc is sufficient, and can be utilised for the carrying out of all the necessary evaporation processes without the use of coal, as is the case at Notodden (*cf.* footnote, p. 705).

THE OXIDATION TOWERS.

The volume of air treated at the Notodden factory is between 700,000 and 800,000 litres per minute, and as it contains a little more than 1 p.c. of nitric oxide, or stated in the form in which all calculations of combined nitrogen are expressed in the works, 30 mg. HNO_3 per litre, the problem of oxidising this gas and absorbing the resulting nitrogen peroxide becomes a very difficult one, for the more dilute the gas the more difficult the operation. The gases leave the furnaces at a temperature of 800°–1000° and are cooled as rapidly as possible (to prevent decomposition of the nitric oxide into nitrogen and oxygen) by passage through a series of tubes contained in four Babcock and Wilcox boilers working at 130 lbs. pressure, and then through tubes in the evaporation tanks, this utilisation of heat having entirely done away with the use of coal in the works. At present provision has not been installed for the fullest possible economy of heat, but when this has been effected it will mean that, in addition to the amount required to evaporate approximately 120,000 litres of water daily, there will be an excess of steam sufficient to generate 1200 kilowatts of electric power.

The temperature of the furnace gases is lowered in the above mentioned manner to 200°–250°, and as the reaction $2NO+O_2=2NO_2$ commences at about 500°, nitrogen peroxide begins to form. The gases are then conducted through a special cooling apparatus composed of a series of aluminium tubes over which water is flowing, where their temperature is further lowered to 50°; then they pass into the so-called 'oxidation chambers,' consisting of vertical iron cylinders with acid-proof lining, where the conversion of nitric oxide into nitrogen peroxide continues till the composition of the gases leaving the chambers is approximately 98 p.c. of air and 2 p.c. of a mixture of 75 p.c. nitrogen peroxide and 25 p.c. nitric oxide.

The Absorption Towers.

The conversion of nitrogen peroxide into nitric acid takes place in the absorption system, consisting of three series of stone towers, whose internal dimensions are 6 × 20 metres, each series containing five towers, three acid towers and two alkali towers. The former are ten-sided, built of granite and bound together with iron rods; they have a capacity of 600 cubic metres, and are filled with broken quartz, over which water, or the dilute nitric acid formed, is constantly flowing.

The alkali towers are cylindrical, of 700 cubic metres capacity, and are made of wood, bound round with iron rods; they are filled with broken quartz, over which a solution of sodium carbonate flows. The three acid towers, in which there is a slightly diminished pressure owing to solution of oxides of nitrogen, absorb 80 p.c. of the nitrous gases, the residue (all but 2 p.c.) being extracted by passage through the two alkali towers with formation of a solution of sodium nitrite containing some sodium nitrate. The total absorption thus amounts to 98 p.c.

Centrifugal fans, constructed of aluminium, are placed on each row of towers to assist the passage of the gases on their way from the furnaces through the absorption system. The absorption of the nitrous gases takes place so that the first tower always contains the strongest acid and the weakest acid is formed in the third tower. The liquid is allowed to flow through the third tower until it attains a strength of 5 volume p.c. HNO_3, when it is pumped to the top of the second tower. Here it circulates till a strength of 20 volume p.c. HNO_3 is reached, when the acid passes to the third tower where in actual practice a 40 volume p.c. acid is formed, though 50 or even 60 p.c. HNO_3 can be produced. The system is arranged so that just as much fresh water is admitted to the third tower as corresponds in quantity with the 40 volume p.c. acid drawn from the first tower.

The main reactions taking place are the absorption of nitrogen peroxide and nitrogen trioxide, with formation of nitrous and nitric acids—

$$2NO_2+H_2O=HNO_3+HNO_2,$$
$$N_2O_3+H_2O=2HNO_2;$$

but with increasing concentration nitrous acid becomes more and more unstable in aqueous solution, so that a further process takes place, resulting in the formation of more nitric acid and nitric oxide $3HNO_2=2NO+HNO_3+H_2O$, and, under certain condition of temperature and amount of water present, the instability of nitrous acid becomes so great that only nitric acid is formed; the practical result being that in the first tower not only the strongest nitric acid, but an acid free from nitrous acid is produced. The nitric oxide passes on from tower to tower, is oxidised and absorbed according to the first of the above equations, so that the amount of nitrous acid increases in each succeeding tower, until in the fifth tower nearly pure sodium nitrite is formed. The raw product of manufacture at Notodden is the 40 volume p.c. nitric acid obtained from the first absorption tower, and an idea of the energy used compared with the combined nitrogen found, may be gathered from the statement that 1 kilowatt year gives rise to 550–600 kilos. of nitric acid (HNO_3).

Among other methods which have been proposed for the absorption of the furnace gases may be mentioned that of Schloessing, in which quicklime in the form of briquettes is treated with the gases while still hot. At first calcium nitrite is formed, but under the influence of air and nitrous gases, this is converted into nitrate, so that the final product, obtained directly, is calcium nitrate in the solid form.

At present no attempt is made further to concentrate this acid, and the four finished products exported from the works are 'Nitrate of Lime,' 'Sodium Nitrite,' 'Ammonium Nitrate,' and 'Sodium Nitrite Nitrate.'

Nitrate of lime. The raw nitric acid is run through a series of granite tanks filled with limestone, until the liquid contains not more than 0·5 p.c. of nitric acid, which is neutralised by the addition of lime. The liquid is then evaporated in vacuum pans until it has a sp.gr. 1·9, and is then run into iron drums holding 380 litres, when it sets to a hard mass and is thus exported for chemical purposes; or it is run on to shallow trays and when cold is broken up, ground to a coarse powder, and sent out as a manure in wooden casks. It varies in appearance from red-brown to black, according to the nature of the limestone from which it is made, and has the following composition—

N=13·1 p.c., corresponding to 77·0 p.c. $Ca(NO_3)_2$
Water . . . . 21·5 ,,
Insoluble in water—
Fe_2O_3; Al_2O_3; humus . 1·5 ,,

The amount produced is about 50 tons per day, or 20,000 tons per annum.

Sodium nitrite. Originally at Notodden no nitrite was prepared. Milk of lime was used as absorbent in the alkali towers, and the resulting liquid was treated with some of the dilute nitric acid from the first tower, when nitrous fumes were evolved, which were again passed into the acid absorption towers

$$Ca(NO_2)_2+2HNO_3=Ca(NO_3)_2+H_2O+NO_2+NO.$$

The nitrate of lime was worked up in the manner described above.

At the present time sodium carbonate is employed in the fourth and fifth absorption towers, and the liquid from these towers is evaporated under ordinary pressure till it has a boiling-point of 130°. It is then run into shallow tanks, allowed to crystallise, centrifuged and dried in a Bühler's drying apparatus, Fig. 10. A is an air heater, B a pump, whereby air raised to a temperature of 100° is forced through the apparatus in the direction indicated by the arrows. The sodium nitrite enters at the entrance roller C and is forced through the drying tube into the cyclone D. The air is filtered in the air filter E and escapes through the outlet tube H. The passage of the sodium nitrite through the apparatus occupies 5–7 seconds, when it collects in the cyclone and is removed directly into casks by means of the outlet roller K.

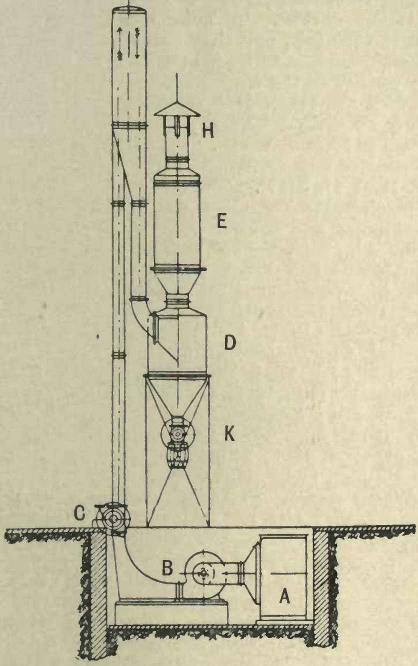


Fig. 10.

The sodium nitrite so obtained, of which about 13 tons are made per day, is a fine white crystalline powder containing 99 p.c. $NaNO_2$, the remaining 1 p.c. being composed of water, sodium nitrate, and sodium carbonate. The mother liquor from the first crop of crystals is again evaporated till it has a boiling-point of 130°, when it yields a second quantity of pure sodium nitrite. On repeating the process for the third time an 80 p.c. sodium nitrite is produced and purified by crystallisation. The mother liquor from the third crop gives rise to—

Sodium nitrite nitrate, which is a yellow, crystalline material containing about 50 p.c. sodium nitrite, 43 p.c. sodium nitrate, and 7 p.c. of moisture, together with some sodium carbonate and sodium chloride. About 2 tons are produced per day, and the substance is used instead of Chile saltpetre in the manufacture of sulphuric acid by the lead chamber process.

Nitrites may also be produced directly from the furnace gases by employing sodium carbonate or milk of lime as absorbing agents, taking care to maintain the temperature between 200° and 300°, and certain other conditions, so that during absorption the gases contain equal quantities of nitrogen peroxide and nitric oxide, when the reaction takes place in accordance with the equation $NO_2+NO+Na_2CO_3=2NaNO_2+CO_2$. The Badische Anilin and Soda Fabrik manufacture in this way at Christiansand all the sodium nitrite they require for the preparation of colouring matters at their Ludwigshafen works.

Ammonium nitrate is prepared at Notodden by neutralising the 40 p.c. nitric acid with pure ammonia liquor (sp.gr. 0·880) imported from England. The resulting liquid is filtered, evaporated in vacuum pans until it has a sp.gr. 1·35, and is then allowed to crystallise. The crystals are centrifuged and dried in a Bühler's apparatus, when they contain 99·9 p.c. NH_4NO_3. Eight tons are made per day, although 15 tons could be manufactured.

Concentrated nitric acid. As already mentioned, no attempt is made at Notodden to manufacture concentrated nitric acid, but at Gelsenkirchen the raw acid (35–40 p.c. HNO_3) is concentrated to 60 p.c. HNO_3 by utilising the heat from the furnace gases; and by distillation with concentrated sulphuric acid a 98 p.c. acid can be produced. During the process the sulphuric acid is reduced in strength to 79–80 p.c., but may again be concentrated.

Another process consists in mixing the dilute nitric acid with polysulphates at a temperature of 110°–130°, and distilling the mixture when the nitric acid is obtained in concentrated form. By raising the temperature of the residue to 250°–300° the water, which has been retained by the polysulphates, is driven off, and the regenerated polysulphates, after cooling to 110°–130°, can be used over again.

Fuller details of the processes referred to will be found in the references given in the text, or in the following:—

Die technische Ausnutsung des atmosphärischen Stickstoffs, Donath und Frenzel, 1907 (Franz Deuticke, Leipzig und Wien).

Zur Stickstoff-Frage, Huber, 1908 (Stämpfli, Bern).

Fabrication électrochimique de l'Acide Nitrique et des Composés Nitrés à l'Aide des Eléments de l'Air, Escard, 1909 (Libraire Dunod et Pinat, Paris).

Critical Considerations on the Prospective Solution of the Nitrogen Problem, Rabius (translated by A. G. Levy), 1907 (Gustav Fischer, Jena).

Etat Actuel de l'Industrie des Engrais Azotes, L. Granier, Revue Universelle des Mines, 1909, 27, 1.

Manufacture of Calcium Carbide by the Alby United Carbide Factories and the Nitrolim Works of the North-Western Cyanamide Company, Engineering, vol. 87.

Engrais Nitrés Synthétiques, Ragondet, Annales de Gembloux, May, 1909 (M. Weissenbruch, Bruxelles).

Utilisation of Atmospheric Nitrogen in the Production of Calcium Cyanamide, Frank, Trans. Faraday Society, 1908.

Caro, Chemical Trade Journal, 1909, 44, 621.

Haber and Koenig, Zeitsch. Elektrochem. 1910, 16, 17. A. C.

NITROGLYCERIN *v.* Explosives.

NITROHYDROCHLORIC ACID *v.* Aqua regia.

NITROMAGNITE or **DYNAMAGNITE** *v.* Explosives.

NITROMETER *v.* Analysis.

NITROPHENINE YELLOW *v.* Primuline and its Derivatives.

NITROPHENOLS AND THEIR HOMOLOGUES. Phenol may be nitrated very readily, and to produce the mono-nitro derivatives it is sufficient to treat it with dilute nitric acid in the cold. The *ortho-* and *para*-nitrophenols, together with some tarry matter, are thus formed. The *ortho-* compound is separated by steam distillation, whilst the non-volatile *para-* compound is purified by repeated crystallisations from xylene (Hofmann, Annalen, 1857, 103, 347; Fritsche, *ibid.* 1859, 110, 150; Schall, Ber. 1883, 16, 1901; Neumann, *ibid.* 1885, 18, 3320).

If the nitric acid is vigorously stirred, during and for about half an hour after the addition to it of the phenol, an 18 p.c. yield of *p*-nitrophenol is obtained without any formation of tar. The best yield is obtained at 25°. Below 4° nitration cannot be effected (Hart, J. Amer. Chem. Soc. 1910, 32, 1105; *v.* Pictet, J. Soc. Chem. Ind. 1911, 683).

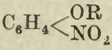
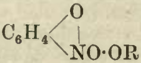
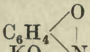
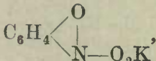
Phenol may be first condensed with an aromatic sulphonic chloride in presence of an alkali, the ester so formed, on nitration, yields, without formation of tarry products, a dinitro derivative, which on hydrolysis with an aqueous solution of a caustic alkali, yields the alkali salt of *p*-nitrophenol, together with that of *o*-nitrotoluene-*p*-sulphonic acid (Eng. Pat. 24193, 1895; J. Soc. Chem. Ind. 1897, 40). *o*-Nitrophenol, almost free from the *p*-isomeride, may be obtained by converting phenol into the *p*-sulphonate, then nitrating it with sodium nitrate and sulphuric acid; on hydrolysis the HSO_3 group is removed (Paul, *ibid.* 1897, 62); or by treating nitro-benzene with potash (Wohl, Ber. 1899, 32, 3486).

m-Nitrophenol is not formed by the direct nitration of phenol, but it may be prepared by boiling diazotised *m*-nitraniline with water (Bantlin, *ibid.* 1878, 11, 2100; Henrique, Annalen, 1882, 215, 323).

The polynitrophenols are obtained by nitrating phenol with concentrated nitric acid, usually in the presence of sulphuric acid; by nitrating the lower nitro compounds or their sulphonates; by treating the hydrocarbon with nitric acid in presence of mercury or mercury compounds, in which case the nitro and hydroxyl groups are introduced simultaneously into the benzene nucleus (Eng. Pat. 17521; D. R. P. 214045; J. Soc. Chem. Ind. 1907, 1194; *ibid.* 1909, 1167; Chem. Zentr. 1908, i. 1005); and by other methods (Wender, Gazz. chim. ital. 1889, 19, 222; Oliveri-Tortorici, *ibid.* 1898, 28, 306; Reverdin and de la Harpe, Chem. Zeit. 1891, 16, 45; Frankland and Farmer, Chem. Soc. Trans. 1901, 1356; Robertson, *ibid.* 1902, 1475; Lobry de Bruyn, Rec. trav. chim. 13, 153; Pinnow and Koch, Ber. 1897, 30, 2857; Reverdin and Bucky, *ibid.* 1906, 39, 2679; Matuschek, Chem. Zeit. 1905, 29, 115; D. R. P. 91314; Frdl. iv. 40).

The nitrophenols are colourless or yellow crystalline substances. They are more acidic than the phenols, and they decompose alkaline carbonates. The nitrophenols may be reduced very readily to the corresponding amines, some of which are themselves valuable dyes, or are readily condensed with suitable aromatic compounds to form dyestuffs. By partial reduction nitroamines may be obtained (Hofer and Jakob. Ber. 1908, 41, 3187). The use of nitrophenols as precipitants for alkaloids is discussed by Rosenthäler and Görner (Zeitsch. anal. Chem. 1910, 49, 340). The constitution of the nitrophenols has given rise to an important series of investigations by Hantzsch and others (Ber. 1902, 35, 1001, 1005; *ibid.* 1906, 39, 1073; *ibid.* 1907, 40, 330, 1556; Zeitsch. physikal. Chem. 1908, 61, 227; *see* also Rabe, *ibid.* 1901, 38, 175; Witt, Ber. 1876, 9, 522; Korczynski, *ibid.* 1909, 42, 167; Chem. Zentr. 1910, ii. 384; Scharwin, J. Russ. Phys. Chem. Soc. 1910, 42, 237; Seyewetz and Poizat, Compt. rend. 1909, 148, 1110; Baly, Edwards and Stewart, Chem. Soc. Trans. 1906, 514).

Whilst themselves colourless, or only faintly coloured, they give rise to two series of highly-coloured alkali salts—yellow and red, and on this account they were regarded as pseudo-acids. This view has been confirmed by the preparation of two series of ethers. The colourless phenol ethers are obtained under ordinary conditions of alkylation, and have the formula $NO_2\cdot C_6H_4OR$. The isomeric red ethers are much more difficult to prepare, owing, it is supposed, to their instability and to the ease with which they change into their colourless isomeride. The red ethers are formed by the action of alkyl iodide on the silver salts of the nitrophenols. The materials must, however, be absolutely pure and dry, and the reaction is commenced at 0° and then raised to ordinary temperature. The red ethers, which have not been obtained quite pure, melt at least 20° below the colourless ethers; they are much more soluble in all solvents, giving coloured solutions, and on standing alone, and more readily in solvents or in the presence of hydrochloric acid, change into the colourless isomerides. The smallest trace of water hydrolyses them, forming the free nitrophenol, and this explains why, when a silver salt of a nitrophenol is alkylated without special precautions, free nitrophenol is often produced.

To explain the formation of the coloured salts and ether, it is supposed that nitrophenols and their derivatives, and also their homologues, may exist in two tautomeric modifications  $C_6H_4{<}\begin{matrix}OR\\NO_2\end{matrix}$ and  $C_6H_4\begin{matrix}/O\\|\\\backslash NO\cdot OR\end{matrix}$ (where R=H, a metal, or an alkyl radicle), of which the first is colourless, the second coloured; thus the constitution of the free colourless nitrophenols corresponds to the first formula, whilst the coloured nitrophenols, being much paler than their salts, correspond partly to the first, partly to the second formula. The coloured ethers correspond to the second formula, whilst the metallic salts, forming two series of coloured salts, have the two formulæ  $\underset{KO_2}{C_6H_4}\begin{matrix}/O\\|\\\backslash N\end{matrix}$ and  $C_6H_4\begin{matrix}/O\\|\\\backslash N{-}O_2K\end{matrix}$, of which the latter probably corresponds with the red salts, the former with the yellow salts. The orange salts sometimes obtained are probably solid solutions of the yellow and red salts (Hantzsch, Ber. 1907, 40, 330).

o-**Nitrophenol** $C_6H_4(NO_2)OH$ forms pale yellow needles or prisms, m.p. 44°, b.p. 214°, sp.gr. 1·447 (Schröder, Ber. 1879, 12, 563; Merz and Ris, *ibid.* 1886, 19, 1749). It has an aromatic smell, is sparingly soluble in cold water, more readily so in hot water, also in alcohol or ether. It behaves as a much stronger acid than the *p*- and *m*-isomerides.

m-**Nitrophenol** forms thick yellow crystals, m.p. 96°, b.p. 194°/70 mm. (Bantlin, *l.c.*); m.p. 93°, sp.gr. 1·827 at 19° (Fels, Zeitsch. Krystalographie, 1900, 32, 374). It is non-volatile in steam, and it is readily oxidised by Caro's reagent on warming, yielding 3- and 4-nitro-catechols, a part of it, however, being decomposed (Bamberger and Czerkis, J. pr. Chem. 1903, [ii.] 68, 480).

p-**Nitrophenol** forms colourless needles, m.p. 114°. It is non-volatile in steam, yields *p*-aminophenol when boiled with zinc-dust and water, and when electrolysed in sulphuric acid forms *p*-aminophenolsulphonic acid. It reacts with alkali sulphide in presence of a copper salt, forming a green dyestuff (D. R. P. 101577; Chem. Zentr. 1899, i. 1091). *p*-Nitrophenol has been proposed for use as an indicator instead of methyl orange (Spiegel, Zeitsch. angew. Chem. 1904, 17, 715; J. Soc. Chem. Ind. 1904, 182; Goldberg and Naumann, *ibid.* 1903, 928). When heated with aqueous ammonia under pressure both the *o*- and the *p*-isomerides yield the corresponding nitraniline (Merz and Riz, *l.c.*). By mixing any of the mononitrophenols with quinine in presence of water, compounds are said to be obtained which are almost insoluble in water or dilute acid, and which may be used as internal antiseptics (U. S. Pat. 1005137 of 1911; J. Soc. Chem. Ind. 1911, 1333).

The nitrophenols may be sulphonated by treating them with fuming sulphuric acid, or in the case of the *ortho*- compound by chlorosulphonic acid. Mercury accelerates the reaction (Post, Annalen, 1880, 205, 38; Nietzki and Lerch, Ber. 1889, 21, 3221; Gnehm and Knecht, J. pr. Chem. 1906, [ii.] 73, 519; *ibid.* 74, 92).

The sulphonic derivatives may also be formed by nitrating the required phenolsulphonic acid (Post and Stuckenberger, Annalen, 1880, 205, 45; Post, Ber. 1874, 7, 1323; D. R. P. 27271; Frdl. i. 324; J. Soc. Chem. Ind. 1885, 203; *see* also D. R. P. 114529; Chem. Zentr. 1900, ii. 1000).

Like phenol itself, the mono- as well as the polynitro compounds form a number of metallic salts, ethers, and other compounds.

2 : 3-**Dinitrophenol** (Bantlin, *l.c.*) has m.p. 144°.

2 : 4-**Dinitrophenol** forms rhombic prisms, m.p. 114°–115° (Gauhe, Annalen, 1868, 147, 67; Pinnow, *l.c.*). It is much more poisonous than picric acid. When warmed with sulphur and sodium sulphide it gives a black dye for cotton (D. R. P. 98437; Chem. Zentr. 1898, ii. 912). Ostromisslensky has prepared another 2 : 4-**dinitrophenol**, m.p. 85·1° (J. Russ. Phys. Chem. Soc. 1906, 38, 1351).

2 : 5-**Dinitrophenol**, yellow needles, m.p. 108°, volatile in steam (Reverdin and Bucky, *l.c.*); m.p. 104° (Bantlin).

2 : 6-**Dinitrophenol**, light yellow, fine needles, m.p. 63°–64° (Hübner, Babcock and Schaumann, Ber. 1879, 12, 1346).

3 : 4-**Dinitrophenol**, long silky colourless needles, m.p. 134° (Bantlin, *l.c.*).

3 : 5-**Dinitrophenol** has m.p. 122° (Lobry de Bruyn, *l.c.*; Heller, Ber. 1909, 42, 2191).

2 : 4 : 6-**Trinitrophenol**, *v.* Picric acid.

2 : 4 : 5-(β-)**Trinitrophenol**, glistening needles, m.p. 96° (Henrique, *l.c.*).

2 : 3 : 6-(γ-)**Trinitrophenol**, small needles, m.p. 117°–118° (Henrique, *l.c.*).

2 : 3 : 5-**Trinitrophenol** is obtained by boiling diazotised trinitroaminophenol with absolute alcohol until nitrogen ceases to be evolved. It forms yellow needles, m.p. 119°–120°, and becomes ochreous and opaque when dried at 100°. It dyes silk and wool with a more orange shade than picric acid (Meldola and Hay, Chem. Soc. Trans. 1909, 1382).

2 : 3 : 4 : 6-**Tetranitrophenol**, golden-yellow needles, m.p. 130°, sometimes with explosion (Nietzki and Blumenthal, Ber. 1897, 30, 184); m.p. 140° (Blanksma, Rec. trav. chim. 1902, 21, 254). It dyes wool and silk an intense red-yellow colour. When boiled with water it forms trinitroresorcinol.

2 : 3 : 5 : 6-**Tetranitrophenol** is known in the form of its ethyl ether, m.p. 115° (Blanksma, *ibid.* 1905, 24, 40).

Pentanitrophenol $C_6(NO_2)_5OH$, m.p. 190°, when boiled with water is transformed into trinitrophloroglucin (Blanksma, *ibid.* 1902, 21, 254).

The polynitrophenols, when treated with potassium cyanide, yield the corresponding purpuric acids (Borsche and Böcker, Ber. 1903, 36, 4357; *ibid.* 1904, 37, 1843, 4388).

Nitraminophenols may be obtained by nitrating acetaminophenols, or, better, acetaminophenol acetate or similar compounds, then eliminating the acetyl group by hydrolysis (Reverdin and Dresel, *ibid.* 1904, 37, 4452), and also by other methods.

4-Nitro-2-aminophenol is obtained by the action of ammonium sulphide on 2 : 4-dinitrophenol. Crystallises with 1 mol. H_2O, m.p. 80°–90°, the anhydrous salt has m.p. 142°–143° (Post and Stuckenberg, *l.c.*; Kehrmann and Gauhe, Ber. 1897, 30, 2132).

5-Nitro-2-aminophenol may be prepared by nitrating the ethenyl derivative of *o*-aminophenol in the cold with a mixture of equal parts of nitric (40°B.) and sulphuric (monohydrate) acids; the product is then decomposed with concentrated hydrochloric acid. It forms yellow needles, m.p. 201°–202°. It yields fast bluish- and greenish-black azo dyes for wool (Eng. Pats. 7910, 7910A, 1905; D. R. P. 165650; J. Soc. Chem. Ind. 1905, 1298).

6-Nitro-2-aminophenol forms red needles, m.p. 110°–111° (Post and Stuckenberg, *l.c.*).

For a number of other mononitro-amino- and acetaminophenols, *see* Hähle, J. pr. Chem. 1891, [ii.] 43, 62; Kehrmann and Gauhe, Ber. 1898, 31, 2403; Meldola and Stephens, Chem. Soc. Trans. 1906, 925; *see* also J. Soc. Chem. Ind. 1905, 796).

When *p*-aminophenol is dissolved in a small quantity of glacial acetic acid, and acetic anhydride is added, the amino group is acetylated. To the solution at 0°, twice the calculated quantity of nitric acid (sp.gr. 1·5), diluted with twice the volume of acetic acid, is added in small portions at a time. The product is then poured into water and neutralised with ammonia, 2 : 6-*dinitro*-4-*acetaminophenol* is thus formed. It forms dense ochreous needles, m.p. 182° (Meldola and Hay, Chem. Soc. Trans. 1905, 1203).

When converted into its sodium derivative and reduced with aqueous sodium sulphide, it yields 2-*nitro*-6-*amino*-4-*acetaminophenol*

$$NHAc{\cdot}C_6H_2(NO_2)(NH_2)OH,$$

brownish-red needles, m.p. 190°, which forms an orange-yellow diazo derivative when treated with nitrous acid (Cassella & Co. D. R. P. 172978, 1906).

4 : 6-Dinitro-2-aminophenol (*Picramic acid*) may be prepared by adding zinc-dust and ammonia solution to a warm aqueous or methyl alcoholic solution of picric acid until the solution is distinctly alkaline. The mixture is boiled for an hour with occasional addition of ammonia, after which it is filtered, the excess of ammonia evaporated on the water-bath, and a slight excess of acetic acid is added. It is then evaporated to dryness, and the residue is recrystallised from boiling water. The acid forms fine red crystals, m.p. 165°, which burn, but do not detonate on sudden heating. It does not precipitate albumin, albumoses, peptone, or alkaloids. Its alkali salts yield deep red solutions, which are turned yellowish-green by acids, and may, therefore, be used as indicators in alkalimetry (Frébault and Aloy, J. Pharm. Chim. 1904, 20, 245; Bull. Soc. chim. 1905, [iii.] 33, 495; Borche and Heyde, Ber. 1905, 38, 3938).

Acetic anhydride reacts with sodium picramate at 60°, and the resulting product, when reduced at 80° by sodium sulphide, and then treated with acid, yields

4-Nitro-2-amino-6-acetaminophenol, which is hydrolysed by acids to 4-*nitro*-2 : 6-*diaminophenol*, the diazonium compound of the latter yielding azo dyes (Cassella, D. R. P. 161341; D. R. PP. 112819, 113241, 111327, 112280, 110711; Chem. Zentr. 1900, ii. 463, 509, 512, 547, 698).

2 : 6 Dinitro-4-aminophenol (iso*picramic acid*) forms thin yellow needles, m.p. 170° (decomp.). The corresponding acetamino derivative, treated with alkali sulphides, forms a compound which readily yields azo dyestuffs for wool, very fast to washing, milling, and light (Reverdin and Dresel, Ber. 1905, 38, 1593; Eng. Pat. 24409, 1903; J. Soc. Chem. Ind. 1904, 1025).

For other dinitroaminophenols, *see* Reverdin and Dresel, *l.c.*; Reverdin, Ber. 1907, 40, 2848; *ibid.* 1909, 42, 1523; Reverdin and Delétra, *ibid.* 1906, 39, 125; Meldola and Hay, Chem. Soc. Trans. 1907, 1481.

2 : 3 : 5-Trinitro-4-acetaminophenol

$$C_6H_2(OH)(NO_2)_3NH{\cdot}COCH_3$$

is obtained by nitrating diacetyl-*p*-aminophenol with cold fuming nitric acid, the mononitrodiacetyl derivative thus obtained is then further nitrated by dissolving it in a mixture of fuming nitric and strong sulphuric acid, when the above trinitro compound is formed. It crystallises in yellow needles, m.p. 178°–179° (decomp.), and owing to the great mobility of the meta- NO_2 group it forms a remarkably active synthetic agent (Meldola, Chem. Soc. Trans. 1906, 1935).

The acetyl group may be removed by dissolving it in concentrated sulphuric acid at the ordinary temperature, then placing the containing vessel in boiling water for a few minutes until a drop of the liquid, mixed with cold water, gives a red precipitate—if the latter is brown the reaction has gone too far and decomposition has set in. The liquid is cooled and poured on to ice. The *trinitroaminophenol* forms deep red needles decomposing at about 145°. It may be diazotised in the cold with sulphuric acid and sodium nitrite (Meldola and Hay, *ibid.* 1909, 1378; Meldola and Kuntzen, *ibid.* 1033; *ibid.* 1910, 444; *ibid.* Proc. 340).

NITROCRESOLS.

The cresols are directly nitrated with difficulty, a small yield of the mononitro products being obtained (Staedel, Annalen, 1883, 217, 49; Khotinsky and Jacopson-Jacopmann, Ber. 1909, 42, 3097). The alkali salts of their sulphonic acid derivatives may be converted into their mononitro derivatives much more readily; the HSO_3 group in the latter cannot, however, be eliminated, but by reduction they may be converted into the corresponding amino compounds which may be readily decomposed into aminocresols and sulphuric acid (Schultze, Ber. 1887, 20, 410).

3-Nitro-*o*-cresol

$$C_6H_3Me(OH)NO_2, (Me : OH : NO_2=1 : 2 : 3)$$

is obtained together with the 5-nitro derivative by dropping a glacial acetic acid solution of *o*-cresol into a cold mixture of 3 parts of nitric acid (sp.gr. 1·4) and 6 of acetic acid (Hirsch, *ibid.* 1885, 18, 1512; Noelting and Wild, *ibid.* 1339). It forms long yellow prisms, m.p. 69·5°, volatile in steam.

4-Nitro-*o*-cresol (Me : OH : NO_2=1 : 2 : 4) is best prepared by diazotising 4-nitro-2-toluidine in 10 p.c. sulphuric acid at 0°, and then dropping the product into boiling dilute sulphuric acid (Ullmann and Fitzenham, *ibid.* 1905, 38, 3790); it forms large yellow crystals, m.p. 118°.

5-Nitro-*o*-cresol, prepared by treating 5-nitro-2-toluidine with sodium nitrite and sulphuric acid, or with concentrated caustic soda, forms fine, white, silky needles which, when dried at 100°, have m.p. 94·6°–95° (Neville and Winther, *ibid.* 1882, 15, 2978).

6-Nitro-*o*-cresol, m.p. 142°–143°, having an intensely sweet smell, is formed from the corresponding nitrotoluidine by treating it with sodium nitrite and sulphuric acid (Ullmann, *ibid.* 1884, 17, 1961).

2-Nitro-*m*-cresol ($CH_3 : OH : NO_2 = 1 : 3 : 2$) is obtained, together with the 4- and 6-nitro derivatives, by nitrating *m*-cresol. It is volatile in steam and soluble in water, but has not been obtained pure. Its methyl ether forms colourless crystals, m.p. 88°–89° (Khotinsky and Jacopson-Jacopmann, *l.c.*).

4-Nitro-*m*-cresol, yellow crystals, m.p. 56°, is formed as above. It is volatile in steam, but insoluble in water, and can thus be separated from the 2-nitro derivative.

5-Nitro-*m*-cresol, m.p. 60°–62°; 90°–91° when anhydrous, is obtained by treating 5-nitro-*m*-toluidine with nitric acid (Neville and Winther, *l.c.*).

6-Nitro-*m*-cresol, m.p. 129°, is obtained as above. It is volatile in steam, and can thus be separated from the 2- and 4-nitro derivatives.

2-Nitro-*p*-cresol ($CH_3 : OH : NO_2 = 1 : 4 : 2$) may be obtained by boiling diazotised 2-nitro-*p*-toluidine (Neville and Winther, *l.c.*), but it is best prepared by nitrating *p*-tolyl carbonate $CO(OC_7H_7)_2$ (m.p. 117°); the 2-nitro-*p*-tolyl carbonate $CO(OC_7H_6NO_2)_2$ thus obtained forms yellow needles, m.p. 143°–144°, which, when hydrolysed with boiling aqueous caustic soda, or sodium carbonate, yields the 2-nitro-*p*-cresol, yellow prisms, m.p. 77° (D. R. P. 206638; J. Soc. Chem. Ind. 1909, 328).

With fuming sulphuric acid 2-nitro-*p*-cresol yields acetyl acrylic acid (Schultz and Löw, Ber. 1909, 42, 577).

3-Nitro-*p*-cresol, formed by treating 3-nitro-*p*-toluidine with nitric acid or concentrated caustic soda, forms yellow needles, m.p. 33·5°, b.p. 125°/22 mm., 114·5°/7·5 mm., sp.gr. 1·2399 at 38·6°/4° (Noelting and Wild, *l.c.*; Brasch and Freyss, Ber. 1891, 24, 1960).

3 : 5-Dinitro-*o*-cresol
($CH_3 : OH : NO_2 : NO_2 = 1 : 2 : 3 : 5$)
forms long yellow crystals, m.p. 86°–87° (Cazeneuve, Bull. Soc. chim. 1900, [iii.] 17, 201; Noelting and Salis, Ann. Chim. Phys. 1885, [vi.] 4, 105). Heated with ammonia at 180° it yields dinitrotoluidine (Barr, Ber. 1888, 21, 1543). It acts as a violent poison (Weyl, *ibid.* 1887, 20, 2835).

2 : 6-Dinitro-*p*-cresol, yellow needles, decomposes when heated, forming a violet sublimate (Knecht, Annalen, 1882, 215, 87).

3 : 5-Dinitro-*p*-cresol, m.p. 85°, is obtained by nitrating *p*-cresol in acetic acid solution with strong nitric acid (Frische, *ibid.* 1884, 224, 138; Staedl, *l.c.*; Chamberlain, Amer. Chem. J. 1897, 19, 533), and by a variety of other methods.

2 : 4 : 6-Trinitro-*m*-cresol, formed when *m*-cresol is nitrated, long, yellow needles, m.p. 109·5° (Murmann, Chem. Zentr. 1904, ii. 436; Noelting and Salis, Ber. 1881, 14, 987; and *l.c.*).

Tetranitro-*m*-cresol $CH_3{\cdot}C(OH)(NO_2)_4$, m.p. 175°, is converted into trinitroorcinol by boiling water (Blanksma, Proc. K. Akad. Wetensch, Amsterdam, 1906, 9, 278).

The relative sensitiveness to the shock of a falling weight of various metallic salts of trinitrophenol and cresol is discussed by Kast (Zeitsch. ges. chiess. and Sprengstoffw. 1911, 6, 7, 31, 67).

Dinitrocresol (Victoria yellow) is sometimes used for colouring food. It may be detected by digesting the finely-powdered sample of macaroni or other food with alcohol, filtering, evaporating to a small bulk and tasting—if it is bitter, picric acid is probably present. Then warm the solution for a few minutes with a little pure hydrochloric acid, cool and drop a fragment of zinc into the basin. After standing in the cold for ½–2 hours the solution will become bright blood-red if dinitrocresol is present, and a beautiful blue in the presence of picric acid (Fleck, J. Soc. Chem. Ind. 1887, 50).

Like the nitrophenols, the nitrocresols also form metallic, amino, and a variety of other derivatives.

2-Ethylphenol or phlorol forms one *mononitro*-derivative, a yellow oil, b.p. 212°–215°, and one *dinitro*- derivative (Béhal and Choaz, Bull. Soc. chim. 1894, [iii.] 11, 309).

NITROXYLENOLS.

3 : 5-Dinitro-1 : 2 : 4-xylenol
$C_6H(OH)(NO_2)_2(CH_3)_2(CH_3{:}CH_3{:}OH{:}NO_2{:}NO_2) = 1 : 2 : 4 : 3 : 5$
forms yellow needles, m.p. 126°–127° (Noelting and Pick; Ber. 1888, 21, 3158).

5-Nitro-1 : 3 : 4-xylenol also forms yellow needles, m.p. 72° (Hodgkinson and Limpach, Chem. Soc. Trans. 1893, 105; Francke, Annalen, 1897, 296, 199).

Symmetrical xylenol has been nitrated by dissolving 5 grms. in 50 c.c. of equal parts of ordinary, and of 20 p.c. fuming, sulphuric acid, the solution is warmed for 15 mins. on the water-bath. After cooling 11·6 grms. of nitric acid of sp.gr. 1·415 are added, the whole, after standing, is warmed on the water-bath, and finally poured into 300 c.c. of water. The precipitate is filtered, washed, and dissolved in boiling water, and the potassium salt of the symmetrical trinitroxylenol is precipitated by adding potassium chloride in excess to the hot solution. It forms brown-yellow crystals, from which the free phenol may be liberated by boiling dilute hydrochloric acid. It forms colourless crystals, m.p. 104°, resembles picric acid in many respects, but is less soluble in water than picric acid and dyes wool in redder shades, whereas the corresponding trinitrocresol gives greenish-yellow colours. Unlike both these substances, it also gives no reaction with potassium cyanide (Knecht and Hibbert, Ber. 1904, 37, 3477; Blanksma, Rec. trav. chim. 20, 422).

Carvacrol forms a 5-*mononitro derivative*
$CH_3(C_3H_7)C_6H_2{\cdot}NO_2(OH)(CH_3 : C_3H_7 : NO_2 : OH = 1 : 4 : 5 : 2)$,
yellow crystals, m.p. 77°–78° (Mazara and Plancher, Gazz. chim. ital. 1891, 21, ii. 155), m.p. 87° (Kehrmann and Schön, Annalen, 1900, 310, 109); and a 3 : 5-*dinitrocarvacrol*, yellow needles, m.p. 117° (Dahmer, *ibid.* 1904, 333, 346).

Thymol yields an almost colourless 6-*nitrothymol*
$CH_3(C_3H_7)C_6H_2(OH)NO_2(CH_3 : C_3H_7 : OH : NO_2 = 1 : 4 : 3 : 6)$,
m.p. 140° (Kehrmann and Schön, *l.c.* 107); a

2 : 6-*dinitrothymol*, m.p. 55° (Oliveri and Tortorici, Gazz. chim. ital. 1898, 28, i. 308).

2 : 5 : 6-*Trinitrothymol*, yellow needles, m.p. 111° (Maldotti, *ibid.* 1900, 30, ii. 365).

NITROCATECHOLS.

3-Nitrocatechol

$C_6H_3(OH)_2NO_2(OH : OH : NO_2 = 1 : 2 : 3)$, obtained by nitrating an ethereal solution of catechol with fuming nitric acid, forms long yellow needles, m.p. 86°, non-volatile in steam (Wesselsky and Benedikt, Monatsh. 1882, 3, 386).

4-Nitrocatechol, yellow needles, m.p. 174°, may be prepared by treating catechol with potassium nitrite and dilute sulphuric acid (Benedikt, Ber. 1878, 11, 362), and by other methods (D. R. P. 81298 ; Frdl. iv. 121 ; Dakin, Amer. Chem. J. 1909, 42, 490). It is also non-volatile in steam.

3 : 5-**Dinitrocatechol**, yellow needles, m.p. 164°, is formed by nitrating catechol diacetate with fuming nitric acid (Nietzki and Moll, Ber. 1893, 26, 2183).

NITRORESORCINOLS.

2-Nitroresorcinol

$C_6H_3(OH)_2NO_2(OH : OH : NO_2 = 1 : 3 : 2)$ may be prepared by adding 22 grms. of resorcinol to 150 c.c. of fuming sulphuric acid (sp.gr. 1·875), and warming on the water-bath; the 2 : 4-disulphonic acid thus formed is then nitrated with a mixture of 12·6 grms. nitric acid (sp.gr. 1·52), and 40 grms. of the fuming sulphuric acid. After 12 hours the mixture is poured into water and distilled with steam (D. R. P. 145190 of 1904). It forms crystals, m.p. 85°, and, when reduced with tin and hydrochloric acid, yields the corresponding amino derivative, whilst if reduced with iron and acetic acid, it forms chiefly benzoylamino resorcinol

$$C_6H_3(OH)_2NH(COC_6H_5),$$

m.p. 187° (Kauffmann and Pay, Ber. 1906, 39, 323). It yields a nitroso, halogen, metallic, and other derivatives (Kauffmann and Franck, *ibid.* 2722 ; *ibid.* 1907, 40, 3999).

2-Nitroresorcinol may be coupled with diazonium chloride and azo dyes have been prepared from the resulting product (Kauffmann and Pay, *l.c.*).

4-**Nitroresorcinol**, m.p. 115°, is formed like the 2-nitro derivative (Ehrlich, Montash. 1887, 8, 426 ; Hemmelmayr, *ibid.* 1905, 26, 185).

5-**Nitroresorcinol** has m.p. 158° (Blanksma, Proc. K. Akad. Wetensch, Amsterdam, 1906, 9, 278).

2 : 4-**Dinitroresorcinol** $C_6H_2(OH)_2(NO_2)_2$ may be obtained by treating the corresponding nitroso compound with cold nitric acid (sp.gr. 1·3) (Kostanecki and Feinstein, Ber. 1888, 21, 3122). It forms yellow needles, m.p. 147°–148° (Hemmelmayr, *l.c.*). For various derivatives and other methods of preparation, *see* Lippmann and Fleissner, Monatsh, 1887, 7, 98 ; Jackson and Koch, Amer. Chem. J. 1899, 21, 511 ; Jackson and Warren, *ibid.* 1891, 13, 179 ; *ibid.* 1904, 32, 297 ; Hemmelmayr, *l.c.*

4 : 6-**Dinitroresorcinol**, m.p. 214·5°, is formed by mixing resorcinol diacetate with 4–5 times its volume of well-cooled, fuming nitric acid (Schiaparelli and Abelli, Ber. 1883, 16, 872).

When 100 grms. of resorcinol is nitrated it yields a dinitro derivative, which, when stirred with 1000 grms. of 20 p.c. ammonia solution at ordinary temperature, yields a brown solution which soon deposits green crystals. The aqueous solution of the latter, when suitably thickened, printed on fabrics and steamed, gives brown shades very fast to soap and light. It can also be applied in conjunction with various acid and basic dyestuffs with or without mordants (D. R. P. 207465 ; J. Soc. Chem. Ind. 1909, 361).

Seven parts of mononitroresorcinol, heated with 10 parts of aniline, and 100 of hydrochloric acid for about an hour on the water-bath, yields a compound which dyes iron-mordanted tissues a greyish-blue and alumina mordanted tissues a blue shade.

Dinitroresorcinol (8 parts), similarly treated with 30 parts of resorcinol and 6 of hydrochloric acid, yields a dyestuff which dyes tissues mordanted with iron oxide, alumina or chromic oxide, yellowish-brown shades.

Mono- and dinitroresorcinol, heated alone with hydrochloric acid, also yield dyestuffs, which, however, are deficient in dyeing power (Poirrier and Ehrmann, Bull. Soc. Ind. Mulhouse, 1906, 76, 69).

2 : 4 : 6-**Trinitroresorcinol** (*Styphnic acid*) may be obtained by the prolonged action of nitric acid on various gums or resins ; or on wood extracts (Böttger and Will, Annalen, 1846, 58, 269) ; by the action of fuming nitric acid on *m*-nitrophenol or on trinitrophenol (Bantlin, Ber. 1878, 11, 2101) ; by the action of a mixture of concentrated nitric and sulphuric acids on resorcinol (Merz and Zitter, Ber. 1879, 12, 681, 2037 ; *cf.* Guerewitsch, *ibid.* 1899, 32, 2425) ; by the oxidation of dinitroresorcinol (Fitz, *ibid.* 1875, 8, 631 ; Bendikt and Hübl, Monatsh. 1881, 2, 326) and by other methods.

Styphnic acid forms large yellow hexagonal crystals, m.p. 175·5° ; is readily soluble in alcohol or in ether and in 88 parts of water at 62. It gives a number of metallic salts, ethers and molecular compounds with various organic compounds (Gibson, Chem. Soc. Trans. 1908, 2098 ; Ullmann and Bruck, Ber. 1908, 41, 3939). Alkylamine derivatives are described by Jerusalem (Chem. Soc. Trans. 1909, 1285).

Tetranitroresorcinol has m.p. 152° (Blanksma, *l.c.*).

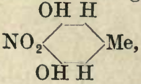
Hydroquinone or *quinol* (1 : 4-dihydroxybenzene) yields a *mononitro derivative*

$$C_6H_3(OH)_2NO_2,$$

m.p. 133°–134° (Elbs, J. pr. Chem. 1893, ii. 48, 179), and a 3 : 5-*dinitroquinol*, pale yellow leaflets, m.p. 135° (Shaw, Chem. Soc. Trans. 1911, 1609).

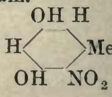
NITRO-ORCINOLS.

Mononitro-orcinol exists in two modifications : α- *derivative*, orange-coloured crystals, m.p. 127°,



, is formed by the interaction of an ethereal solution of orcinol and the molecular equivalent of fuming nitric acid (sp.gr. 1·515). Is volatile in steam.

β- *Modification*, m.p. 122°,



, is

formed like the α- derivative, but is non-volatile in steam. It forms brown crystals containing benzene of crystallisation, and yields green potassium and yellow silver salts (Henrich and Meyer, Ber. 1903, 36, 885).

2 : 4-**Dinitro-orcinol** $C_6H(CH)_3(OH)_2(NO_2)_2$ forms deep yellow leaflets, m.p. 164·5° (Henrich, Monatsh. 1897, 18, 162); another dinitro-derivative known as **β-dinitro-orcinol,** m.p. 109°–110°, has also been described (Leeds, Ber. 1881, 14, 483).

Trinitro-orcinol $C_6CH_3(OH)_2(NO_2)_3$, formed by nitrating orcinol and also by other methods (Merz and Zeller, *ibid.* 1879, 12, 2038; Cazeneuve and Hugouneuq, Bull. Soc. chim. 1888, 50, 643), long yellow needles, m.p. 162°–163·5°, is feebly explosive above its melting-point.

NITROPYROGALLOLS.

5-**Nitropyrogallol**
$C_6H_2(OH)_3NO_2,H_2O(OH : OH : OH : NO_2 = 1 : 2 : 3 : 5)$
is obtained by the action of nitric acid on pyrogallol in ethereal solution at 0°. Forms brownish-yellow needles, or prisms which lose water of crystallisation at 100°, then melt at 205° (Barth, Monatsh. 1882, 1, 882).

4-**Nitropyrogallol,** m.p. 162°, is formed by boiling nitropyrogallol carbonate with water (Einhorn, Cobliner and Pfeiffer, Ber. 1904, 37, 114).

4 : 6-**Dinitropyrogallol,** yellow needles, m.p. 208°, is formed by the action of a mixture of sulphuric and nitric acids on pyrogallol carbonate (Einhorn, Cobliner, and Pfeiffer, *l.c.*).

NITROPHLOROGLUCINOLS.

Phloroglucinol yields a **mononitro derivative** $C_6H_2(OH)_3(NO_2)(OH : OH : OH : NO_2 = 1 : 3 : 5 : 2)$ when nitrated with weak nitric acid. It forms reddish-yellow leaflets (Hlasiwetz, Annalen, 1861, 119, 200).

Trinitrophloroglucinol $C(OH)_3(NO_2)_3$ is formed by treating phloroglucinol triacetate or trimethyl phloroglucinol with fuming nitric acid (Nietzki and Mol, Ber. 1893, 26, 2185; Blanksma, *l.c.*). Yellow crystals; loses water of crystallisation at 100°, sublimes at 130°, m.p. 167° (anhydrous), explosive at higher temperatures. A large number of halogen nitro derivatives of the nitrophenols and their homologues are known: for some recent literature *see* Dahmer, *l.c.*; D. R. PP. 160304, 234742; J. Soc. Chem. Ind. 1905, 886; *ibid.* 1911, 884; Zincke and Klostermann, Ber. 1907, 40, 679; Heller, *ibid.* 1909, 41, 2191; and *l.c.*; Zincke and Breitweiser, *ibid.* 1911, 44, 176; Robertson, Chem. Soc. Trans. 1908, 788; Railford, Amer. Chem. J. 1910, 44, 209; *ibid.* 1911, 46, 417; Erp, Rec. trav. chim. 1910, ii. 14, 187; Zincke, Annalen 1911, 381, 28.

p-**NITROPHENYLHYDRAZINE** *v.* HYDRAZINES.

NITROPHENYLHYDRAZONES *v.* HYDRAZONES.

p-**NITROPHENYLNITROSAMINE** *v.* DIAZO-COMPOUNDS.

NITROSO COLOURING MATTERS *v.* QUINONEOXIME DYES.

NITROSOPHENOL and **NITROSOPHENOL COLOURING MATTERS** *v.* art. PHENOL AND ITS HOMOLOGUES.

'**NITROSULPHATE**' **OF IRON** *v.* *Ferric chloride*, arts. DYEING; IRON.

NITROSTARCH *v.* EXPLOSIVES.

NITROSUGAR *v.* EXPLOSIVES.

NITROSULPHURIC ACID *v.* SULPHUR.

NITROTOLUENE *v.* TOLUENE.

NJAVE OIL *v.* OILS, FIXED, AND FATS.

NJIMO WOOD. This wood is obtained from the interior of the Cameroons, and contains a principle which is said to act like pepsin. The drug is found in commerce partly in billets with but little bark, partly as thick circular sections of the root uniformly covered with bark. The wood of both stem and root possesses a beautiful yellow colour, that of the former being dashed with red. It is easily reduced to powder with a rasp, and possesses an odour like musk. It contains numberless circular pores, which contain yellow resin. The alcoholic extract of the drug is yellow by transmitted light, but exhibits a green fluorescence resembling uranium glass. It appears to contain no alkaloid. The resin contains a bitter substance with a faint aromatic smell (Hugo Schulz, Pharm. Zeit. 31, 350; J. Soc. Chem. Ind. 5, 501).

Cyclo-**NONANONE** *v.* AZELAIC ACID.

NONDECATOIC ACID $CH_3[CH_2]_{17}COOH$ is obtained from octadecyl cyanide (Schweitzer, J. 1884, 1193); m.p. 66·5°, b.p. 297°–299° (100 mm.).

NONOIC ACIDS $C_9H_{18}O_2$.

1. *n-Nononic acid* or *Pelargonic acid*

$$CH_3[CH_2]_7COOH$$

is contained as an ether in the oil from *Pelargonium roseum* (Pless, Annalen, 59, 54), and may be obtained by the oxidation of oil of rue (from *Ruta graveolens* [Linn.]) (Perrot, *ibid.* 105, 64), and of oleic acid (Redtenbacher, *ibid.* 59, 52). Also formed by the oxidation of stearolic acid ($C_{18}H_{32}O_2$) (Limpach, *ibid.* 190, 197); by boiling normal octyl cyanide with potash (Zincke and Franchimont, *ibid.* 164, 333); by melting undecylenic acid with potash (Krafft, Ber. 1882, 1691); and by heating the barium salt of sebacic acid with sodium methoxide (Mai, Ber. 1889, 2136); m.p. 12·5°, b.p. 253°–254°, sp.gr. 0·9068 at 17°/17°.

The characteristic odour of the quince is probably due to ethyl pelargonate. This ester (b.p. 227°–228°; sp.gr. 0·8655 17·5°/4°) is prepared commercially for flavouring common wines, brandy, &c., from the oxidised products of oil of rue.

2. *isoNonoic acid, methylhexyl acetic acid,* or *α-methyloctoic acid* $CH_3[CH_2]_5CH(CH_3)COOH$ is formed by boiling methylhexyl carbinol cyanide with potash (Kullhem. Annalen, 173, 319); b.p. 244°–246° (corr.), sp.gr. 0·9032 at 18°/. Almost insoluble in water; readily soluble in alcohol and ether.

3. *isoHepthyl acetic acid* or *β-methyloctoic acid* $CH_3[CH_2]_5CH(CH_3)CH_2{\cdot}CO_2H$. Obtained by heating *iso*heptyl malonic acid; b.p. 232°. Insoluble in water; soluble in alcohol and ether (Venable, Ber. 13, 1652).

NONTRONITE. A hydrated ferric silicate of a light-green colour, which, on the expulsion of water, changes to a dark chestnut-brown; opaque, fracture uneven; lustre resinous; unctuous to the touch, and somewhat harder than talc. Specimens found at Heppenheim, in the Bergstrasse, and at Andreasberg gave numbers agreeing with the formula

$$Fe_2O_3{\cdot}3SiO_2,5H_2O$$

(Thorpe, Proc. Lit. and Phil. Soc. Manchester, 1869, 1).

NOPAL. The Mexican name of the cactaceous opuntia, upon which the cochineal insect (*Coccus cacti*) breeds.

NORDHAUSEN ACID. *Fuming oil of vitriol* or *pyrosulphuric acid, v.* SULPHURIC ACID.

NORMAL POWDER *v.* EXPLOSIVES.

NORWAY SPRUCE RESIN *v.* RESINS.

NOSEAN *v.* LAPIS-LAZULI.

NOSOPHEN *v.* SYNTHETIC DRUGS.

NOTTINGHAM WHITE. *Flake white v.* PIGMENTS.

NOVACULITE *v.* OILSTONE AND WHETSTONE.

NOVAINE *v.* CARNITINE.

NOVARGAN, NOVASPIRIN *v.* SYNTHETIC DRUGS.

NOVOCAINE. Trade name for *p*-aminobenzoyldiethylaminoethanol hydrochloride used as a substitute for cocaïne. Fine white needles, m.p. 156°, very soluble in water (*v.* SYNTHETIC DRUGS).

NOYAU *v.* LIQUEURS AND CORDIALS.

NUCIN or **JUGLONE.** This substance, obtained by Vogel and Reischauer from walnut husks, has been shown by Bernthsen to be an oxynaphtho-quinone $C_{10}H_6O_3$ (Ber. 1884, 1945).

NUN. This name is given to the fatty product of an insect found in Yucatan. It is a yellowish-brown fatty mass, which has a neutral reaction, absorbs oxygen from the air, melts at 48·9°, and resolidifies between 26·7° and 24·9°; dissolves easily in ether, benzene, chloroform, or oil of turpentine, but is insoluble in alcohol; saponifies with difficulty, yielding a pungent-smelling acid called *niïc acid,* and a volatile oil, together with palmitic and stearic acid. Ammonia colours it red. Its solution in turpentine oil is converted, by exposure to the air, into a resinous syrup (A. Schott, Chem. News. 22, 110).

NUT-GALLS *v.* GALL-NUTS.

NUTMEG. The nutmeg is the kernel of the fruit of *Myristica fragrans* (Houtt) (*v.* Mace). When gathered the fruit is slowly dried, either in the sun or by artificial heat, the hard shell is removed and the nutmegs (except in the case of those from Penang) washed in milk of lime. The nuts are then sorted into grades according to their size, the larger and denser being the most valuable. Those which are shrivelled are reserved for the production of ground nutmeg, of which, however, little, if any, appears on the market.

The true nutmeg is oval or nearly spherical in shape, from 20 to 25 mm. long and from 15 to 18 mm. wide. It is wrinkled longitudinally with a groove marking the position of the raphe. In cross section it has a marbled appearance. It has a pleasant and characteristic odour and a hot aromatic taste.

Composition.—The preponderating constituents are a fixed oil, starch, albuminoids, and fibre; the flavour and therapeutic action are due to the volatile oil.

According to Winton, Ogden, and Mitchell (U.S. Dep. Agric. Bureau of Chemistry, Bulletin 66, 1902), nutmeg has the composition—

	Max.	Min.
Moisture	10·83	5·79
Ash, total	3·26	2·13
,, sol. in water	1·46	0·82
,, insol. in HCl	0·01	0·00
Ether extract, volatile	6·94	2·56
,, ,, non-volatile	36·94	28·73
Alcohol extract	17·38	10·42
Reducing matter by acid conversion } calc. as starch	25·60	17·19
Starch by diastase method	24·20	14·62
Crude fibre	3·72	2·38
Nitrogen	1·12	1·05

(For earlier analyses by Richardson, *v.* U.S. Dept. of Agric. Div. of Chemistry, Bull. 13, pt. 2, 1887.)

The sole use of nutmeg is as a flavouring agent, but the volatile oil is employed in medicine as an aromatic and carminative. In large doses it produces epileptiform convulsions.

The expressed oil of nutmeg (*Adeps myristicae*) is used in plasters and hair lotions as a mild stimulant. It consists mainly of the fixed oil, but usually contains substantial proportions of the volatile oil also. When freed from this it has the following constants:—m.p. 29°–30° C.; saponification value, 184–186; iodine value, 56–59·5 (Parry, Food and Drugs, p. 235).

Adulteration.—As nutmegs are almost invariably sold whole, *i.e.* unground, adulteration is very rare in this country.

The substitution of the long nutmeg (*M. Argentea*) cannot be regarded as legitimate, being much inferior in flavour, still less that of wild nutmegs from *M. Malabarica* or other species of *Myristica.* Both would be detected at once by the complete absence of aroma, and also by their different shape and size. Worm-eaten nuts may be passed off as sound after stopping the holes and coating with lime. This will be revealed by careful inspection. More or less exhausted nuts may be detected by the reduced fat content.

Standards.—The United States standards for nutmeg are as follows: The fixed ether extract shall be not less than 25 p.c., the ash not greater than 5 p.c., the ash insoluble in hydrochloric acid not greater than 0·5 p.c., and the crude fibre not over 10 p.c.

C. H. C.

NUTMEG BUTTER *v.* MYRISTICA FATS.

NUTMEG-OIL (syn. *Oil of Mace*) is the essential oil of the nutmeg, and is extracted by bruising the fruit and submitting the paste to the action of steam; after which the mass is pressed between metal plates, when the oil slowly exudes. The yield of oil reaches 2–3 p.c. of the nutmegs so treated. The colour of this oil is reddish-yellow; it possesses the aroma of the nutmeg and is employed for scenting soaps and perfumery; and sometimes also in medicine.

The purest commercial oil of nutmeg is resolvable by fractional distillation into the following bodies:—1. A soft brown resin (about 2 p.c. of the oil) not volatile at 300°, and having the composition $C_{40}H_{56}O_5$. 2. Liquids boiling at

260°–280° and 280°–290°, the composition of which may be represented by the formula $(C_{10}H_{13}O_2)_n$. 3. An oxidised oil, $C_{10}H_{16}O$, boiling at 212°–218°. 4. A mixture, boiling at 173°–179° (about 15 p.c. of the original oil), of a terpene $C_{10}H_{16}$, with a small quantity of cymene. 5. A hydrocarbon boiling at 163°–164°, consisting of a terpene with a trace of cymene, amounting to 70 p.c. of the original oil.

From these results it may be inferred that the hydrocarbon boiling at 167°, called by Gladstone myristicene (Chem. Soc. Trans. [ii.] 10, 3), is a mixture of two or more terpenes with perhaps a little cymene.

The oxidised body ($C_{10}H_{16}O$) is myristicol. It is converted by heat into an isomeric (or polymeric) modification boiling at a higher temperature, and subsequently into a resin having the same composition. Myristicol treated with dehydrating agents yields cymene, and when treated with phosphorus pentachloride it is converted into a compound $C_{10}H_{15}Cl$, which is resolved by prolonged boiling into hydrogen chloride and cymene.

The cymene contained in the portion of the nutmeg hydrocarbon which boils at 163°–164°, may be isolated by treating the mixture with sulphuric acid so as to polymerise the terpene present (the cymene is not altered by the treatment), then shaking with water and distilling in a current of steam. The cymene thus obtained is quite pure, and amounts to about 8 p.c. of the hydrocarbon boiling at 163°–164°.

The terpene of nutmeg-oil may be converted into cymene by combining it with bromine and distilling the resulting dibromide $C_{10}H_{16}Br_2$, whereby it is resolved into 2HBr and $C_{10}H_{14}$ (Wright, Chem. Soc. Trans. [ii.] 11, 549), *v.* OILS, ESSENTIAL.

NUTS. The name given to various seeds, some the produce of large trees, *e.g.* walnut, chestnut; others of shrubs, *e.g.* filbert; some even of small leguminous plants, *e.g.* pea nuts.

Nuts are, as a rule, rich in nitrogenous matter and in oil, and when palatable and digestible, afford a concentrated and nutritious food.

The following analyses, chiefly from American sources (Bull. 28, U.S. Dept. of Agric. 1899), will serve to show the average composition of the edible portions of many varieties of nuts:—

	Water	Protein	Fat	Carbo-hydrates	Ash
Almonds . .	4·8	21·0	54·9	17·3	2·0
Beechnuts .	4·0	21·9	57·4	13·2	3·5
Brazil nuts .	5·3	17·0	66·8	7·0	3·9
Chestnuts, fresh	45·0	6·2	5·4	42·1	1·3
Chestnuts, dried	5·9	10·7	7·0	74·2	2·2
Cocoanut . .	14·1	5·7	50·6	27·9	1·7
Filberts . .	3·7	15·6	65·3	13·0	2·4
Hickory nuts .	3·7	15·4	67·4	11·4	2·1
Pea nuts . .	9·2	25·4	38·6	24·4	2·0
Pecaus . :	2·7	9·6	70·5	15·3	1·9
Pistachio nuts .	4·2	22·3	54·0	16·3	3·2
Walnuts . .	2·5	18·4	64·4	13·0	1·7

H. I.

NUX VOMICA (*Noix vomique*, Fr.; *Krahenaugen, Brechnuss*, Ger.). Among the numerous species of *Strychnos* distinguished for their toxic properties the best known is *S. Nux vomica* (Linn.), a medium-sized tree which is found throughout Southern and Eastern Asia and in the northern part of Australia. The seeds of the fruit of this tree constitute the nux vomica of commerce. They were introduced into Europe during the sixteenth and seventeenth centuries, and have gradually become an important article of *materia medica*. They are known in the market as 'Bombay,' 'Cochin,' and 'Madras' seeds. The finest specimens which have been examined are grown in Ceylon. In small doses nux vomica acts as a powerful nervous stimulant affecting certain nerve centres, particularly the medulla oblongata. Other parts of the tree possess similar physiological activity, notably the bark, which has attracted attention as an adulterant of cusparia or angustura and as such is called False Angustura Bark (*v.* CUSPARIA BARK). For further botanical and historical particulars, *v.* Flück. a. Hanb. 428; Bentl. a. Trim. 178; Oberlin and Schalgdenhauffen (J. Pharm. Chim. [iv.] 28, 225); Dunstan and Short (Pharm. J. [iii.] 13, 1053; 15, 1 and 156); Rosoll (Monatsh. 5, 94); Greenish (Pharm. J. [iii.] 15, 60); and Ford, Ho Kai and Crow (*ibid.* [iii.] 17, 927).

The poisonous action of nux vomica depends upon the presence of the two well-known bitter alkaloids, *strychnine* and *brucine*. The former was isolated from the seeds in 1818 by Pelletier and Caventou (Ann. Chim. Phys. [ii.] 10, 142; 26, 44), and the latter, a year later, from the bark and seeds, by the same chemists (*ibid.* [ii.] 12, 118; 26, 53). That strychnine is also present in the bark was shown by Shenstone in 1877 (Pharm. J. [iii.] 8, 445; 9, 154). These alkaloids are widely distributed among the species of the *Strychnos* genus. The *S. Ignatii* (Berg.), a climbing plant of the Philippine Islands, the seeds of which constitute the St. Ingatius' Beans, contains both alkaloids. Strychnine indeed was discovered by Pelletier and Caventou in the seeds of this plant (*cf.* Flückiger and Meyer, Pharm. J. [iii.] 12, 1; Flück. a. Hanb. 431; Bentl. a. Trim. 179; Crow *ibid.* [iii.] 17, 970; and Ford, Ho Kai and Crow, *ibid.* [iii.] 18, 75). Strychnine and brucine are found also in *S. Tieuté* (Lesch.) of Java, the active ingredient in the Upas-Tieuté arrow poison (Pelletier and Caventou); in *Lignum colubrinum* or snake-wood, from *S. colubrina* (Linn.), a Malabar tree (Berdenis, J. 1866, 710; H. G. Greenish, Pharm. J. [iii.] 9, 1014), and *S. Gauthieriana* (Piérre), the tree which yields the *hoang-nan* of China (*cf.* Planchon, J. Pharm. Chim. 1877, 384; Räber, Y.-Bk. Ph. 1881, 138). The Indian drug *bidara laut* derived from *S. ligustrina*, examined by H. G. Greenish, was found to contain brucine only (Pharm. J. [iii.] 9, 1013). Other poisonous species of *Strychnos* depend upon the alkaloid curarine for their activity (*v.* CURARA); and the African shrub *akazga*, apparently belonging to the same genus, contains a nearly related base *akazgine* (Frazer, J. pr. Chem. 104, [i.] 51).

For the extraction of the alkaloids from the seeds, besides the process employed by Pelletier and Caventou, numerous other methods have been suggested. The most noteworthy are those of Corriol (J. Pharm. Chim. [i.] 11, 492), Soubeiran (*ibid.* [iii.] 45, 230), Winckler (Mag. Ph. 19, 261), Neuhaus (Neu. Jour. Trommsdorf, 11, 2, 198), Duflos (Berz. J. 28, 2, 208), O. Henry

(J. Pharm. Chim. [ii.] 16, 752), N. E. Henry (*ibid.* [ii.] 8, 401), Lebourdais and Tilloy (*ibid.* [iii.] 23, 406), Wittstein (Darstell. und Prüfung, 215), Wittstock (Berz. Lehrb. 3rd ed. 6, 296), and Geiseler (Arch. Pharm. [ii.] 2, 73). Of these that of Wittstein is the best known and has formed the basis of most of the methods now in use. In all cases it is necessary in the first place to reduce the seeds to a powder, an operation which is rendered difficult by their horny nature. Perhaps the best mode of procedure is that recommended by Dunstan and Short (Pharm. J. [iii.] 13, 1053). The seeds are split and then subjected to a temperature of 100° for 3 hours, after which treatment they admit of being powdered in a drug-mill. The powder, according to Wittstein, is exhausted with 40 p.c. alcohol and the solution obtained is distilled and evaporated until the residue is equal in weight to the powder employed. A solution containing one-fiftieth of this weight of normal lead acetate is then added and the precipitated lead salts separated. The filtrate is concentrated to one half, mixed with calcined magnesia and allowed to stand a week, when the alkaloids will have precipitated. They are extracted from the precipitate by treatment with 80 p.c. alcohol, and on evaporating this solution are obtained in an impure condition. Washing with 40 p.c. alcohol removes the brucine and colouring matter and leaves the strychnine. Ammonia is now generally substituted for magnesia, when only 12 hours' standing is necessary. Crude strychnine thus obtained may be purified by further washing with 40 p.c. alcohol, or as suggested by Prescott (Y.-Bk. Pharm. 1879, 97) more dilute alcohol may be advantageously employed until the washings cease to give the colour reaction with nitric acid for brucine. Another plan is to convert it into a salt, such as the nitrate, recrystallise the salt several times and regenerate the base. Strychnine consists of rhombic prisms (Schabus, J. 1854, 516; Kenngott, J. 1855, 567) which melt at 268° (Löbisch and Schoop, Monatsh. 6, 858) and have a sp.gr. of 1·359 at 18° (Clarke, Ber. 12, 1399). Solubility in 100 parts of cold water, 0·014; benzene, 0·607; 95 p.c. alcohol, 0·936; ether, 0·08; fusel oil, 0·55 (Dragendorff, J. 1865, 739; *cf.* Crespi, Gazz. Chim. ital. 13, 175). Many of the neutral salts of strychnine are almost insoluble in water, and hence precipitation of the alkaloid occurs where, as is sometimes the case, salts of strychnine are prepared for medical administration in aqueous solution together with alkaline bromides or iodides (*cf.* Lyons, Pharm. J. [iii.] 8, 1048). For other characters and reactions of strychnine *v.* VEGETO-ALKALOIDS.

To obtain brucine from the mixed alkaloids extracted from nux vomica several methods are employed beside those already mentioned, and the seeds are sometimes worked directly for this base. The latter plan was adopted by Shenstone, who prepared brucine quite free from strychnine. The powdered seeds were extracted with alcohol containing one-sixth part of water, and the solution concentrated by distillation and evaporation to the consistence of a thick syrup. From this the alkaloids were extracted by water containing 0·3 p.c. of sulphuric acid. To the acid solution an excess of sodium carbonate was added, and the precipitate, which formed after a few hours, was collected and dissolved in chloroform. The chloroformic solution was then shaken several times with water, to which sulphuric acid was gradually added. The first washings were kept alkaline, but the last ones were made distinctly acid. In this way crystallisation during the operation is prevented. The solution of alkaloidal sulphate was next treated in a shallow dish with an atmosphere of ammonia gas, when some of the base separated in crystals. These were washed with dilute alcohol, which on spontaneous evaporation left brucine, not quite free, however, from traces of strychnine. These were finally removed by conversion into hydriodide and regeneration of the alkaloid (Chem. Soc. Trans. 39, 453). The crude alkaloids may also be separated by taking advantage of the different behaviour of brucine and strychnine acetates when heated on a water-bath, when the strychnine salt loses its acid and becomes comparatively insoluble in water (Flückiger, Arch. Pharm. [iii.] 6, 404); or of the action of dilute nitric acid on the picrates (Gerock, *ibid.* [iii.] 27, 158); or of the different solubility of their chromates (Horsley, J. 1856, 758); or of their ferrocyanides (Dunstan and Short, Pharm. J. [iii.] 14, 290; *cf.* Beckurts, Ph. Centh. 4, 325). By the last-mentioned process the mixed alkaloids, in a dilute solution containing a slight excess of sulphuric acid, are treated with potassium ferrocyanide, when after standing several hours the whole of the strychnine is precipitated, leaving the brucine in solution. Brucine crystallises from dilute alcohol in monoclinic prisms or plates containing $4H_2O$ (Lüdecke, Ber. 10, 838), which lose water at 105° and melt at 178° (Claus and Röhre, Ber. 14, 773). The physiological action is similar but less intense than that of strychnine; but, unlike strychnine and like curarine, it is not poisonous when taken into the stomach, but acts fatally when injected under the skin (Brunton, Chem. Soc. Trans. 47, 143). It is very slightly soluble in cold water, though much more so than strychnine. It is soluble in cold alcohol, chloroform, and volatile oils; but insoluble in ether and fats. For other characters and reactions, *v.* VEGETO-ALKALOIDS.

Nux vomica seeds also contain *igasuric acid*, discovered by Pelletier and Caventou (Ann. Chim. Phys. [ii.] 10, 167; 26, 54), with which the alkaloids are supposed to be combined, and a small proportion of a glucoside, *loganin*, $C_{25}H_{34}O_{14}$, first obtained by Dunstan and Short from the fruit pulp which contains it in larger quantities (Pharm. J. [iii.] 14, 1025; 15, 4). The 'igasurine' of Desnoix (J. Pharm. Chim. [iii.] 25, 202) and Schützenberger (Compt. rend. 46, 1234) has been shown by Jörgensen (J. pr. Chem. [ii.] 3, 175) and Shenstone (Chem. Soc. Trans. 37, 235; 39, 453) to be impure brucine. Igasuric acid is isolated from the lead precipitate obtained in the preparation of the alkaloids. The igasuric acid obtained by Pelletier and Caventou was crystalline while other investigators have always obtained it in an amorphous state. It would seem to be a variety of tannic acid (Ludwig, Arch. Pharm. [iii.] 2, 137; Corriol, J. Pharm. Chim. 19, 155; Marsson, Annalen, 72, 296), and Sander (Arch. Pharm. 235, 133) has regarded it as identical with caffetannic acid. Gorter, however (*ibid.* 247, 197), finds that it is identical with the chlorogenic acid $C_{32}H_{28}O_{19}$, obtained by him from coffee berries. Loganin consists of colourless prisms which melt at 215°. It dissolves easily in water and alcohol, but less so in chloroform or benzene. Warmed with sulphuric acid it develops a red colour which changes to purple. Boiled with dilute acids it breaks up into glucose and *loganetin*. It occurs in the pulp of the fruit of Ceylon nux vomica to the extent of 5 p.c. (Dunstan and Short). In addition to these constituents nux vomica seeds contain about 11 p.c. of *proteids* (Flück. a. Hanb.); 4 p.c. of *fat* or fatty oil (Flück. a. Hanb.; Meyer, J. 1875, 856; T. E. Greenish, Pharm. J. [iii.] 12, 581; Dunstan and Short; Harvey and Wilkes, J. Soc. Chem. Ind. 24, 718), together with *mucilage* and *sugar*.

Several methods have been suggested for the estimation of the alkaloids in nux vomica. The most important are those of Dragendorff (C. Wertbestimmung, St. Petersburg, 1874; Zeitsch. Chem. [ii.] 2, 27) and Dunstan and Short (Pharm. J. [iii.] 13, 665 and 1053). Dragendorff's method, which gives accurate results, consists in extracting the powdered seeds with dilute sulphuric acid, nearly neutralising the solution with magnesia, and evaporating to a syrup. From this the alkaloids are extracted by treating it first with 90 p.c. and afterwards with 50 p.c. alcohol. The alcoholic solutions are then distilled until the residue is concentrated to one-fifth of the original volume. The slightly acid solution is then shaken with benzene, which removes fat and other substances, but does not dissolve the alkaloidal salts. Treatment with magnesia sets the alkaloids free and they are extracted by benzene or chloroform, the solution evaporated and the residue dried and weighed. The method of Dunstan and Short is simpler. The powdered seeds are exhausted with a mixture of three volumes of chloroform and one volume of alcohol. From this solution the alkaloids are separated by shaking with dilute sulphuric acid, which dissolves them as acid sulphates. By treatment of the acid solution with ammonium hydroxide and chloroform, the free bases are extracted, and on evaporation of the chloroform solution are obtained in a sufficient state of purity for weighing. Examined by this method, 'Bombay' seeds gave from 3·14 to 3·90 p.c.; 'Cochin' seeds 3·04 and 3·60 p.c., and 'Madras' seeds 2·74 and 3·15 p.c. of total alkaloids (Dunstan and Short). Keller's method (Chem. Soc. Abstr. 1894, 490; 1897, 84) in which the powdered beans are extracted with a mixture of ether and chloroform gives very accurate results.

A method for the estimation of strychnine and brucine when mixed as in the alcoholic extract of nux vomica was based on the insolubility of strychnine ferrocyanide in dilute sulphuric acid, the corresponding brucine salt being soluble (Dunstan and Short, Year Book Pharm. 1883, 469; Holst and Beckurts, Arch. Pharm. [iii.] 25. 313). This method, however, according to Schweissinger (*ibid.* [iii.] 12, 579, 609; Stoeder, Chem. Zentr. 1899, i. 506), does not give a satisfactory separation. Other methods are the oxidation of brucine by potassium permanganate which leaves the strychnine unaltered (Sander, Zeitsch. anal. Chem. 37, 132), or similar oxidation by nitric acid (Keller, Zeitsch. Oesterr, Apoth.-Ver. 1903, 587; Gordin, Arch. Pharm. 240, 641; Howard, Annalen, 30, 261; Reynolds and Sutcliffe, J. Soc. Chem. Ind. 25, 512).

The percentage of strychnine in the total alkaloids from nux vomica varies from 43·9 to 45·6. The alkaloids in the St. Ignatius' bean contain a larger percentage of strychnine, 60·7–62·8 (Sander, Arch. Pharm. 235, 133).

The experiments of Siebold (Pharm. J. [iii.] 7, 283), Dunstan and Short (*ibid.* [iii.] 14, 292, 441, and 443), and Conroy (*ibid.* [iii.] 14, 461) proved that the pharmaceutical preparations of nux vomica, the extract and tincture, vary materially in alkaloidal strength. To employ only the alkaloids for medical purposes would obviate this want of uniformity, but they are not believed to possess the whole of the therapeutic activity represented by the extract or tincture. The liquid extract of nux vomica of the British Pharm. 1898, is, therefore, standardised to contain 1·5 grams of strychnine in 100 c.c. the alkaloid being estimated by the ferrocyanide process. A. S.

NYCANTHES ARBOR-TRISTIS (Linn.). This is a large shrub with rough leaves and sweet scented flowers occurring in the sub-Himalayan and Tarai tracts; also in Central India, Burmah, and Ceylon. The flowers open towards evening and fall to the ground on the following morning. The corolla tubes are orange coloured and give a beautiful but fleeting dye, which is mostly used for silk, sometimes in conjunction with 'kusum' or turmeric, occasionally with indigo and kath (Watts, Dict. Econ. Prod. of India, 1891, 5, 434).

According to Hill and Sirkar (Chem. Soc. Trans. 1907, 91, 1501) these flowers yield a red crystalline colouring matter *nycanthin*. An aqueous decoction treated with 1 p.c. of hydrochloric acid, is warmed gently for several hours, the precipitate collected and extracted with boiling alcohol. The extract heated with 1 p.c. hydrochloric acid deposits the colouring matter in red flakes which are washed with alcohol, and crystallised from pyridine or phenylhydrazine.

Nycanthin separates from pyridine in minute regular hexagons, and from phenylhydrazine in rhombic crystals; these are yellow, while wet, but brick red when dry, and melt between 225° and 230°. It dissolves in alkalis to form a yellow solution from which it appears to be reprecipitated unchanged by acids, and contains no methoxyl group. With sulphuric acid it gives a most intense blue colour, which, however, rapidly turns yellow, and in this respect resembles bixin, the colouring matter of annatto (*Bixa Orellana* [Linn.]).

The analyses of Hill and Sirkar (*l.c.*) agree closely with $C_{20}H_{27}O_4$ or $C_{15}H_{20}O_3$, but of these formulæ the former appears to be preferable. *Acetylnycanthin* $C_{20}H_{26}O_4 \cdot C_2H_3O$, and the bromine compound $C_{20}H_{15}O_{18}Br_5$, amorphous powders, have been prepared by these authors. Mannitol was also isolated from the flowers.

For dyeing purposes the material (silk or cotton) is simply steeped in a hot or cold decoction of the flowers. The addition of alum and lime juice to the dye-bath is said to render the colour more permanent.

According to Perkin (private communication) the flowers of the *Cedrela Toona* (Roxb.), also employed as a dyestuff in India, yield a small quantity of crystalline red colouring matter, which closely resembles and is probably identical with nycanthin. A. G. P.

O.

OAK-BARK. The oak tree is generally barked from the beginning of May till the middle of July. The barkers make a longitudinal incision with a mallet furnished with a sharp edge, and a peculiar incision by means of a barking-bill. The bark is then removed by peeling-irons, the separation being promoted, when necessary, by beating the bark. It is stacked in pieces about 2 feet long (*v.* Leather).

OAK-GALLS *v.* Gall nuts.

OAK-VARNISH *v.* Varnish.

OATS *v.* Cereals.

OBLITINE *v.* Carnitine.

OBREGUIN. A substance intermediate in character between the fats and resins, occurring in Mexico on the twigs of *Althaea rosea* (Cav.). Nearly insoluble in water; easily soluble in ether, chloroform, or turpentine oil. On evaporation its solutions form a colourless, odourless mass, of the consistency of turpentine. Saponifiable by alkalis.

OBSIDIAN. A vitreous volcanic rock, generally jet-black or of dark bottle-green tint, and nearly opaque, except on the thin edges, which are translucent. Obsidian results from the rapid cooling of rocks of acid type, such as rhyolite, the corresponding glass in the basic series being termed *tachylyte.* Microscopic examination of obsidian usually reveals the presence of numerous enclosures, known as crystallites and microlites, which may be so abundant as to render the rock opaque and devitrified. Many obsidians present a banded structure, while others are spherulitic. An analysis of obsidian from Iceland gave: SiO_2, 75·28; Al_2O_3, 10·22; Fe_2O_3, 4·24; CaO, 1·81; MgO, 0·25; K_2O, 2·44; Na_2O, 5·53; H_2O, 0·23 p.c. Obsidian, when fractured, presents a sharp-cutting edge, and hence in parts of Mexico where the material is abundant, as at the Cerro de Navajas ('Hill of Knives'), it was used by the Aztecs for knives, razors, and arrow-heads. It has also been employed by savages in other volcanic countries. Obsidian has occasionally been cut and polished as a gem-stone, but displays too little colour, even when thin, and is, moreover, too soft for general use. A dark variety with a silvery sheen is, however, used for ornamental purposes in Siberia, while a brownish-red streaked variety, known as 'mahogany-obsidian,' has been employed to a limited extent as a decorative material in the United States. On Obsidian Cliff, Yellowstone National Park, *v.* J. P. Iddings, Seventh Ann. Rep. U.S. Geol. Sur. 1888. F. W. R.

OCCLUSION (*occludo*, to enclose). Graham's term for the process of absorption or condensation of gases within the pores of a substance, *e.g.* the absorption of hydrogen by platinum and palladium, or the condensation of marsh-gas or fire-damp in coal.

OCHRE. A name applied to various native pigments, distinguished according to colour as yellow, brown, and red ochres, and consisting essentially of ferric hydroxides (represented by the mineral species limonite and turgite), usually more or less earthy by admixture with clay or sand. Deposits of fine yellow ochre occur in the Lower Greensand of Shotover Hill, near Oxford. Red and brown ochres are commonly associated with iron-ores, especially with the hæmatite occurring in pockets in the carboniferous limestone, and have been worked in South Wales, the Forest of Dean, near Bristol, at Brixham in Devonshire, Ulverston in Lancashire, and near Workington in Cumberland. Some of the finest ochres of commerce are obtained from France, and are known as Auxerre and Rochelle ochres. In the United States, ochres are worked in connection with many deposits of iron-ore, especially in Virginia and Pennsylvania. Ochre is deposited by the water of chalybeate springs and by the waters issuing from mines; in some cases such material is collected. Red ochre is formed as a by-product in the roasting of iron-pyrites. Some ochres are so pure as to be ready for use after having been simply dried, ground, and bolted; while others require careful preparation by washing and levigating. Sometimes the material is roasted to obtain the required shade of deep brown or red. The value of an ochre depends, not only on its colour, but on the proportion of oil required to be mixed with it for use as a pigment. The presence of finely-divided silica is not always detrimental to an ochre, inasmuch as it may enable the paint to adhere to fibres of the wood to which it is applied, and by filling up spaces may improve its covering power. Coarse ochre is extensively employed in the manufacture of oilcloth and linoleum, while the finer kinds of ochre are valued by the paper-maker for staining the pulp to its required tint, being especially used in the manufacture of brown paper. In commerce the term 'ochre' is frequently restricted to the pale yellowish-brown varieties. In mineralogy, on the contrary, it is extended to a variety of metallic oxides and other compounds formed as products of alteration and occurring as earthy incrustations on the minerals from which they have been derived by atmospheric action. Thus the mineralogist recognises such bodies as antimony-ochre, bismuth-ochre, molybdic-ochre, nickel-ochre (an arseniate), uranium-ochre (a sulphate), and wolfram-ochre. *See* G. P. Merrill, The Non-Metallic Minerals, 2nd ed. 1910; T. L. Watson, Ochre Deposits of Georgia, Bull. Georgia Geol. Survey, 1906, No. 13 (*v.* Umber). L. J. S.

OCHROITE *v. Cerium metals.*

OCRE DE RU. *Brown ochre v.* Pigments.

OCTITOL *v.* Carbohydrates.

OCTOIC ACIDS. $C_8H_{16}O_2$.

1. *n. Octoic acid* or *caprylic acid*

$CH_3[CH_2]_6COOH$.

Exists as a glyceride in butter, and in human fat, and especially in cocoa-nut oil. It is also found in cheese, among the products of the distillation of fat by superheated steam, and in many fusel oils, partly free and partly in combination with different alcohol radicles. It may be prepared by oxidising normal octyl alcohol (Zincke, Annalen, 152, 9) or by the dry distillation of oleic acid (Gottlieb. *ibid.* 57, 63). It melts at 16·5° and boils at 237·5°, sp.gr. 0·9100 at 20°/4°. Sparingly soluble in cold water: 400 parts of water at 100° dissolve 1 part of the acid; readily soluble in alcohol or ether (Zincke, *l.c.*).

2. *Dipropylacetic acid, α-propylvaleric acid* $(C_3H_7)_2CH{\cdot}COOH$ is obtained by boiling ethyl dipropylacetoacetate with potash (Burton, Amer. Chem. J. 3, 389), or by heating dipropylmalonic acid (Fürth, Monatsh. 3, 319; *v.* also method of Oberreit, Ber. 1896, 2000); b.p. 219·5°, sp.gr. 0·9215 at 0°/4°. Sparingly soluble in water.

3. *Iso-octoic acid* is obtained by the oxidation of *iso*-octylalcohol (Williams, Chem. Soc. Trans. 1879, 128), b.p. 218°–220°, sp.gr. 0·911 at 20°/4°.

4. *Octoic acid* from *iso*dibutylene

$C(CH_3)_3CH_2{\cdot}CH(CH_3)COOH$

formed by the oxidation of the hydrocarbon; boils at about 215° with partial decomposition (Butlerow, Annalen, 189, 72). Probably identical with *iso*-octoic acid.

5. *Ethylbutylacetic acid, α-ethylhexoic acid* $CH_3[CH_2]_3CH(C_2H_5)COOH$. Obtained by the oxidation of corresponding alcohol (Raupenstrauch, Monatsh. 8, 115).

6. *Ethylisobutylacetic acid, α-ethyl-γ-methylvaleric acid* $(CH_3)_2CH{\cdot}CH_2{\cdot}CH(C_2H_5)COOH$. Obtained by heating ethyl*iso*butylacetoacetate with alkali and alcohol (Guye and Jeanprêtre, Bull. Soc. chim. [iii.] 13, 183), b.p. 219°–220° (729 mm.); sp.gr. 0·906 at 20°/4°.

OCTYL *Capryl* C_8H_{17}. The eighth alcohol-radicle of the series C_nH_{2n+1}. Like other members of this series, it cannot exist in the free state; when liberated from its compounds it is converted into dioctyl $C_{16}H_{34}$, a body isomeric and perhaps identical with ceryl hydride.

The compounds of this radicle occur in petroleum, in the seeds of the common- and cow-parsnip, and in the products of the distillation of some varieties of coal.

OCTYL ALCOHOL $C_8H_{17}{\cdot}OH$. A large number of isomeric alcohols with this formula are possible, but only the following have been prepared:—

(1) **Normal octyl alcohol,** *α-hydroxy octane* $CH_3[CH_2]_7OH$, occurs in the fruit of *Heracleum Sphondylium* (Linn.), the cow-parsnip, as the acetic acid ester (Zincke, Annalen, 152, 1; Möslinger, *ibid.* 185, 26); and as the acetate and butyrate in the oil of *Heracleum villosum* (Fisch.) (Franchimont, Ber. 1871, 822). Oil expressed from the ripe fruit of *Peucedanum sativum* (Benth. and Hook.), the common parsnip, is almost pure octyl butyrate (Renesse, Annalen, 166, 80). It boils at 195·5° and has sp.gr. 0·8375 at 0° (Zander, Annalen, 224, 84).

(2) **Methyl hexyl carbinol,** *β-hydroxy octane* $CH_3[CH_2]_5CH(OH)CH_3$, b.p. 179°–179·2° at 762 mm. (Schiff, *ibid.* 220, 103), 177·6°–177·8° at 745·4 mm. (Brühl, *ibid.* 203, 28); sp.gr. 0·8193 at 20°/4° (Brühl). Heat of combustion 1,262,105 cal. (Lugunin, Ann. Chim. Phys. [v.] 25, 141).

It is formed by the distillation of alkaline ricinoleates with excess of potash (Moschnin, Annalen, 87, 111; Bouis, *l.c.*; Städeler, J. 1857, 358; Dachauer, Annalen, 106, 269; Schorlemmer, *ibid.* 147, 222). By the distillation of the saponified oil of the seed of *Jatropha curcas* (Linn.) (Silva, Zeitsch. Chem. 1869, 185).

It is a limpid, oily, inactive liquid, with a strong aromatic odour, soluble in alcohol, ether, wood-spirit, and acetic acid; insoluble in water. It dissolves phosphorus, sulphur, iodine, fused zinc chloride, fats, resins, and copals.

Preparation.—Castor oil (which contains sodium ricinoleate) is distilled with excess of potash; the portion which passes over between 176°–180° is collected and purified by fractional distillation.

On oxidation it yields, first, methyl-hexyl ketone $MeCOC_6H_{13}$; subsequently acetic and normal caproic acids are formed. It reduces silver oxide (but not nitrate) when heated with it, forming a metallic mirror. With hydrochloric acid, phosphorus pentachloride, bromine or iodine and phosphorus, &c., it exhibits the usual reactions of secondary alcohols. The ketone $C_6H_{11}Cl_2{\cdot}CO{\cdot}CCl_3$ is produced on saturation with chlorine (A. Brochet, Bull. Soc. chim. [iii.] 13, 120).

(3) **Methyl** *iso***hexyl carbinol,** *β-hydroxy-ζ-methyl heptane* $CH_3{\cdot}CH(OH)[CH_2]_3CH(CH_3)_2$ is produced by the reduction of methyl *iso*hexyl ketone $CH_3{\cdot}CO[CH_2]_3CH(CH_3)_2$ (Welt, Ann. Chim. Phys. [vii.] 6, 135). It boils at 167°–169°, and has a sp.gr. 0·8174 at 21°. It is optically active $[\alpha]_D^{24°}=4{\cdot}69°$.

(4) **Methyl dipropyl carbinol,** *δ-hydroxy-δ-methyl heptane* $CH_3{\cdot}C(C_3H_7)_2OH$, has been prepared by Gortaloff and Saytzeff by the action of 262 grams methyl iodide and excess of zinc on 70 grams butylene (J. pr. Chem. [ii.] 33, 204). It is a liquid boiling at 161·5°, and of sp.gr. 0·82479 at 20°. On oxidation with chromic acid it yields chiefly acetic and propionic acids.

(5) **γ-Hydroxy-δ-ethyl hexane**

$(C_2H_5)_2CH{\cdot}CH(OH)C_2H_5$

may be prepared from bromoacetyl bromide and zinc ethyl (Winogradow, Annalen, 191, 140). It boils at 164°–166°, and on warming with hydrogen iodide yields the iodide.

(6) **Diethylpropylcarbinol,** *δ-hydroxy-δ-ethyl hexane* $(C_2H_5)_2C(C_3H_7)OH$ is prepared from butyl chloride and zinc ethyl (Butlerow, Bull. Soc. chim. [ii.] 5, 17). The product is left for several days till it becomes viscid, it is then heated, acidified with hydrochloric acid and distilled. It has an alcoholic, camphoraceous odour, is lighter than water, in which it is slightly soluble and boils at 145°–155°. On oxidation with chromic acid it yields propionic and acetic acids.

(7) **Diethyl** *iso***propyl carbinol,** *γ-hydroxy-δ-methyl-γ-ethyl pentane* $CH(CH_3)_2C(OH)(C_2H_5)_2$ is produced together with ethyl *iso*propyl carbinol and ketone from *iso*butyryl chloride (1 mol.) and zinc ethyl (2 mols.). The reagents are

mixed and allowed to stand in ice for three days and subsequently left together for five or six months, after which the mixture is treated with ice water (Grigorovitch and Pawloff, J. Russ. Phys. Chem. Soc. 23, 169). It boils at 159·5°–161° at 750 mm. and has sp.gr. 0·8463 at 0°.

(8) **Di*iso*butyl hydrate** $C_8H_{17}OH$. Two alcohols of this name are known. (1) A primary alcohol of unknown constitution. It boils at 179°–180° at 765 mm. (uncorr.) remains fluid at −17° and has sp.gr. 0·841 at 0°/4°, 0·828 at 20°/4° (Williams, Chem. Soc. Trans. 1879, 127). (2) A secondary alcohol obtained mixed with the primary and separated from it by fractionation. It boils at 160°–163°/75·5 mm. and has sp.gr. 0·820 at 15°/4°.

(9) ***Iso*dibutol,** *β-hydroxy-βδδ-trimethylpentane* $(CH_3)_3C{\cdot}CH_2{\cdot}C(CH_3)_2OH$, boils at 146·5°–147·5°, and has sp.gr. 0·8417 at 0°/0°. It is a colourless viscid liquid, with a musty camphoraceous odour. It is prepared from di*iso*butylene hydriodide and silver hydroxide. On oxidation it yields acetone, trimethylacetic acid, acetic acid, and octoic acid $C_8H_{16}O_2$, and a ketone $C_7H_{14}O$ (Butlerow, Annalen, 189, 53).

(10) **Octylene hydrate** $C_8H_{17}OH$ is of uncertain constitution. The iodide results from the action of hydriodic acid on octylene. The alcohol is a clear liquid, boiling at 174°–178°, and of sp.gr. 0·811 at 0°. On oxidation acetic acid, caproic acid, and a ketone $C_8H_{16}O$ are obtained.

OCTANES, C_8H_{18}. Eighteen isomeric hydrocarbons having this formula are theoretically possible, and of these twelve have been prepared. Two of these occur in American petroleum (Mabery and Hudson, Amer. Chem. J. 1897, 19, 255), and are found in the portion boiling between 115° and 130°. *n*-Octane is found among the light oils obtained by distilling Wigan cannel coal at a low temperature (Schorlemmer, Chem. Soc. Trans. 1862, 419). Ligroin consists essentially of hydrocarbons having the formulæ C_7H_{16} and C_8H_{18} (Pelouze and Cahours, Annalen, 127, 197).

(1) ***n*-Octane,** *octyl hydride* $CH_3[CH_2]_6CH_3$, b.p. 125·6° (corr.), sp.gr. 0·71883 at 0°/4° (Thorpe, Chem. Soc. Trans. 1880, 217); b.p. 124·7°/760 mm., sp.gr. 0·7068 at 15°/15°, $n_{\mathrm{D}}^{25^\circ}$ 1·3963 (Clarke, J. Amer. Chem. Soc. 1911, 33, 520; *cf.* Schorlemmer, Annalen, 161, 281).

Occurs in American petroleum; prepared by reducing *sec*-octyl iodide with zinc and hydrochloric acid (Schorlemmer, *ibid.* 152, 152), or *n*-octyl iodide with sodium amalgam (Zincke, *ibid.* 152, 15); by the action of sodium on *n*-butyl iodide (Schorlemmer, *l.c.*); by heating sebacic acid with baryta (Riche, *ibid.* 117, 265).

Colourless liquid, having a faint ethereal smell. On warming with nitric acid (sp.gr. 1·42) mono- and dinitro-octane, acetic, succinic and oxalic acids, and carbon dioxide are obtained (Worstall, Amer. Chem. J. 1898, 20, 212).

(2) **β-Methylheptane,** *iso-octane*
$CH_3[CH_2]_4CH(CH_3)_2$,
b.p. 116·0°/761 mm.; sp.gr. 0·7035 at 15°/15°; $n_{\mathrm{D}}^{25^\circ}$ 1·3944. Has been synthesised by Clarke (J. Amer. Chem. Soc. 1909, 31, 107).

(3) **γ-Methylheptane**
$CH_3[CH_2]_3CH(CH_3)CH_2{\cdot}CH_3$,
b.p. 117·6°/760 mm.; sp.gr. 0·7167 at 15°/15°; $n_{\mathrm{D}}^{25^\circ}$ 1·4022. Has been synthesised by Clarke (*ibid.* 558). The method of Welt (Ann. Chim. Phys. [vii.] 6, 121) does not yield a pure product.

(4) **δ-Methylheptane**
$CH_3[CH_2]_2CH(CH_3)[CH_2]_2CH_3$,
b.p. 118·0°/760 mm.; sp.gr. 0·7217 at 15°/15°; $n_{\mathrm{D}}^{25^\circ}$ 1·3978. Has been synthesised by Clarke (Amer. Chem. J. 1908, 39, 87).

(5) **βγ-Dimethylhexane**
$CH_3[CH_2]_2CH(CH_3)CH(CH_3)_2$,
b.p. 113·9°/758 mm.; sp.gr. 0·7246 at 15°/15°; $n_{\mathrm{D}}^{25^\circ}$ 1·4075. Has been synthesised by Clarke (J. Amer. Chem. Soc. 1911, 33, 520).

(6) **βδ-Dimethylhexane**
$CH_3{\cdot}CH_2{\cdot}CH(CH_3)CH_2{\cdot}CH(CH_3)_2$,
b.p. 110·0°/763 mm.; sp.gr. 0·7083 at 15°/15°; $n_{\mathrm{D}}^{25^\circ}$ 1·3986. Has been synthesised by Clarke (*ibid.* 1908, 30, 1144).

(7) **βε-Dimethylhexane,** *diisobutyl*
$(CH_3)_2CH[CH_2]_2CH(CH_3)_2$,
b.p. 108·53° (corr.), sp.gr. 0·711 at 0°/4° (Thorpe, Chem. Soc. Trans. 1880, 219); b.p. 108·25°/760 mm.; sp.gr. 0·6991 at 15°/15°, $n_{\mathrm{D}}^{25^\circ}$ 1·3930 (Clarke, J. Amer. Chem. Soc. 1909, 31, 585; *cf.* Schiff, Annalen, 220, 88).

Prepared by the action of sodium on *iso*butyl iodide (Wurtz, *ibid.* 96, 365) or on a mixture of *iso*amyl and *iso*propyl iodides (Schorlemmer, *ibid.* 144, 188; Kolbe, *ibid.* 69, 261); for other methods, *v.* Clarke, *l.c.* Colourless mobile liquid with ethereal odour and burning taste. Oxidation with chromic acid yields acetic acid and carbon dioxide.

(8) **γδ-Dimethylhexane**
$CH_3{\cdot}CH_2{\cdot}CH(CH_3)CH(CH_3)CH_2{\cdot}CH_3$,
b.p. 116·5°/759 mm.; sp.gr. 0·7270 at 15°/15°; $n_{\mathrm{D}}^{25^\circ}$ 1·4038 (Clarke, J. Amer. Chem. Soc. 1911, 33, 520). Prepared by the action of sodium on β-iodobutane (Norris and Green, Amer. Chem. J. 1901, 26, 313).

(9) **γ-Ethylhexane**
$CH_3[CH_2]_2CH(C_2H_5)CH_2{\cdot}CH_3$,
b.p. 118·8°–119°/766 mm.; sp.gr. 6·7175 at 15°/15°; $n_{\mathrm{D}}^{25^\circ}$ 1·3993. Has been synthesised by Clarke and Riegel (J. Amer. Chem. Soc. 1912, 34, 674), who state that it is probably one of the hydrocarbons found by Mabery and Hudson in American petroleum.

(10) **ββγ-Trimethylpentane**
$CH_3{\cdot}CH_2{\cdot}CH(CH_3)C(CH_3)_3$,
b.p. 110·5°–110·8°/760 mm.; sp.gr. 0·7219 at 15°/15°; $n_{\mathrm{D}}^{25^\circ}$ 1·4164. Has been synthesised by Clarke and Jones (*ibid.* 170).

(11) **β-Methyl-γ-ethylpentane**
$CH_3{\cdot}CH_2{\cdot}C(C_2H_5)CH(CH_3)_2$,
b.p. 114·0°/760 mm.; sp.gr. 0·7084 at 15°/15°; $n_{\mathrm{D}}^{25^\circ}$ 1·3996. Has been synthesised by Clarke (Amer. Chem. J. 1908, 39, 574).

(12) **Hexamethylethane** $C(CH_3)_3C(CH_3)_3$, a crystalline substance; m.p. 96°–97°; b.p. 105°–106°. Prepared by the action of sodium on *tertiary*-butyl iodide (Lwow, Bull. Soc. chim. [ii.] 35, 169).

Octyl chlorides.

Normal chloride, *a-chlorooctane*
$CH_3[CH_2]_6CH_2Cl$,

b.p. 179·5°–180°; sp.gr. 0·8802 at 16°, 0·87857 at 15° (Perkin, J. pr. Chem. [ii.] 31, 495).

Preparation.—By the action of hydrochloric acid gas on octyl alcohol (Zincke, Annalen, 152, 4). A limpid liquid, soluble in absolute alcohol and in ether, insoluble in water.

Secondary chlorides. (1) *β-Chlorooctane* $CH_3[CH_2]_5CHCl{\cdot}CH_3$, b.p. 175° (Bouis, Annalen, 92, 398), 170°–172° (Schorlemmer, Chem. Soc. Trans. 1876, 419), 168°–172° (Pelouze and Cahours, Annalen, 129, 91); sp.gr. 0·892 at 18° (Schorlemmer), 0·895 at 16° (Pelouze and Cahours).

Formation.—By the action of hydrogen chloride or phosphoric chloride on methylhexylcarbinol (Bouis); by the action of hydrogen chloride on octylene (Berthelot, Annalen, 104, 185); by the action of chlorine on octane (Schorlemmer; Würtz, J. 1863, 509; Pelouze and Cahours).

Properties.—A colourless liquid, with a strong smell of oranges.

Reactions.—It does not precipitate salts of silver. It is decomposed by potassium or sodium in the cold, yielding dioctyl $C_{16}H_{34}$. By repeated distillation with sodium, hydrogen is evolved and octylene C_8H_{16} is formed.

(2) The octyl chloride prepared from petroleum octane exhibits the same reactions as that obtained from the alcohol, but on treatment with concentrated acetic acid and potassium acetate, octylene and octyl acetate are formed in equal quantities, whereas the chloride from the carbinol yields three times as much octylene as octyl acetate (Schorlemmer, Annalen, 152, 152).

(3) *Diisobutyl chloride*, b.p. 165°; sp.gr. 0·8834 at 10·5° (Schorlemmer, *ibid.* 144, 190).

Tertiary chlorides. (1) *δ-Ethyl-δ-chlorohexane* $CH_3{\cdot}CH_2{\cdot}CCl(C_2H_5)CH_2{\cdot}CH_2{\cdot}CH_3$, b.p. 155°. A liquid with a peculiar, unpleasant odour. Prepared by the action of phosphoric chloride on the diethylpropylcarbinol (Butlerow, Bull. Soc. chim. [ii.] 5, 17).

(2) *Diethyl isopropylcarbinol chloride, δ-methyl-γ-ethyl-γ-chloropentane.* From diethyl*iso*propyl carbinol and phosphorus pentachloride (Grigorovitch and Pawloff, J. Russ. Phys. Chem. Soc. 23, 169). Boils at 150°–155° with decomposition.

(3) *Isodibutol chloride. βδδ-trimethyl-β-chloropentane* $(CH_3)_3C{\cdot}CH_2{\cdot}CCl(CH_3)_2$. Boils with decomposition at 145°–150°; sp.gr. 0·890 at 0°. It is formed by the action of fuming hydrochloric acid on di*iso*butylene at 100° (Butlerow, Annalen, 189, 51).

Octyl bromides.

(1) **Normal,** *α-bromooctane* $CH_3[CH_2]_6CH_2Br$, b.p. 198°–200°; sp.gr. 1·116 at 16°; 1·1178 at 13° (Perkin, Chem. Soc. Trans. 1896, 1237). A colourless liquid prepared by the action of bromine and phosphorus on *n*-octyl alcohol.

(2) **Secondary,** *β-bromooctane*

$CH_3[CH_2]_6CHBr{\cdot}CH_3$

b.p. 187·5°–188·5° at 741 mm.; sp.gr. 1·0989 at 22° (Lachowicz, Annalen, 220, 185).

Preparation.—By treating methylhexyl carbinol with bromine and phosphorus, or by saturating the carbinol with hydrogen bromide at 0°, and heating for a few hours to 100°.

Properties.—It is an oily liquid, resembling the chloride in smell; it is soluble in alcohol but not in water. It boils with decomposition and leaves a carbonaceous residue when distilled. It precipitates silver salts in alcoholic solution, but less readily than the iodide.

Octyl iodides.

Normal, *α-iodooctane* $CH_3[CH_2]_6CH_2I$, b.p. 220°–222°; sp.gr. 1·338 at 16° (Zincke, Annalen, 152, 1).

Preparation.—By the action of iodine and phosphorus or of hydrogen iodide on the alcohol (Möslinger, *ibid.* 185, 55). It is a colourless liquid which reddens on warming; it is soluble in absolute alcohol or in ether, but insoluble in water (Zincke).

Secondary iodides. (1) *β-iodooctane*

$CH_3[CH_2]_5CHI{\cdot}CH_3$

It boils with decomposition at 211° (Bouis, Ann. Chim. Phys. [iii.] 44, 131); 193° (Squire, Chem. Soc. Trans. 1855, 108).

Preparation.—By the action of iodine and phosphorus on methylhexylcarbinol. It is an oily liquid with an odour of oranges, reddening on exposure to light. With sodium or potassium it behaves like the chloride. When heated with mercury, mercurous iodide, octylene, and free hydrogen are formed. The alcoholic solution precipitates silver salts.

(2) *Octylene hydriodide*, b.p. 120°; sp.gr. 1·33 at 0°, 1·314 at 21°. An amber-yellow liquid insoluble in water; it is decomposed by light, and by the action of mercury in the cold.

Tertiary iodide. *Isodibutol iodide, βδδ-trimethyl-β-iodopentane* $(CH_3)_3C{\cdot}CH_2{\cdot}CI(CH_3)_2$ is formed by the action of hydriodic acid on di*iso*butylene. It is decomposed by water (Butlerow, Annalen, 189, 52).

Octyl ethers. *Normal octyl ether* $(C_8H_{17})_2O$. From *iso*heptyl carbinol, b.p. 280°–282°; sp.gr. 0·8050 at 17°, 0·82035 at 0°/0° (Dobriner). An oily liquid easily soluble in hot alcohol or ether. It is prepared by the action of sodium octoxide on the *iso*primary iodide (Möslinger, *ibid.* 185, 57; Dobriner, *ibid.* 243, 10).

Mixed ethers. *Methyl normal octyl ether* $CH_3{\cdot}O{\cdot}C_8H_{17}$, boils at 173°; sp.gr. 0·8014 at 0°/0° (Dobriner, *ibid.* 243, 4).

Ethyl normal octyl ether, boils at 189·2°; sp.gr. 0·8008 at 0°/0° (Dobriner, *l.c.*).

Propyl normal octyl ether, boils at 207·0°; sp.gr. 0·8039 at 0°/0° (Dobriner, *l.c.*).

Butyl normal octyl ether, boils at 225·7°; sp.gr. 0·8069 at 0°/0° (Dobriner, *l.c.*).

Amyl normal octyl ether, boils at 220°; sp.gr. 0·6080 at 20°/ (Wills, J. 1853, 509).

Heptyl normal octyl ether, boils at 278·8°; sp.gr. 0·8182 at 0°/0° (Dobriner, *l.c.*).

All are colourless, mobile liquids, soluble in alcohol and ether, but not in water, prepared by the action of iodides of the radicles on sodium octoxide (Wills).

Octyl sulphides. (1) *Primary sulphide* $(C_8H_{17})_2S$. Boils with decomposition over 310°; sp.gr. 0·8419 at 17°/17°. A faintly-yellow mobile liquid soluble in warm alcohol, and miscible with ether. It is prepared by the action of an alcoholic solution of potassium sulphide on normal octyl chloride (Möslinger, Annalen, 185, 60). Sulphuric acid forms with it a white amorphous mass probably of *octyl sulphone* $(C_8H_{17})_2SO_2$; mercuric chloride gives crystalline needles of $C_8H_{17}S{\cdot}HgCl_2$. It forms no compound with the alkyl iodides.

(2) *Secondary sulphide.* An oily liquid

lighter than water and having an unpleasant smell. It is prepared by heating an alcoholic solution of sodium sulphide with secondary octyl iodide until the mixture becomes turbid, and then allowing the sulphide to separate out. It is slightly soluble in alcohol and decomposes on heating.

Methyl hexyl ketone $C_6H_{13}\cdot CO\cdot CH_3$. A liquid with an aromatic odour, b.p. 171°; sp.gr. 0·817 at 17°. It is obtained as a by-product in the preparation of the alcohol, also by the oxidation of the alcohol, and by the distillation of a mixture of calcium œnanthylate and calcium acetate (Staedler, J. pr. Chem. [i.] 72, 241). On oxidation it yields acetic and caproic acids. With the acid sulphites of the alkaline metals it forms compounds which crystallise in pearly scales.

Ethereal salts of primary octyl. The following constants have been determined by Gartenmeister (Annalen, 233, 249):—

	B.p. °	Sp.gr. $\frac{0°}{0°}$	Sp.gr. $\frac{\text{B.p.}}{0°}$	Ratio of vol. at b.p. to vol. at 0°	Specific volume
Formate .	198·1	0·8929	0·7156	1·2477	220·3
Acetate .	210·0	0·8847	0·6981	1·2672	245·8
Propionate	226·4	0·8833	0·6860	1·2876	270·5
Butyrate .	242·2	0·8794	0·6751	1·3028	295·6
Valerate .	260·2	0·8784	0·6618	1·3272	322·6
Caproate .	275·2	0·8748	0·6509	1·3440	349·6
Heptoate	290·4	0·8757	0·6419	1·3651	376·2
Octoate .	305·9	0·8755	0·6318	1·3858	404·3

These esters are all colourless liquids soluble in or miscible with alcohol and ether. The first six are prepared by the action of the silver salts of the acids on the bromides or iodides of octyl. The heptoate is prepared by the action of sulphuric and heptoic acids on octyl alcohol. The octoate is obtained as a by-product in the oxidation of octyl alcohol.

Normal octyl acetate occurs naturally in the ethereal oil of *Heracleum Sphondylium* (Linn.); it is a mobile fluid with a pleasant odour of apples and a burning spicy taste. The butyrate occurs in the oil of the seeds of *Peucedanum sativum* (Benth. and Hook.).

Octyl acetoacetic ester $C_{14}H_{26}O_3$, b.p. 280°–282° (not corr.); sp.gr. 0·9354 at 18·5°/17·5°. A clear, highly refractive liquid, obtained by the action of sodium acetoacetate on octyl iodide. It decomposes on hydrolysis into octyl acetone and octyl acetic acid (Guthzeit, Annalen, 204, 2).

Octyl benzoate $C_6H_5\cdot COOC_8H_{17}$, b.p. 305°–306°. A colourless liquid with a weak aromatic odour easily soluble in alcohol and ether (Zincke, *ibid.* 152, 1).

Octyl sulphuric acid is prepared from concentrated sulphuric acid and octyl alcohol. The barium salt $Ba(C_8H_{17}SO_4)_2$ forms large anhydrous nacreous plates very slightly soluble in hot water and alcohol. The potassium salt

$$KC_8H_{17}SO_4$$

forms a white soluble semi-crystalline mass with a soapy feel.

Octyl nitrite, b.p. 175°–177°; sp.gr. 0·862 at 17°. Obtained by heating octyl alcohol saturated with nitrous acid to 100° (Eichler, Ber. 12, 1887).

Octyl allophanate $NH_2CO\cdot NH\cdot COOC_8H_{17}$. Shining needles melting at 155°–160°, soluble in hot alcohol. Obtained by the action of chloroformamide on the alcohol.

Ethereal salts of secondary octyl. From methylhexylcarbinol.

Secondary octyl acetate, b.p. 193° (Bouis, Annalen, 44, 135); 191°–192° (Dachauer, *ibid.* 106, 269). A mobile liquid with a pleasant fruity odour, lighter than water, soluble in alcohol and ether, and also without change in not too concentrated sulphuric acid. It is easily saponified by potash. It is prepared (1) by the action of acetic acid or of an alkaline acetate and sulphuric acid upon the secondary alcohol; (2) by the action of silver or potassium acetate on the haloid compounds of the secondary alcohol; (3) by the action of acetyl chloride on sodium octoxide.

The *monochloroacetate* is prepared by passing hydrogen chloride into a mixture of equivalent quantities of the alcohol and monochloroacetic acid and heating for 30 hours. B.p. 234°; sp.gr. 0·9904 at 10°. It is a colourless neutral mobile oil with an ethereal odour and burning taste. It is soluble in alcohol and ether.

The *di-* and *tri-chloracetates* are prepared in a similar manner by substituting dichloro- or trichloroacetic acid. The trichloroacetate requires less heating. The former boils at 244°, the latter at 260°. They are colourless ethereal oils, lighter than water (Gehring, Compt. rend. 104, 1000).

Secondary octyl nitrate $C_8H_{17}O\cdot NO_2$. A liquid with a pleasant smell resembling ethyl acetate. It begins to boil at 80° but soon decomposes. It is lighter than water, is soluble in alcohol, and is prepared by the action of silver nitrate on octyl iodide in alcoholic solution (Bouis).

Secondary octyl nitrite $C_8H_{17}O\cdot NO$. A dark-yellow mobile liquid, b.p. 165°–166°; sp.gr. 0·881 at 0°. Obtained by the action of glyceryl trinitrite on the alcohol. It is soluble in ether and chloroform, and is decomposed by acids and by alcohol (Bertoni, Chem. Zentr. 1887, 35).

Secondary octyl sulphuric acid is obtained by the action of concentrated fuming sulphuric acid on methylhexyl carbinol. It is a colourless syrupy strongly acid liquid, easily soluble in water and alcohol; the diluted acid is decomposed on boiling into secondary octylic alcohol and sulphuric acid. It dissolves iron, zinc, &c., with evolution of hydrogen, and completely neutralises the bases.

The *barium salt* forms flexible nacreous plates containing three molecules of water on separating from a hot solution, or mammillary aggregations with two molecules of water on evaporating in a vacuum. It is soluble in water and alcohol, and has at first a bitter, then a sweet taste. It turns red on standing, blackens at 100°, and decomposes without melting.

The *calcium salt* forms white laminæ with a soapy feel and bitter taste.

The *potassium salt* $KC_8H_{17}SO_4,\frac{1}{2}H_2O$ forms white shining plates with a greasy feel; the taste is at first bitter, then sweet. It is soluble in water and alcohol, reddens and is decomposed at 100°.

Octyl phosphoric acid is formed by digesting octyl alcohol with glacial phosphoric acid. It forms soluble salts with lead or barium (Bouis).

Octyl palmitate and **stearate** are formed by prolonged heating of the alcohol with the respective acids to 200° in sealed tubes. The palmitate melts at 8·5°, the stearate at −4·5° (Hanhart, Compt. rend. 47, 230).

Octyl carbamate is formed by the action of cyanogen chloride on the alcohol, b.p. 135° (under 20 mm. pressure). It is very soluble in alcohol, from which it separates out in colourless crystals melting at 54°–55°. At ordinary pressures it boils with decomposition at 230°–232°, with partial conversion into cyanuric acid.

Octyl thiocyanate $C_8H_{17}\cdot S\cdot CN$, b.p. 142°, is formed by the action of KCNS on the secondary iodide (Jahn, Ber. 8, 805).

Octyl thiocarbimide $C_8H_{17}\cdot N:CS$. A colourless liquid, b.p. 234°, formed by Hofmann's reaction from octylamine by mixing with carbon disulphide in alcoholic or ethereal solution, evaporating to dryness and adding silver nitrate or mercuric, or ferric chloride to the solution of amine salt of the resulting carbaminic acid, and distilling in steam.

Octyl thiocarbamide $C_8H_{17}\cdot NH\cdot CSNH_2$, m.p. 112·5°, formed by the action of ammonia on the preceding compound. It is soluble in alcohol and ether, and separates out from its solution in colourless laminæ (Jahn, Ber. 8, 803).

OCTYLAMINES.

Only the following have been prepared—

(1) **Primary amines.**

(*a*) **Normal octylamine,** *α-aminooctane*

$$CH_3[CH_2]_6CH_2\cdot NH_2$$

is prepared by heating *n*-octyl iodide with alcoholic ammonia to 100° (Renesse, Annalen, 166, 85). It is also produced by treating octyl alcohol with ammonio-zinc chloride at 280° (Merz and Gasiorowski, Ber. 1884, 629); and by reducing nitrooctane with iron filings and acetic acid (Eichler, *ibid.* 1879, 1885); and in a purer condition by decomposing octyl phthalimide with concentrated hydrochloric acid at 200° (Mugdan, Annalen, 298, 145).

It is a colourless basic oil which takes up CO_2 from the air, and boils at 175°–177°/745 mm. In contact with water it forms white crystalline needles. With bromine and potash an oily compound $C_8H_{17}NBr_2$ is formed, which is converted on boiling with soda into heptyl cyanide $C_7H_{15}CN$ (Hofmann, Ber. 1884, 1920). The *hydrochloride* $C_8H_{17}NH_2,HCl$ is easily soluble in water and alcohol; the *platinichloride*

$$(C_8H_{17}NH_2)_2H_2PtCl_6$$

forms yellow leaves soluble with difficulty in alcohol and water; the *picrate*

$$C_8H_{17}NH_2\cdot C_6H_2(NO_2)_3OH$$

crystallises from alcohol in oblong tables, melting at 112°–114° (Hoogewerff and Dorp, Rec. trav. chim. 6, 387).

(*b*) **Secondary octylamine,** *β-aminooctane,* is prepared by treating secondary octyl iodide from castor oil with ammonia; or methyl hexyl carbinol with ammonio-zinc chloride at 280° (Merz and Gasiorowski, Ber. 1884, 364). It boils at 162·5° (Jahn, *ibid.* 1875, 805); 175° (Bouis, J. 1855, 526); sp.gr. 0·786. It is a colourless, bitter, very caustic inflammable liquid with an ammoniacal fishy odour. It is insoluble in water, but precipitates metallic salts and dissolves silver chloride. On heating with secondary octyl iodide, ammonium iodide, octylene, polyoctylenes and the iodide of secondary octylamine are formed (Jahn, *l.c.*). The *hydriodide* $C_8H_{20}NI$ forms large plates easily soluble in water; the *hydrochloride* $C_8H_{20}NCl$ is a very deliquescent solid which crystallises *in vacuô* in large nacreous plates; the *aurichloride* $C_8H_{20}NAuCl_4$ forms shining yellow laminæ, resembling lead iodide; the *platinichloride* $(C_8H_{20}N)_2PtCl_6$ separates from boiling solution in brilliant golden yellow scales soluble in alcohol or ether.

(2) **Secondary amines.**

(*a*) **Dinormal octylamine** $C_8H_{17})_2NH$ is produced together with *n*-octylamine by the action of ammonia on octyl iodide (Renesse, Annalen, 166, 85); or by treating octyl alcohol with ammonio zinc chloride at 280° (Merz and (Gasiorowski). It crystallises in needles, melting at 36°, and boiling at 297°–298°. It is soluble in alcohol and ether, and has a strong tallow-like odour. The *hydrochloride* forms plates soluble in alcohol; the *platinichloride*

$$(C_{16}H_{35}N\cdot HCl)_2\cdot PtCl_4$$

crystallises in small scales.

(*b*) **Di-secondary-octylamine** $(C_8H_{17})_2NH$ is prepared by heating methyl hexylcarbinol and ammonio-zinc chloride to 280° (Merz and Gasiorowski). It is an oil with an aromatic odour boiling at 260°–270°. The *hydrochloride* $C_{16}H_{36}NCl$ forms small leaves; the *platinichloride* $(C_{16}H_{35}N\cdot HCl)_2PtCl_4$ forms a brown mass; the aurichloride $C_{16}H_{35}NHAuCl_4$ crystallises from alcohol in golden yellow laminæ.

(3) **Tertiary amines.**

(*a*) **Tri-normal-octylamine** $(C_8H_{17})_3N$ is formed in moderate quantity along with the mono- and di- compounds by heating octyl alcohol with ammonio-zinc chloride to 260°–280°. When pure it forms a white crystalline mass, but is usually obtained as a nearly colourless oil of agreeable odour. It boils at 365°–367°, is readily soluble in ether and absolute alcohol, but not in water. Most of its salts are liquid; the *platinichloride* $((C_8H_{17})_3NHCl)_2PtCl_4$ forms a glutinous mass insoluble in water.

(*b*) **Tri-secondary-octylamine** $(C_8H_{17})_3N$ is obtained in the same way from methylhexyl carbinol. It is a liquid boiling at 370°. It forms an oily hydrochloride. The *platinichloride* $(C_{24}H_{51}NHCl)_2PtCl_4$ is a reddish-brown resin.

Primary octyl phosphine. B.p. 184°–187°; sp.gr. 0·8209 at 17°. A limpid, mobile, highly refractive liquid, soluble in alcohol, ether, benzene, and glacial acetic acid. It is obtained by the action of phosphonium iodide and zinc oxide upon normal octyl iodide at 170° (Möslinger, Annalen, 185, 65).

Nitric acid oxidises the solution in glacial acetic acid to *octylphosphinic acid,* an amorphous compound soluble in hot acetic acid. Oxygen, bromine, and iodine act less energetically upon octyl phosphine than upon the phosphines of the lower members of the series. Fuming hydriodic acid forms *octyl phosphonium iodide* $PH_3C_8H_{17}I$, a semi-crystalline mass which decomposes on standing, or on solution in ether or benzene.

Octonitrile, *heptyl cyanide* $C_7H_{15}CN$, boils at 194°–195°; sp.gr. 0·8201 at 13·3° (Felletar, J. 1868, 634); b.p. 198°–200° (Hofmann, Ber. 1884, 1410).

n-**Octyl cyanide,** *pelargonic nitrile,* boils at 214°–216°; sp.gr. 0·786 at 16°/4° (Hell and Kitrosky, *ibid.* 1891, 985; Eichler, *ibid.* 1879, 1888).

Octoamide, *caprylamide* $C_7H_{15}CO\cdot NH_2$, crystallises in leaves melting at 97°–98° (Aschan, Ber. 1898, 2348), 110° (Felletar, J. 1868, 624).

It is prepared by dropping the acid chloride into ammonia (Aschan, *l.c.*), or by heating ammonium octoate (Hofmann, Ber. 1882, 983). It is very slightly soluble in boiling water, and not at all in cold.

Nitro-octane. A liquid boiling at 205°–212°, obtained together with octyl nitrite by the action of silver nitrite on primary octyl iodide (Meyer, Annalen, 171, 23; Eichler, Ber. 1879, 1883).

Octyl nitrolic acid $C_8H_{16}NO{\cdot}NO_2$. An oily body formed from nitro-octane by saturating its solution in 10 volumes of water with nitrous fumes. Concentrated sulphuric acid decomposed it into octoic acid and nitrous oxide (Eichler, Ber. 12, 1885).

BENZENE DERIVATIVES OF PRIMARY OCTYL.

Octylbenzene $C_6H_5{\cdot}C_8H_{17}$. A colourless oil with a sweet taste, b.p. 261°–263° (uncorr.); sp.gr. 0·849 at 15°/15°; b.p. 262°–264°; sp.gr. 0·852 at 14° (Ahrens, Ber. 1886, 2717) (Schweinitz, *ibid.* 640). It is obtained by the action of sodium on a mixture of bromobenzene and normal octyl bromide in ethereal solution; or from bromobenzene, normal octyl iodide and sodium (Lepinski, Ber. 1898, 938). It is miscible with alcohol, ether, or benzene.

Chloro-octylbenzene $C_6H_4ClC_8H_{17}$ is a yellowish odourless oil soluble in alcohol and ether, b.p. 270°–275°. It is prepared by the action of chlorine and iodine on octylbenzene (Ahrens, Ber. 1886, 2719).

Bromo-octylbenzene $C_8H_{17}{\cdot}C_6H_4Br$, b.p. 285°–287°, resembles the chloro derivative, and is prepared by warming octyl benzene with bromine water (Schweinitz, Ber. 1886, 642).

p-**Iodo-octylbenzene.** A heavy oil, b.p. 318°–320°, prepared from *p*-amino-octylbenzene (*q.v.*) by the diazo- reaction (Beran, Ber. 1885, 136). By treating octylbenzene, diluted with petroleum, with iodine and mercuric oxide, a yellow oil is obtained, which is probably identical with the preceding compound.

The corresponding derivative of the secondary alcohol (from castor oil) is a yellow oily liquid, b.p. 304°–305°. On oxidation with chromic acid both yield *p*-iodobenzoic acid.

m-**Nitro-octylbenzene** $NO_2{\cdot}C_6H_4{\cdot}C_8H_{17}$. Crystallises in long needles which melt at 123°–124° and sublime at a high temperature. It is prepared by the action of fuming nitric acid upon octylbenzene in the cold. It is slightly soluble in alcohol and chloroform. With potassium permanganate it yields *m*-nitrobenzoic acid (Ahrens, Ber. 1886, 2725).

o-**Nitro-octylbenzene** is a thick yellow aromatic oil which decomposes at 100°. It is prepared by treating octylbenzene with fuming nitric acid and warming after filtering off the precipitated crystals of *m*-nitro-octyl benzene (Ahrens, *l.c.*).

p-**Nitro-octylbenzene** which forms small yellow lustrous needles melting at 204°, and soluble in alcohol or ether, is found in the residue from the meta- and ortho- compounds (Ahrens, *l.c.*).

Dinitro-octylbenzene $C_8H_{17}{\cdot}C_6H_3(NO_2)_2$ forms crystals melting at 226°, but subliming below this temperature. It is soluble in alcohol and ether and is formed by the action of fuming nitric acid on the crystals of the meta- compound (Ahrens).

o-**Amino-octylbenzene hydrochloride**

$$C_8H_7{\cdot}C_6H_4{\cdot}NH_2,HCl$$

occurs in small lustrous white plates which redden on heating. It is formed by reducing the nitro derivative with tin and hydrochloric acid (Ahrens, Ber. 1886, 2717).

p-**Amino-octylbenzene,** a colourless liquid, b.p. 310°–311°, volatilises in steam. It is obtained by the action of aniline hydrochloride, or of aniline and zinc chloride on primary octyl alcohol (from *Heracleum* oil). A similar derivative may be prepared from the secondary alcohol (from castor oil), b.p. 290°–292° (corr.) (Beran, Ber. 1885, 132).

Formylphenoctylamine, *formylamino-octylbenzene,* $C_8H_{17}{\cdot}C_6H_4{\cdot}NH{\cdot}CHO$ is obtained by the action of formic acid on *p*-aminoctylbenzene. It forms scales which melt at 56° and are soluble in alcohol or ether (Beran, Ber. 1885, 135).

Acetylphenoctylamine, *acetylamino-octylbenzene* $C_8H_{17}{\cdot}C_6H_4NH{\cdot}C_2H_3O$, is formed from *p*-amino-octylbenzene and acetic anhydride. It forms thin plates melting at 93°, and soluble in alcohol or ether (Beran).

Benzoylphenoctylamine, *benzoylamino-octylbenzene* $C_8H_{17}{\cdot}C_6H_4NHBz$, is obtained from *p*-amino-octylbenzene and benzoyl chloride. It forms scales melting at 117° and soluble in alcohol or ether. The corresponding derivative of the secondary alcohol forms white needles melting at 109° (Beran).

p-**Octylbenzonitrile** is obtained by distilling formylphenoctylamine with zinc-dust; b.p. 312°. It is converted by oxidation into *p*-octylbenzoic acid.

Octylbenzene sulphonic acid. A thick syrupy strongly acid liquid formed by the action of Nordhausen acid on octylbenzene. Silver salt $C_8H_{17}{\cdot}C_6H_4{\cdot}SO_3Ag,H_2O$. Barium salt

$$(C_{14}H_{21}SO_3)_2Ba,H_2O.$$

Lead salt $(C_{14}H_{21}SO_3)_2Pb,3H_2O$ (Schweinitz, Ber. 1886, 640).

TOLUENE DERIVATIVES OF PRIMARY OCTYL.

Amino-octyltoluene (*Toloctylamine*)

$$C_8H_{17}C_6H_3MeNH_2$$

is prepared by treating the normal alcohol with *o*-toluidine and zinc chloride. It is a colourless oil which boils at 324°–326°, and forms a well-crystallised hydrochloride, sulphate, and oxalate (Beran, Ber. 1885, 146).

Acetyltoloctylamine $C_8H_{17}{\cdot}C_7H_6{\cdot}NHAc$ forms slender white needles, m.p. 81°, soluble in alcohol and ether (Beran, *l.c.*).

Benzoyltoloctylamine $C_8H_{17}{\cdot}C_7H_6{\cdot}NHBz$ forms lustrous scales, m.p. 117°, soluble in alcohol. These toluene derivatives are prepared in a manner analogous to the corresponding benzene derivatives (Beran, *l.c.*).

THIOPHEN DERIVATIVES OF PRIMARY OCTYL.

(Schweinitz, Ber. 1886, 644 *et seq.*)

Octylthiophen $C_8H_{17}{\cdot}C_4H_3S$ is formed by the action of sodium on octyl bromide and iodothiophen, b.p. 257°–259°; sp.gr. 0·8181 at 20·5°/20·5°. It is soluble in ether.

Bromo-octylthiophen $C_4SH_2Br{\cdot}C_8H_{17}$ boils at 285°–290° and solidifies at 5°.

Iodo-octylthiophen $C_4SHI{\cdot}C_8H_{17}$ is a yellow oil which solidifies at 0°; sp.gr. 1·2614 at 20°/20°.

Both the bromo and iodo compounds are prepared analogously to the corresponding benzene derivatives.

Octylacetothienone $C_8H_{17}\cdot C_4SH_2\cdot COMe$, an oil with a garlic-like odour, b.p. 350°–355°, and **Octyldiacetothienone** $C_8H_{17}\cdot C_4SH(COMe)_2$, a yellow syrup, are prepared by the action of acetyl chloride and aluminium chloride on octylthiophen.

Octylthiophen-di-carboxylic acid

$$C_8H_{17}\cdot C_4SH(COOH)_2$$

is obtained in microscopic needles melting at 185°, by the action of potassium permanganate on the mono and diacetyl derivatives. Barium, copper, and silver salts have been prepared.

$\beta\beta$-Methyloctylthiophen $C_8H_{17}\cdot C_4SH_2Me$ is obtained by the action of sodium on $\beta\beta$-methyl iodothiophen and octyl bromide. It is a colourless oil boiling at 270°–275°, and on strongly cooling it solidifies to a crystalline mass which melts at 10°. The monobromo derivative $C_8H_{17}C_4SHMeBr$ melts at 20°.

OCUBA WAX *v.* Wax.

ODORINE. A volatile base found by Unverdorben in bone-oil. Probably impure picoline.

iso-**ŒNANIC ACID** *v.* Heptoic acids.

ŒNANTHIC ACID *v.* Heptoic acids.

ŒNANTHIC ETHER. According to Liebig and Pelouze (Annalen, 19, 241), there is found in wine a small quantity of a body termed by them œnanthic ether. It is a very mobile liquid, with a strong vinous smell, and of a disagreeable taste; readily soluble in ether and alcohol, but very sparingly soluble in water. This ether is now prepared commercially for flavouring common wines, brandy, &c., from the oxidised products of oil of rue. According to A. Fischer (Annalen, 115, 247) the artificial product is a mixture of capric and caprylic acids. Many fusel oils contain both these acids, and amyl caprate is found in several Hungarian wines.

ŒNANTHOL, *œnanthaldehyde, heptaldehyde, normal œnanthic,* or *heptoic aldehyde,* $C_6H_{13}CHO$, is one of the products of the dry distillation of alkaline ricinoleates and of the action of nitric acid on stearic and margaric acids. It is also formed when fats and oils turn rancid (Scala, Chem. Zentr. 1898, i. 439).

The following method of preparation may be employed:—

Castor oil, which consists essentially of the glyceride of ricinoleic acid, is rapidly distilled until the residue becomes resinous, thus converting the greater part of the ricinoleic acid into œnanthol and hendecatoic acid:—

$$C_{18}H_{34}O_3 = C_6H_{13}CHO + C_{11}H_{20}O_2.$$

The distillate is rectified, and the part coming over between 90° and 180° is shaken with a saturated solution of acid sodium sulphite, and is warmed and filtered. The mass of the double salt $C_6H_{13}CHO\cdot HNaSO_3,H_2O$, separating out on cooling, is pressed between filter paper, mixed with a solution of sodium carbonate, and distilled in a current of steam. The œnanthol which floats on the distillate is separated and dried over anhydrous sodium sulphate or calcium chloride (Bussy, Annalen, 1846, 60, 246; Erlenmeyer and Sigel, *ibid.* 1875, 176, 342).

The yield of œnanthol is increased when the castor oil is distilled under reduced pressure (Krafft, Ber. 1877, 10, 2035; Jourdan, Annalen, 1880, 200, 102).

A better yield is obtained by distilling the ethyl or preferably the methyl ester of ricinoleic acid at ordinary pressure. The distillate is redistilled, treated with sodium bisulphite and the crystalline mass thus obtained is washed with ether and well drained. The œnanthol can then be isolated in the ordinary way (Haller, Compt. rend. 1907, 144, 462).

Œnanthol is also prepared by the following process: Castor oil or rape oil is heated in an iron boiler to 160°, and air is blown through, the source of heat is then removed and the temperature of the mass rises spontaneously to 220°. The vapours are condensed and the oily layer is treated with sodium bisulphite. The œnanthol is then separated as above (D. R. P. 167137; Frdl. 1905–07, 40).

Œnanthol reacts with diazoacetic ester yielding non-crystalline ethyl œnanthyliden-1:2-dioxynonylate, b.p. 200°/14 mm. On saponification the latter yields an acid which on boiling with acetic acid decomposes with formation of œnanthol (Dieckmann, Ber. 1910, 43, 1027).

Œnanthol is a highly refractive, very mobile, colourless liquid, of pungent aromatic smell, boiling at 154° at 747 mm. pressure, and having at 15° a sp.gr. of 0·8231 (Perkin, jun., Ber. 1882, 15, 2802; D. R. P. 126736, 1902), b.p. 152·2°–153·2° (corr.) sp.gr. 0·82264 at 15° (Perkin, Chem. Soc. Trans. 1884, 476), b.p. 42°–43°/10 mm., sp.gr. 0·8250 at 20° (Semmler, Ber. 1909, 42, 1161). It is slightly soluble in water, and dissolves in all proportions in alcohol and ether. Œnanthol rapidly oxidises on exposure to air. It reduces silver nitrate.

When heated at 190° in sulphuric acid, it blackens and a small quantity of carbon monoxide and much sulphur dioxide are evolved (Bistrzycki and Fellmann, Ber. 1910, 43, 776).

With nitric acid, œnanthol yields dinitrohexane, hydroxylamine and heptoic acid (Ponzio, J. pr. Chem. 1896, [ii.] 53, 431). Œnanthol reacts with cyanacetic acid in the presence of piperidine forming $\alpha\gamma$-dicyano-β-hexyl-glutaric acid, m.p. 142° (D. R. P. 156560; Frdl. 1902–04, 738; *see* also Guareschi, Chem. Zentr. 1903, ii. 193; Annalen, 1903, 325, 205). It also reacts with malonic acid forming Δ' nonylenic acid (D. R. P. 156560; Harding and Weizmann, Chem. Soc. Trans. 1910, 299).

Œnanthol condenses with aniline (Miller, Ber. 1892, 25, 2020); with aniline sulphite (Eibner, Chem. Zentr. 1901, i. 1360; Speroni, Annalen, 1902, 325, 354); with acetone (Rupe and Hinterlach, Ber. 1907, 40, 4764); with oxalacetic ester in presence of ammonia (Simon and Conduché, Ann. Chim. Phys. 1907, [viii.] 12, 5), and with hydrazobenzene (Russow, J. pr. Chem. 1909, [ii.] 80, 511). It also reacts with a number of other substances (Fittig and Reechelmann, Annalen, 1889, 255, 126; Miller, *l.c.*; Fischer and Giebe, Ber. 1897, 30, 3054; Knoevenagel, Ber. 1898, 31, 730; Claisen, *ibid.* 1014; Neuberg and Neimann, *ibid.* 1902, 35, 2049; Lees, Chem. Soc. Proc. 1902, 213; Tschitschenko, J. Russ. Phys. Chem. Soc. 1906, 38, 482; Schlotterbeck, Ber. 1907, 40, 479; Braun, *ibid.* 1908, 41, 2169; Semmler, *l.c.*).

Œnanthaldoxime boils at 100·5°/14 mm. It only solidifies partially and the solid part melts at 55·5° (Bourgeois and Dambmann, Ber. 1893, 26, 2856). It forms a number of derivatives (Goldschmidt and Zanoli, Ber. 1892, 25, 2573; Comstock, Amer. Chem. J. 1897, 19, 485; Conduché, Ann. Chim. Phys. 1908, [viii.] 13, 5; Irvine and Moodie, Chem. Soc. Trans. 1908, 102).

ŒNANTHYLIC ACID *v.* Heptoic acid.

ŒNOCYANIN, the colouring matter of black grapes and red wines, is of colourless origin, and becomes blue through oxidation, and probably hydration, which may be shown by placing a green grape picked from a bunch which is just beginning to turn red in a vacuum of 1–2 mm. over boiled sulphuric acid for 3 or 4 days, or sufficient time to allow of the grape becoming hard and dry. The colour becomes yellow, but, on admitting air, moisture and oxygen are rapidly absorbed, the colour changing to blue black at the same time (Maumené, Compt. rend. 95, 924). Œnocyanin cannot be extracted from grape marcs and lees of wine, but is obtained from red wines destined for distillation by the following method: the wine is treated with sufficient basic lead acetate to precipitate the colouring matter, the precipitate is collected on a filter and washed until the filtrate contains only traces of lead (24 hours). The precipitate is weighed moist and the dry substance and lead oxide are determined in an aliquot portion. The remainder is then treated with exactly the calculated quantity of sulphuric acid and filtered hot. The colouring matter passes into the filtrate and is obtained in the form of a syrup soluble in water or alcohol by evaporating the solution to the required consistency after adding glycerol in the proportion of 10 grams of glycerol to the extract from 1 litre of wine. The solution of œnocyanin thus obtained is used for increasing the colour of poor wine and also for colouring confectionery and liqueurs. Œnocyanin is not a uniform substance and its proportion in red wines varies from 9·2 to 18·7 grams per litre (Cari Mantrand, Bull. Soc. chim. 1906, 35, 1017, 1022).

ŒNOLIN. The name given to the natural red colouring matter of wine precipitable by lime or basic lead acetate. Is brown-red whilst moist, but nearly black when dry, giving a violet-red or brown-red powder, readily soluble in alcohol, and in water acidulated with vegetable acids. Is said to have the composition $C_{20}H_{20}O_{10}$, and to form a lead compound $C_{20}H_{18}O_{10}Pb$ (Glénard, Compt. rend. 47, 268; Varenne, Bull. Soc. chim. [ii.] 29, 109). For the estimation of œnolin and œnotannin in wines, *v.* F. Jean, Compt. rend. 93, 966.

ŒNOMETER. A hydrometer designed for determining the alcoholic strength of wines.

OIL-GAS *v.* Gas, oil.

OIL, MINERAL, *v.* Petroleum.

OIL OF AMBER *v.* Oils, essential, and Resins.

OIL OF HARTSHORN *v.* Bone oil.

OIL OF VITRIOL *v.* Sulphuric acid.

OILS, ESSENTIAL. The word 'oil' appears to be derived from the Greek *elaia*, the olive tree, through the Latin *oleum*, and the French *huile*. It would seem to have been originally applied to liquids which like olive oil are insoluble in water, combustible, and more or less viscid, and this may be regarded, save for a few unimportant exceptions, such as oil of vitriol, as the signification which the word has retained.

Two kinds of oil are recognised, fixed or fatty oils (*v.* Oils, Fixed, and Fats) and essential or volatile oils.

A scientific definition of the term 'essential' or volatile oils is not possible, but they may be for general purposes defined as substances of an oily nature obtained from, as a rule, vegetable sources, possessed usually of odour, generally liquid, although sometimes semi-solid at ordinary temperatures, and volatile without decomposition.

The constituents of some essential oils are decomposed either in whole or part when the oils are distilled by themselves, and some even under steam distillation.

The essential oils occur in various parts of the plant, in some instances distributed throughout the plant, in others restricted to a particular portion, *e.g.* in the petals of the flowers as in the rose, in the bark and leaves as in the cinnamon, and in the flower and rind of the fruit as in the orange and lemon.

The functions of the essential oil in plant life are not thoroughly understood. Obviously the more powerful odours are of value in attracting insects for fertilisation by pollen, but this has no direct connection with the plant life.

The majority of essential oils are probably correctly classified as by-products of the changes of cell life in the plant, the oils in some instances occurring in conjunction with resins, forming a series of bodies known as oleo-resins.

The researches of Charabot and his colleagues on the varying proportions of oil in plants at different periods of their growth, as well as differences in the constitution of such oils, have been of great value in determining the suitability of soil, and conditions for the growth of plants for distillation of essential oils, and also for determining the period for collection of distillation material.

Space does not permit of reference to the detail of such experiments, but a few of the general conclusions may be thus briefly summarised:—

The odorous compounds first appear in the young green organs of plants, and continue to form and accumulate until the flowering period, when the activity slackens. They migrate by diffusion from the leaf to the stem, and thence into the inflorescence. A portion enters into solution and penetrates into the tissues where it becomes deposited. When fertilisation takes place, a quantity of essential oil is consumed in the inflorescence, or is lost by evaporation. Probably the green organs continue to produce odorous constituents, but experiments show that during fertilisation there is a net loss of these bodies. It is therefore obvious that in most cases the best yield of essential oil is obtained before fertilisation takes place. After fertilisation the oil again increases in the green parts of the plant.

Esters have their origin in the green parts of the plant by the direct combination of acids on the alcohols previously formed. Esterification appears to be assisted by enzymes which act as dehydrating agents. Chlorophyll, however, appears to be the important factor in effecting the condensations which build up complex substances from simpler bodies.

The addition of mineral salts to the soil, such as the chlorides of potassium, sodium and ammonium, sulphates of sodium, potassium, ammonium, iron and manganese, nitrates and phosphates of sodium and potassium, appears to favour the formation of esters in peppermint plants.

In some instances oils are formed as a result of the decomposition of a glucoside by a ferment, as in the case of almond oil from the glucoside amygdalin by the ferment emulsin. The general characters of essential oils vary over a very wide range, and even essential oils of the same species grown in different parts of the world may show considerable variations in constitution. As a class the oils are lighter than water, although to this rule there are exceptions, such as cinnamon, cassia, clove, wintergreen, &c. They are almost insoluble in water, although sufficiently so to impregnate water with their odour. As already stated the majority of the volatile oils are liquid at ordinary temperatures, the oils consisting of liquid constituents or solid constituents dissolved in liquids.

In some instances the oils are semi-solid or almost solid in character. Although the words are of little scientific value the solid portion of oils are still described as *stearoptenes*, and the liquid portions as *oleoptenes* or *elœoptenes*.

The methods of production may be divided into three principal classes.

(1) Distillation :
    (*a*) From the plant ;
    (*b*) From oleo-resinous exudations.
(2) Mechanical processes.
(3) Extraction by solvents.

1. The methods of production of volatile oils by distillation from the wood, leaves, flowers or fruit by means of water, which is the usual method employed, have been much modified in recent years, and much attention has been devoted to improvements in modes of distillation and condensation. In some few instances fire heat is still used for distillation, the practice being retained by some of the distillers of lavender and peppermint oils in the Mitcham district. The usual method, however, is to pass steam through the material suitably arranged on trays—for example, in the case of the umbelliferous fruits, or to pass live steam through the material.

All the essential oils are readily volatile in the vapour of water. Many of the essential oils are distilled from their primary material under reduced pressure, the vapour passing over at a much lower temperature, with the corresponding advantage that the oil is not subjected to temperature likely to lead to decomposition. Modern stills have a capacity of 600–1200 gallons or more, and are usually made of copper with removable domes having water-sealed joints with latch fastenings to keep them in position. They are mounted on brickwork bases with steel framework, and have bottoms raised in the centre to effect absolute drainage. The stills are fitted with discharge pipes and also with steam heating coils constructed of copper with traps for the condensed water, which is led back into a tank for feeding the steam boiler. The still heads taper to a narrow pipe which leads to the condenser. The false bottom and cages in which the material is placed rest upon brackets fitted into the inside of the still. They are usually made of galvanised iron and the false bottom is perforated to enable the water to drain away. Above the stills chain lifting tackle is fitted to steel girders to facilitate emptying and refilling.

The condensers usually consist of coils surrounded by cold water, which is kept continually flowing through them from the bottom upwards. The condensed distillate is collected in separators fitted with strainer plates and a series of draining taps. The condensed water is forced back into the stills by steam ejectors to be used in a subsequent distillation.

Distillation from oleo-resinous exudations. Many of the oleo-resins of different degrees of viscidity are used for the distillation of volatile oils—the most important being the oleo-resin used for the distillation of turpentine, and the essential oil distilled from such bodies as copaiba, &c. The oleo-resin is caused to exude from the living tree by making incisions, usually V-shaped, after stripping off the bark. The incisions are first made about 8 inches above the root, and the oleo-resin which exudes is collected in wooden vessels. The exudation commences about March and continues till the end of August or the beginning of September. The crude oleo-resin thus obtained is then distilled with water.

2. *Mechanical production.* Mechanical processes are employed in the case of lemon, orange, bergamot, and lime oils, which are obtained from the peel of the fruit. *The sponge process*, which is usually employed in Sicily, and Calabria, is essentially as follows : The fruit is first soaked in water for a short time and the peel is then removed in three slices, each slice being pressed flat by the fingers against a sponge. The oil glands are burst by the pressure and the oil, together with a considerable quantity of water and some juice, is absorbed by the sponge. The sponge is squeezed from time to time into a bowl and the oil separated from the water and filtered in closed filters.

The Écuelle process is employed in Northern Italy and the South of France. An écuelle is a saucer-shaped vessel, 8–10 inches in diameter, made of tinned copper, the inside of which is covered by short spikes about a quarter of an inch long. The bottom is connected by a hollow tube through which the oil passes to a collecting vessel. The whole fruit is placed on the écuelle and by rapid rotatory motion the oil glands are burst and the oil is ejected. An oil of inferior quality is obtained by subjecting the residual fruits to pressure or by macerating in warm water. A still inferior oil is obtained by distillation.

In the *Scorzetta process* the fruits are cut into halves, the pulp is removed by a spoon and the peel is twisted and pressed against a sponge. The pulp is used for the production of lemon juice and the peel is salted.

Machines are also used for the production of these oils, especially that of bergamot, by means of which the fruits are brought into contact with small knives which puncture or rupture the oil glands. The oil is drawn out of the vessel by means of vacuum pumps and steam is sometimes admitted to facilitate the process. Machine made oils, however, are usually inferior to those produced by hand processes. An illustration of one form of mechanical press is figured in the Perfumery and Essential Oil Record, March, 1910, 61.

3. *Extraction by solvents.* Extraction processes are employed principally for the delicate floral essences which are partially decomposed by distillation, such as jasmine and tuberose. Three kinds of processes are used, (*a*) those in which a volatile solvent is used; (*b*) those in which a non-volatile oil or fat is employed; and (*c*) those in which a current of moist air is used.

The volatile solvents commonly employed are alcohol, benzene, ether, chloroform, light petroleum, carbon disulphide, acetone, and tetrachlorethane. The simplest form of extraction is by percolation, either in the cold or at the boiling-point of the solvent on the principle of the Soxhlet apparatus. On the removal of the solvent a mixture of oil, resin, and colouring matter results, from which floral essences are prepared by solution in alcohol. In some cases the extracts are purified by distillation under reduced pressure with steam.

The extraction by non-volatile solvents is typified by the *enfleurage process.* A pure neutral fat, such as purified lard, is melted in trays, technically known as 'chassis,' and the fresh flowers are laid on the fat for a short time, then removed and replaced by fresh flowers until the fat has become saturated. The fat is then removed and sold as 'pomades,' which are employed in the manufacture of perfumes, being extracted by means of warm alcohol in closed vessels. Olive oil is also used for jasmine and violet flowers, the fresh flowers being macerated in the oil or placed on trays containing linen cloths soaked in the oil. The oil is then pressed out and may be extracted by means of alcohol.

In the *moist air process,* hot air is passed through a series of wet sponges and then over the flowers and into a volatile solvent which retains the perfume, and which can afterwards be removed. The advantage of this process is that only volatile bodies are extracted, colouring matters and resins being left in the raw material.

The main constituents of essential oils may be conveniently divided into the following important classes: terpenes and sesquiterpenes, alcohols, aldehydes, ketones, phenols and allied compounds.

Terpenes. The principal terpenes occurring in essential oils are pinene, camphene, fenchene, limonene, dipentene, terpinene, terpinolene, phellandrene, sylvestrene, carvestrene, thujene, sabinene, santene. The first three belong to the bicyclic series, the structure being in the form of a double ring. The other terpenes may be regarded as derivatives of cymene, which they closely resemble in molecular constitution. Limonene, dipentene, carvestrene, sylvestrene, and terpinolene may be regarded as dihydrocymenes, containing two ethylene linkages and have the formula $C_{10}H_{16}$. Menthene and carvo-menthene are tetrahydrocymenes and have the formula $C_{10}H_{18}$. On reduction they yield hexahydrocymenes. The terpenes are characterised by the melting-points of their derivatives.

Sesquiterpenes. These have the general formula $C_{15}H_{24}$ and boil at a temperature above 250°. They have a high refractive index and yield halogen derivatives which are somewhat difficult to purify. The more important ones occurring in essential oils are cadinene, caryophyllene, cedrene, humulene, santalene, and zingiberene. Olefinic sesquiterpenes occur in oils of citronella, lime, and lemon.

For further details as to characters and composition of this class of substances *see* art. TERPENES.

Alcohols. The alcohols of the paraffin series found in essential oils comprise geraniol, linalool, nerol, and citronellol. These belong to the unsaturated series containing one or more double linkages.

Alcohols of the benzene series are benzyl, cinnamyl, and anisyl alcohols and phenyl-ethyl-alcohol. Terpineol, terpene hydrate, borneol. pulegol, thujyl alcohol, fenchyl alcohol, sabinol and menthol are derivatives of the terpenes. Among sesquiterpene alcohols, santalol, cedrol, guaiol, patchouli alcohol, and the so-called 'camphors' of cubebs and matico may be mentioned. With the exception of santalol these are solid compounds.

Esters of many of these alcohols also occur in essential oils, chiefly those of acetic, propionic, butyric, valeric, tiglic, benzoic, salicylic, cinnamic, and anthranilic acids. The percentage of esters is found by saponification with alcoholic potash and many oils are valued according to their ester content. It should be pointed out, however, that probably other constituents absorb potash under the conditions of saponification and the determination of the saponification number is not strictly a measure of the esters present. It is useful, however, for purposes of comparison. Two to five grammes of the oil are heated on a water-bath for an hour with 20 c.c. of normal alcoholic potash and the excess of potash titrated with normal sulphuric acid.

The alcohols are determined by acetylation and subsequent estimation of the acetic esters formed. The usual method of procedure is to heat 10 c.c. of the oil with an equal volume of acetic anhydride and 2 grams of anhydrous sodium acetate for 2 hours to boiling-point. The oil is then thoroughly washed by shaking with successive quantities of water and afterwards dried by shaking with anhydrous sodium sulphate. 2–5 grammes of the acetylated oil is then neutralised and saponified with 20 c.c. of normal alcoholic potash for an hour and the excess of potash titrated with normal acid, using phenolphthalein as indicator. The percentage of alcohol in the original oil is calculated from the formula $\frac{M}{1000} \times \frac{X \times 100}{W-(0{\cdot}042X)} =$ p.c. alcohol, where M is the molecular weight of the alcohol, W the weight of acetylated oil, and X the number of c.c. of normal alcoholic potash absorbed.

Aldehydes. The aldehydes of the paraffin series found in essential oils are furfural, acetaldehyde, citral, and citronellal. Those belonging to the benzene series are benzaldehyde, salicylic aldehyde, cinnamic aldehyde, anisic aldehyde, and cumic aldehyde.

The usual method employed for the determination of cinnamic aldehyde in cinnamon and cassia oils and for the determination of citral in lemongrass oil is as follows:—

Five c.c. of the oil are shaken with a hot solution of sodium bisulphite (35 p.c.), freshly prepared, and heated in a water-bath for an hour, or until the solid aldehyde bisulphite compound is completely dissolved. A flask with the neck graduated in tenths of a cubic centimetre is employed and the uncombined oil is driven up into the neck of the flask and the volume noted after cooling. The difference between the volume of the original oil and the volume of the residual oil represents the proportion of citral or cinnamic aldehyde, and multiplied by 20 gives the percentage by volume.

For the determination of citral in lemon oil the hydroxylamine process is recommended (*see* Perfumery and Essential Oil Record, November, 1910, 263–264).

Ketones. The more important ketones occurring in essential oils are carvone, pulegone, menthone, camphor, fenchone, and thujone. Methyl-heptyl-ketone and methyl-nonyl-ketone occur in the oil of rue and methyl-heptenone in the oils of lemongrass, citronella, and lignaloe.

The best absorption process for the estimation of carvone is as follows:—

Five c.c. of the oil is introduced in a 200 c.c. flask with the neck graduated in tenths of a cubic centimetre. 25 c.c. of a 20 p.c. solution of neutral sodium sulphite is then added and a few drops of phenolphthalein solution. It is then placed in a water-bath and thoroughly shaken, when a red colour is immediately produced due to the liberation of free caustic alkali. A 10 p.c. solution of acetic acid is added from a burette to maintain neutrality, and the mixture heated until no more free alkali is liberated, the time required being usually about 45 minutes. The uncombined oil is then driven into the neck of the flask and the volume read off after cooling. The difference between the volume of the original oil and that of the residual oil multiplied by 20 will give the percentage by volume of carvone. For pulegone in oil of pennyroyal litmus is a better indicator.

The above process may also be used for the determination of benzaldehyde in almond oil, cinnamic aldehyde in cinnamon and cassia oils and citral in lemongrass oil.

Phenols (*v. also* art. TERPENES AND TERPENE DERIVATIVES). The chief phenols found in essential oils are thymol, carvacrol, and eugenol (*q.v.*). These bodies are soluble in solutions of alkaline hydroxides, and may be extracted by shaking the oils with a solution of caustic potash or soda. They differ from acids in not being soluble in alkaline carbonates.

The method usually adopted for the estimation of phenols in essential oils is as follows: 5 c.c. of the oil is heated for an hour in a water-bath with a 5 p.c. aqueous solution of potash with frequent agitation. A flask with the neck graduated in tenths of a cubic centimetre is employed for the purpose, and the uncombined oil is driven into the graduated neck by the addition of a further quantity of potash solution. The proportion of phenols absorbed is calculated by deducting the measure of uncombined oil from the volume of the original oil, which gives the proportion of phenols by volume. If the proportion by weight is required the specific gravity of the oil and the uncombined portion must be taken into account.

Phenol derivatives. Anethole is the methyl ether of *p*-propenyl phenol. It is the chief constituent of anise oil and star anise oil and also occurs in oil of fennel. It is a crystalline substance, melting at 21° and boiling at 232°; sp.gr. 0·986 at 25°.

Iso-anethole (*estragole*) is the methyl ether of *p*-allyl-phenol. It occurs in estragon oil, and also in anise and fennel oils. It is a colourless liquid having a density of 0·971 and boiling at 215°–216°.

Safrole is the methylene ether of allylpyrocatechol. It is the principal constituent of sassafras oil, and occurs in the high boiling fractions of camphor oil and in cinnamon leaf oil. It is a colourless liquid, boiling at 233°; sp.gr. 1·108.

Other phenol derivatives are diosphenol, found in oil of buchu, chavicol, a constituent of bay oil and betel leaf oil, and chavibetol, occurring in betel leaf oil.

Unclassified constituents of essential oils. Apiole occurs in oil of parsley and its isomer dill-apiole in East Indian oil of dill.

Cineol or eucalyptol occurs in oils of wormseed, cajeput and eucalyptus, and in smaller quantities in oils of rosemary, lavender, spike, sage, laurel, cinnamon, and camphor.

Compounds containing nitrogen and sulphur occur in essential oils derived from plants rich in albuminous matter. The more volatile compounds, such as trimethylamine and sulphuretted hydrogen (the latter being formed during the distillation of carraway oil) are usually lost in the distillation process.

Hydrocyanic acid occurs together with benzaldehyde in oil of bitter almonds. Carbon disulphide is found in black mustard oil, dimethyl sulphide in American peppermint oil and allyl sulphide in oil of garlic. Allyl-*iso*thiocyanate is the chief constituent of black mustard oil, resulting from the decomposition of the glucoside potassium myronate in the presence of the ferment myrosin. It is obtained synthetically from allyl iodide and potassium thiocyanate.

EXAMINATION OF ESSENTIAL OILS.

Physical characters. In the analysis of essential oils it is usual to first determine the physical characters, such as the specific gravity, optical rotation, refractive index, boiling range, and solubility.

The *specific gravity* is the density at 15° compared with the weight of an equal volume of water at the same temperature, and is usually taken by means of a specific gravity bottle of 10 c.c. or 25 c.c. capacity. Anise oil and otto of rose are generally taken at 20° and 30° respectively in comparison with water at 15°C. Oils which contain water should be first dried by agitation with anhydrous sodium sulphate.

Optical rotation. The optical rotation of essential oils is usually taken in a 100 mm. tube by means of a polarimeter, using sodium light. The specific rotation applied to pure substances is the optical rotation in a 100 mm. tube divided by the specific gravity. It is expressed by the term $[\alpha]_D$.

The refractive index is the ratio of the sine of the angle of incidence to the sine of the angle of refraction for the D line (sodium light) and is expressed by the term n_D. It is usually given for a temperature of 20° and decreases with rise of temperature to the extent of 0·0004 to 0·0006 for each degree Centigrade. Refractometers are of various types, but the direct reading instrument made by Zeiss is the one most suitable for the examination of essential oils (*v.* REFRACTOMETER). The temperature is kept constant by passing a stream of water through the two prisms between which the oil is placed.

The melting-point of an oil is best determined by placing about 3 c.c. in a test-tube, and congealing it by immersion in a freezing mixture. The tube is then immersed in a beaker of water and the temperature of the water slowly raised until the oil is just completely melted, a thermometer being used to stir the oil continuously. For crystalline solids a capillary tube should be employed.

The boiling-point of a substance depends on the pressure of the atmosphere, the standard pressure being equal to 760 mm. of mercury. The correction for variation of pressure is made as follows: $T=T_1+0{\cdot}0375\ (760-p)$ where T is the true boiling-point, T_1 the observed boiling-point, and p the observed pressure. For accurate determination a correction may be made for the portion of the stem of the thermometer not surrounded by the vapour of the boiling liquid. This is made as follows: $T=T_1+0{\cdot}000154\ t.d.$ where T is the true boiling-point, T_1 the observed boiling point, t the number of degrees exposed to the atmosphere and d the difference between the temperature of the boiling liquid and that of the surrounding atmosphere.

Fractional distillation of essential oils is usually carried out under reduced pressure which should not exceed about 25 mm. A three-bulbed flask or a fractionating column is sometimes used, better separations being thus obtained. The characters of the various fractions are exceedingly useful in detecting adulteration.

Methods for the determination of alcohols, esters, aldehydes, ketones, and phenols are given under the various constituents.

Solubility. The solubility of an oil is often a good criterion of purity. It is usually determined by shaking 1 c.c. of the oil with 1, 2, 3, or more c.c. of alcohol of various strengths. The strengths generally employed are 70, 80, 90, and 95 p.c., and these must be carefully adjusted to the correct specific gravity. Each oil has a definite solubility value and the test serves to detect adulteration or the presence of oxidised or resinified products. Petroleum floats in 70 p.c. alcohol, fixed oils sink. A definite standard temperature should be adopted, say 20°C.

DETECTION OF ADULTERANTS.

Turpentine oil may be readily detected in oils which contain no pinene, the latter being the chief constituent of turpentine oil. It is usually found in the first fraction distilled, and generally reduces the specific gravity and affects the solubility. Its presence is proved by the formation of pinene hydrochloride (m.p. 125°) and its nitrosochloride (m.p. 103°).

Cedar wood, copaiba, and *gurjun balsam oil.* These are usually found in the last fractions since their chief constituents are sesquiterpenes. They have a high refractive index and high specific gravity, and are only soluble in absolute alcohol. Copaiba oil rotates −5° to −35° (African +20°), cedarwood oil −25° to −45°, and gurjun balsam −35° to −130°.

Alcohol may be detected by its low boiling-point, low specific gravity, low refractive index, and by the iodoform test. Oils containing alcohol form milky mixtures with water. It may be extracted by washing the oil with water.

Acetone may be detected in a similar manner.

Fatty oils leave an oily stain when exposed on blotting paper. With the exception of castor oil they are insoluble in alcohol. They usually increase the ester value of an oil and increase the non-volatile residue. Fatty oils have a very high boiling-point, and are therefore found in the residue left on distillation, where they may be detected by the acrolein test.

Artificial esters have usually a high boiling-point and may be detected in the last fractions of an oil by saponifying with aqueous potash and identifying the products of hydrolysis.

Glyceryl acetate, ethyl citrate, tartrate, oxalate, and succinate have been used for adulteration purposes.

Petroleum (mineral oil, kerosene, &c.) is less soluble in alcohol than most oils. It has a low specific gravity and refractive index, and is not saponified by potash. It is also unaffected by nitric and sulphuric acids.

PRINCIPAL ESSENTIAL OILS.

Absinthe oil (wormwood oil) is distilled from the leaves and tops of *Artemisia absinthium* (*N.O. Compositæ*), a herbaceous plant growing in Europe, Northern Africa, and Northern Asia, and cultivated in the United States of America. The yield is from 0·5 to 1·0 p.c. It is of a dark green or bluish colour having a sp.gr. of 0·920–0·955. It contains thujone (tanacetone), thujyl alcohol, acetic and valeric esters, phellandrene, pinene, and cadinene. It is used in the preparation of absinthe, in conjunction with other essential oils (*v.* ABSINTHE).

Ajowan oil is distilled from the fruit of *Carum ajowan* (Bentham and Hooker) or *Ptychotis ajowan* (D.C.) (*N.O. Umbelliferæ*). Cultivated in India, Egypt, Persia, and Afghanistan. The yield is from 3 to 4 p.c.; sp.gr. 0·900–0·930; slightly dextro-rotatory. Contains thymol (40–55 p.c.), cymene, and a terpene hydrocarbon. Ajowan oil is the chief source of thymol (methyl *iso*propyl phenol), which is extracted from the oil by freezing or by means of caustic soda, precipitating with hydrochloric acid and recrystallising from alcohol. Thymol melts at 50°–51°, and boils at 230°.

Bitter almond oil. Obtained by distillation with water from the marc left after expression of the fixed oil from the seeds of bitter almonds *Prunus Amygdalus*, var. *amara* (*N.O. Rosaceæ*). The oil results from the action of a nitrogenous ferment *emulsin*, found in both sweet and bitter almonds, on the glucoside amygdalin which exists only in the bitter almond. The reaction occurs in the presence of moisture as follows:—

$$\underset{\text{Amygdalin.}}{C_{20}H_{27}NO_{11}}+2H_2O=\underset{\text{Benzaldehyde.}}{C_7H_6O}+\underset{\text{Hydrocyanic acid.}}{HCN}+\underset{\text{Glucose.}}{2C_6H_{12}O_6}$$

Benzylcyanhydrin is formed by the interaction of the benzaldehyde with the hydrocyanic acid. The yield of essential oil varies, partly according to the quality of the almonds, partly according to the proportions of sweet almonds mixed with the bitter. The marc yields on an average 1 p.c. of oil corresponding to about 0·5 p.c. from the original almonds; sp.gr. 1·045–1·070; it is optically inactive and consists of benzaldehyde (about 90 p.c.), hydrocyanic acid (4–6 p.c.), and benzylcyanhydrin or mandelonitrile ($C_6H_5 \cdot CH(OH)CN$).

The hydrocyanic acid may be removed by redistillation with lime and ferrous sulphate or by agitation with sodium acid sulphite, crystallising the double salt and distilling the crystals with caustic soda. Essential oil of almonds is very rapidly oxidised on exposure to moist air forming benzoic acid, but when carefully dried by immersing in it a piece of calcium chloride it is said to keep indefinitely. It may be adulterated with artificial benzaldehyde or with alcohol. The former, if free from chlorine compounds, is impossible to detect; the latter is detected by shaking with water and applying the iodoform test to the washings.

A similar oil almost identical in character with oil of bitter almonds is obtained from peach and apricot kernels.

Amber oil is a mixture of terpenes boiling between 130° and 140° obtained by the destructive distillation of amber. Mixed with rectified spirit and ammonia it was formerly used in medicine under the name *Eau de Luce*. By the action of nitric acid a mixture of resins is produced, formerly known as 'artificial musk.' Genuine oil of amber is now very rarely found in commerce, much of the oil used medicinally for embrocations being obtained from amber resin (*colophony* (*q.v.*)) by destructive distillation.

Anise oil. Distilled from the fruit of *Pimpinella Anisum* (Linn.) (*N.O. Umbelliferæ*), grown in Europe, and from the fruit of the star anise, *Illicium verum* (Hook.) (*N.O. Magnoliaceæ*), cultivated in China. The latter is the source of most of the anise oil of commerce. The yield of oil from the star anise fruits is 2–4 p.c., that from the pimpinella anise seldom exceeding 2 p.c. The characters and constituents of the two oils are practically identical; sp.gr. 0·975–0·990 at 20°/15°, rising on keeping; 0°–2° seldom dextrorotatory; μ1·552–1·558; soluble in 3 vols. of 90 p.c. alcohol; it congeals about 10°, remelting at 15°–19°. It contains anethole 80–90 p.c., methyl chavicol, anisic aldehyde, anisic acid, anisic ketone, pinene, phellandrene, and safrole. Important changes take place in the oil on keeping, the melting-point being lowered and the density increasing. It is employed medicinally as a carminative and expectorant and as a flavouring agent.

Asafœtida oil. Distilled from the gum resinous exudation from the root of *Ferula Assa-fœtida* (Linn.) (*N.O. Umbelliferæ*), and probably other species growing in Persia and Afghanistan. It yields by distillation 3–7 p.c. of oil; sp.gr. 0·975–0·990; rotation about −10°. It contains organic sulphur compounds having the formulæ $C_7H_{14}S_2$, $C_8H_{16}S_2$, $C_{10}H_{20}S_2$, pinene, and a sesquiterpene. The proportion of sulphur compounds present varies according to the species of *Ferula* from which the gum resinous exudation has been obtained.

Bay oil. Distilled from the leaves of *Pimenta acris* (Kostel) (*Myrcia acris* [DC.]) (*N.O. Myrtaceæ*), largely grown in the West Indies. The yield is from 2 to 3 p.c.; sp.gr. 0·965–0·995; rotation −0° 30′ to −2°. It contains eugenol, methyl-eugenol, chavicol, methyl-chavicol, pinene, dipentene, phellandrene, myrcene, and citral. When distilled with water the oil separates into two layers, one lighter, the other heavier, than water. These are mixed to obtain a normal oil. It is sometimes adulterated with other eugenol-containing oils, notably those of clove and pimento.

Bergamot oil. Obtained by expression from the peel of the fresh unripe fruit of *Citrus Bergamia* (Risso) (*N.O. Rutaceæ*) cultivated in Calabria and Sicily. The process used for extraction is similar to that used for lemon oil. One hundred fruits yield 2½–3 ozs. of oil, which is limpid and of yellowish or greenish-yellow colour; sp.gr. 0·881–0·886; rotation +8° to +24°, rarely exceeding +18°; esters calculated as linalyl acetate, 36–42 p.c.; non-volatile matter after heating 2 hours on water-bath, 5–6 p.c. It contains linalool, linalyl acetate, octylene, pinene, camphene, limonene, dipentene, limene (sesquiterpene), bergaptene (stearoptene). The oil is subject to considerable adulteration with added esters, including terpinol acetate, ethyl citrate, &c., together with terpenes from allied species of citrus.

Buchu oil. Distilled from the leaves of *Barosma betulina* (Bartl. & Wendl.), and other species (*N.O. Rutaceæ*), a shrub indigenous to Cape Colony. It yields from 1 to 2 p.c. of oil; sp.gr. 0·940–0·960. It contains diosphenol, limonene, dipentene, menthene, the constituents varying according to the species of *Barosma* used for distillation (*see* Pharm. J. 3rd series, 796–797).

Cajuput oil. Distilled from the leaves of *Melaleuca Leucadendron* (Linn.) (*N.O. Myrtaceæ*), indigenous to India, North Australia, the Malay Archipelago, and the Molucca Islands. It is a green or bluish-green limpid oil having an aromatic camphoraceous odour resembling eucalpytus oil; sp.gr. 0·919–0·930; rotation 0°–4°. It contains cineol (45–60 p.c.), terpineol, pinene, butyric, valeric, and benzoic aldehydes. The green colour of the oil is due to contamination with copper, which can be removed by distillation or by shaking the oil with a solution of citric or tartaric acid or potassium ferrocyanide.

Calamus oil. Distilled from the rhizome of the sweet flag, *Acorus Calamus* (Linn.) (*N.O. Aroideæ*), found on the banks of many European rivers and cultivated in India. The yield is from 1·5 to 3·5 p.c.; sp.gr. 0·960–0·970; rotation +10° to +35°. It contains pinene and a sesquiterpene and unidentified oxygenated constituents. The Japanese oil is probably derived from the rhizome of *Acorus gramineus* (Soland). It has a density of 0·990–1·000. It is used in the preparation of cordials and liqueurs and in perfumery.

Camphor oil. A by-product in the manufacture of camphor from the wood of the camphor tree, *Cinnamomum Camphora* (Nees & Eberm.) (*N.O. Lauraceæ*), found in China, Japan, and Formosa. The oil varies considerably in character, but may be divided into two distinct classes, (1) the light fractions consisting principally of terpenes, (2) the heavy fractions containing more or less safrole, which is largely used in the preparation of heliotropin: sp.gr. (1) 0·860–0·950, (2) 0·950–1·100; rotation (1) +12° to +32°, (2) 0° to +12°. Camphor oil contains camphor, terpineol, safrole, eugenol, cineol, pinene, phellandrene, dipentene, and cadinene.

Cananga oil *v. Ylang Ylang.*

Caraway oil. Distilled from the fruit of *Carum Carvi* (Linn.) (*N.O. Umbelliferæ*), which is cultivated in England, Holland, Germany. Russia, and Morocco. The yield is from 4 to 6 p.c.: sp.gr. 0·900–0·920; rotation +75° to +82°; refractive index (25°) 1·485–1·497; at least 50 p.c. should distil above 200°. It contains carvol or carvone (45–55 p.c.), limonene, dihydrocarveol, and dihydrocarvone. Much of the oil is partially decarvonised, the carvone being employed extensively for the production of the liqueur 'Kummel' (*v.* LIQUEURS).

Cardamom oil. Distilled from the seeds of *Elettaria Cardamomum* (Maton), var. *β.* (*N.O. Zingiberaceæ*), growing wild, and cultivated in Ceylon, Malabar, and Mysore. The cultivated Ceylon variety furnishes the greater part of the oil of commerce. The yield is from 3 to 8 p.c.: sp.gr. 0·924–0·947 at 25°; rotation +22° to +46°. The wild Ceylon oil is inferior in quality, having a density of 0·895–0·910 and a rotation of +12° to +13°. Cardamom oil contains cineol 5–10 p.c., *d*-terpineol, limonene, and terpinene.

Cascarilla oil. Distilled from the bark of *Croton Eluteria* (Benn.) (*N.O. Euphorbiaceæ*), a native of the Bahama Islands; the yield is from 1·5 to 3 p.c.: sp.gr. 0·890–0·930; rotation +2° to +5°. It contains cymene, limonene, eugenol, cascarillic, stearic, and palmitic acids, and two sesquiterpenes.

Cassia oil. Distilled from the bark, leaves, and twigs of *Cinnamomum Cassia* (Blume.) (*N.O. Lauraceæ*), indigenous to Cochin China and cultivated in China. The yield is from 0·5 to 2 p.c.: sp.gr. 1·050–0·065; rotation +1° to −1°; refractive index 1·585 to 1·605; soluble in 3 vols. 70 p.c. alcohol. It contains cinnamic aldehyde 75–85 p.c., cinnamic esters, and terpenes. It may be adulterated with resin, petroleum, and fatty oils. The oil is sold in various grades according to cinnamic aldehyde percentage, the lower grades being usually reduced by the addition of resin.

Cedarwood oil. Distilled from the bark of *Juniperus virginiana* (Linn.), the red cedar (*N.O. Cupressineæ*). Often obtained from the waste shavings from the manufacture of cedar pencils: sp.gr. 0·940–0·960; rotation −25° to −45°; refractive index, 1·50–1·51. The chief constituent is cedrene (sesquiterpene). It contains 8–10 p.c. of cedrol or cedar camphor, which is a crystalline sesquiterpene alcohol melting at 78°–80°. It is largely used in perfumery and soap manufacture as a fixative for perfumes, and for microscopic purposes on account of its high refractive index. Cedar leaf oil, obtained from the leaves of *J. virginiana*, is dextro-rotatory +55° to +65°, and has a sp.gr. of 0·883–0·888. It contains limonene, cadinene, borneol, and bornyl esters.

Commercial cedar leaf oil is probably derived from *Thuya occidentalis* (Linn.), and other allied trees. It has a density of 0·860–0·920 and optical rotation −3° to −24°.

Cherry laurel oil is distilled from the leaves of *Prunus Lauro-cerasus* (Linn.) (*N.O. Rosaceæ*), an evergreen shrub indigenous to south-eastern Europe and Asia Minor. It has a density of 1·050–1·065 and contains benzaldehyde, prussic acid, and traces of benzyl alcohol. It differs very little from oil of bitter almonds. It is obtained as a by-product in the preparation of cherry laurel water (B.P.), which is standardised to contain 0·1 p.c. of prussic acid, and is used for medicinal purposes.

Cinnamon oil. Distilled from the bark of *Cinnamomum zeylanicum* (Nees) (*N.O. Lauraceæ*), a native of Ceylon. The yield is from 0·5 to 1 p.c.: sp.gr. 1·000–1·040; rotation 0° to −1°; refractive index 1·565–1·582; soluble in 3 vols. of 70 p.c. alcohol. It contains cinnamic aldehyde (55–75 p.c.), terpenes (phellandrene) and traces of eugenol. Oils containing a high aldehyde content (over 75 p.c.) may contain cassia oil or artificial cinnamic aldehyde. These oils have a higher refractive index than 1·582. English distilled oils have a low specific gravity, low aldehyde content, and a much finer aroma than heavier oils.

Cinnamon leaf oil, distilled from the leaves and twigs of the same tree, contains 75–85 p.c. of eugenol and safrole, and only traces of cinnamic aldehyde: sp.gr. 1·045–1·060; rotation −1° to +1°; refractive index 1·533–1·536. The oil distilled from the root contains eugenol, safrole, camphor, benzoic aldehyde, and benzoic esters.

Citron or **cedrat oil.** Obtained by expression from the rind of the fruit of *Citrus Medica* (Linn.) (*N.O. Rutaceæ*). The citron is very similar to lemon oil but contains a slightly higher percentage of citral. It is not now an article of commerce, but efforts are being made to grow the fruit in Corsica for the production of the oil. Factitious oils are offered under both names composed of the oils of other species of *Citrus*.

Citronella oil is distilled from the fresh grass *Andropogon Nardus* (Linn.), (*Cymbopogon Nardus* [Rendle]) (*N.O. Gramineæ*), which is largely grown in Ceylon and in the Straits Settlements. The yield is from 0·5 to 1·0 p.c.; the Ceylon oil has sp.gr. 0·900–0·915; rotation 0° to −21°; refractive index 1·480–1·482: the Java oil has sp.gr. 0·885–0·910; rotation 0° to −10°; refractive index 1·465–1·468. Citronella oil contains geraniol, citronellal, camphene, dipentene, limonene, and traces of linalool, borneol, methyl heptenone, methyl eugenol, and sesquiterpenes. It is largely used in cheap soap perfumery. The Ceylon oil contains a large proportion of geraniol, the total acetylisable constituents amounting to 58–65 p.c. In the Java variety the citronellal predominates and the proportion of acetylisable constituents is higher (75–90 p.c.) since citronellal is converted into *iso*pulegol acetate on acetylation. There are at least two varieties of citronella grass cultivated: (1) the 'Lena batu' type; (2) the 'Mahi Penghiri' type. The Ceylon oil is largely adulterated with Russian petroleum, the proportion of 12½–15 p.c.

having passed the solubility test which has been long in vogue. Attempts are being made to establish a standard for the sale of the Ceylon oil on geraniol content in the same way as cassia and other essential oils are on their percentage of odorous constituents.

Clove oil is distilled from the flower buds of *Eugenia caryophyllata* (Thunb.) (*N.O. Myrtaceæ*), indigenous to the Molucca Islands and cultivated in Zanzibar and Pemba, Sumatra, Penang, Madagascar, Seychelles, Mauritius, and West Indies. The yield is from 15 to 20 p.c.; the stems yield about 6 p.c. It has sp.gr. 1·047–1·065 (eugenol 1·070; caryophyllene 0·908); rotation 0° to −1·30°; refractive index 1·528–1·540; soluble in 3 vols. of 70 p.c. alcohol. It contains eugenol (85–95 p.c.) and eugenol esters, caryophyllene, methyl alcohol, furfural, traces of amyl methyl ketone and methyl benzoate. The oil is very largely used for the production of vanillin.

Copaiba oil is distilled from the oleo-resin or balsam of copaiba, which is an exudation from the trunk of *Copaifera Lansdorfii* (Desf.) and other species of copaiba (*N.O. Leguminosæ*), indigenous to Brazil and northern S. America. The Para variety gives the highest yield of oil (60–65 p.c.), the Bahia yielding about 50 p.c., the Maranham and Maracaibo about 40 p.c.: sp.gr. 0·895–0·918; rotation −7° to −25° (occasionally higher); refractive index 1·495–1·500. It is chiefly composed of sesquiterpenes (caryophyllene). African copaiba oil is dextro-rotatory about +20°, but lævo-rotatory oils can be obtained from the wood of young branches. Gurjun balsam oil has a lævo-rotation of −35° and upwards. It gives an intense violet colour when dissolved in glacial acetic acid and treated with a few drops of nitric acid.

Coriander oil is distilled from the fruit of *Coriandrum sativum* (Linn.) (*N.O. Umbelliferæ*), cultivated in most European countries. Russian, Moravian, and Thuringian fruits yield 0·8–1·0 p.c.; French, Dutch, and Italian 0·4–0·6 p.c.: sp.gr. 0·870–0·885; rotation +8° to +13°; refractive index 1·463–1·467; soluble in 3 vols. of 70 p.c. alcohol. It contains coriandrol (*d*-linalool) and *d*-pinene. The body which gives the characteristic odour is unknown. It may be adulterated with orange and lemon terpenes or turpentine oil, which affect the solubility and the rotation.

Cubeb oil is distilled from the dried unripe fruit of *Piper Cubeba* (Linn.) (*N.O. Piperaceæ*), chiefly imported from Java. The yield is from 10 to 18 p.c.; sp.gr. 0·910–0·930; rotation −25° to −40°; refractive index 1·495–1·496; soluble in 3–10 vols. of 90 p.c. alcohol. It contains dipentene, *l*-pinene, camphene, cadinene, and cubeb camphor, a crystalline sesquiterpene alcohol (m.p. 68°–70°, b.p. 245°).

Cummin oil is distilled from the fruits of *Cuminum Cyminum* (Linn.) (*N.O. Umbelliferæ*), also known as the Roman caraway. It is cultivated in Syria, Morocco, Malta, and the East Indies. The yield is from 2·5 to 4·0 p.c.; sp.gr. 0·910–0·930 (East Indian 0·893–0·899); rotation +4° to +8°; good oils dissolve in 3 vols., but inferior oil may require 8–10 vols. of 80 p.c. alcohol. It contains cuminic aldehyde (cuminal) 20–30 p.c., cymene, and a dextro-rotatory terpene, b.p. 156°, probably pinene.

Dill oil is distilled from the fruit of *Anethum* (*Peucedanum*) *graveolens* (Benth. & Hook.), *N.O. Umbelliferæ.* Indigenous to the Caucasus and Mediterranean countries, cultivated in Bavaria, Thuringia, and Roumania. The yield is from 3 to 4 p.c.; sp.gr. 0·895–0·915 (usually over 0·900); rotation +70° to +80°; refractive index 1·483–1·488; soluble in 3 vols. of 90 p.c. alcohol, 5–8 vols. of 80 p.c. alcohol. It contains carvone (40–60 p.c.), limonene, and phellandrene, but no dill apiol. East Indian and Japanese dill oils obtained from *Anethum* (*Peucedanum*) *Sowa* (Roxb.) have a sp.gr. 0·948–0·970, and a rotation of +41° to +51°. They contain dill apiol, a body heavier than water, b.p. 285°.

Eucalyptus oil. Distilled from the leaves of many species of *Eucalyptus* (*N.O. Myrtaceæ*), that of *Eucalyptus globulus* (Labill.) being chiefly prized though the oils of other species often contain more eucalyptol. The bulk of the oil of commerce is now derived from *E. dumosa* (A. Cunn.), but several hundred species are known and employed for distillation. *See* Baker and Smith's researches (Pharm. J. 4, [ix.] 315; [xvii.] 314; [xxi.] 356, 382). Indigenous to Australia, Tasmania, and New Zealand; cultivated in Spain, Algeria, and California. The yield is from 0·8 to 1·5 p.c. The following are the characters of oils of high eucalyptol content as required by the British Pharmacopœia: sp.gr. 0·910–0·930; rotation +10° to −10°; refractive index 1·469–1·475; cineol (eucalyptol) 55–80 p.c.; most oils are soluble in 3 vols. of 70 p.c. alcohol. Oils containing much phellandrene and but little cineol such as that of *E. amygdalina* (Lab.) have a lower density (0·855–0·890) and a higher lævo rotation (−25° to −80°). Eucalyptus oil contains cineol (eucalyptol), pinene, phellandrene, cymene, piperitone, aromadendrene, aromadendral, esters of eudesmic acid, eudesmol or eucalyptus camphor, and traces of amyl alcohol, valeric, butyric, and caproic aldehydes. The medicinal reputation of eucalyptus oil was largely founded on oils from *E. amydalina*, which are of low eucalyptol content. It is not by any means proved that the value of the oil is dependent on eucalyptol.

The oils of *Eucalyptus citriodora* (Hook.) and *E. maculata* (Hook.) do not contain cineol, but consist almost entirely of citronellal. They have sp.gr. 0·870–0·905; rotation 0° to +2°.

Geranium oil (*Rose-Geranium oil* or *Pelargonium oil*) is distilled from the leaves of *Pelargonium odoratissimum* (Soland), *P. capitatum* (Soland), and *P. roseum* (R.Br.) (*N.O. Geraniaceæ*). Indigenous to South Africa, but largely cultivated in France, Spain, Algeria, and the island of Reunion. The yield is 0·15 to 0·35 p.c.; soluble in 3 vols. of 70 p.c. alcohol.

Geranium oil contains geraniol, citronellol, and probably linalool, acetic, butyric, tiglic, and valerianic esters. The Spanish oil commands the highest price. The French and Algerian oils come next, and the Bourbon, which is usually darker in colour and has a characteristic odour, is of lowest value (*v.* table on p. 738).

Indian geranium oil (*Turkish Geranium oil*) *v. Palmarosa oil.*

Ginger oil is distilled from the rhizome of *Zingiber officinale* (Rosc.) (*N.O. Zingiberaceæ*): indigenous to tropical Asia, and cultivated in the East and West Indies and in Africa. The yield

——	French	Algerian	Reunion (Bourbon)	Spanish
Sp.gr.	0·895–0·905	0·890–0·900	0·890–0·895	0·889–0·898
Rotation	−7° to −10°	−6° to −10°	−8° to −11°	−10° to −15°
Esters calculated as geranyl tiglate	22–28 p.c.	20–29 p.c.	27–34 p.c.	35–42 p.c.
Total alcohols as geraniol .	about 75 p.c.	about 75 p.c.	about 80 p.c.	about 70 p.c.

is from 1 to 3 p.c.; sp.gr. 0·872–0·885; rotation −25° to −45°; refractive index 1·4885–1·4950. It contains phellandrene, camphene, and a sesquiterpene zingiberene, also traces of cineol, borneol, and citral.

Ginger grass oil is an inferior kind of palmarosa oil. Its botanical source is still uncertain, though it is probably derived from a species of *Andropogon* (*N.O. Gramineæ*). It has sp.gr. 0·930–0·940; rotation +18° to +32°; esters 10–25 p.c.; total alcohols calculated as geraniol 70–90 p.c. It contains geraniol, geranyl acetate, dihydrocuminol, and traces of limonene, dipentene, carvone, and an aldehyde not identified.

Juniper oil is distilled from the berries of *Juniperus communis* (Linn.) (*N.O. Coniferæ*) and is produced chiefly in Hungary, where it is obtained as a by-product in the manufacture of gin. The Italian berries produce the best yield of oil, viz. 1–1·5 p.c. The oil has sp.gr. 0·860–0·890, increasing with age; rotation −3° to −12°, occasionally slightly higher; refractive index 1·472–1·488; soluble when freshly distilled in 4 vols. of 95 p.c. alcohol. It contains pinene, cadinene, juniper-camphor, and a small proportion of esters. Pinene occurs to the extent of 25–60 p.c., and cadinene to the extent of 15–25 p.c. Juniper-camphor consists of a sesquiterpene alcohol (m.p. 165°–166°).

Lavender oil, principally used in commerce is distilled from the fresh flowering herb *Lavandula vera* (DC.) [*L. officinalis* (Chaix.)] (*N.O. Labiatæ*), and other species growing on the higher slopes of the Alps. The distillation is carried out on the spot by means of portable stills, to save cartage of the fresh herb. The oil distilled in the lower districts is inferior to that of the higher. It has sp.gr. 0·883–0·895 (occasionally higher); rotation −3° to −9°; esters calculated as linalyl acetate 25–45 p.c.; total alcohols as linalool 60–70 p.c.; soluble in 3 vols. of 70 p.c. alcohol. Contains linalool, geraniol, nerol, linalyl acetate, pinene, limonene, traces of cineol and thymol and a small quantity of sesquiterpene.

English lavender oil, distilled in Surrey, Suffolk, and Hertfordshire, has similar characters, but contains only 7–10 p.c. of esters calculated as linalyl acetate. It contains more cineol than the French oil, which may be adulterated with artificial esters, ethyl oxalate, citrate, tartrate, benzoate, succinate, benzyl benzoate, &c. Admixture with spike oil is detected by the odour, and by the reduction of ester percentage.

Spike lavender oil or *spike oil* is distilled from the flowering herb *Lavandula Spica* (Cav. Desc.), which grows in the lower mountainous regions of France, Spain, and Italy. Sp.gr. 0·905–0·915; rotation +1° to +4°; total alcohols calculated as borneol 25–45 p.c.; esters as linayl acetate 4–6 p.c.; soluble in 3 vols. of 70 p.c. alcohol. Contains linalool, borneol, camphor, cineol, terpineol, *d*-camphene, and a sesquiterpene.

Lemon oil is obtained by mechanical means from the fresh peel of *Citrus Limonum* (Risso) (*N.O. Rutaceæ*), which is largely cultivated in Southern Italy and Sicily. It is also grown in Spain, Portugal, Southern France, and in the West Indies, California, and Australia. It is produced in Sicily between November and March. Sp.gr. 0·857–0·862; rotation +57° to +65°; refractive index (25°) 1·474–1·476. Contains limonene (about 90 p.c.), pinene (traces), citral (4–5 p.c.), octyl, nonyl, and decyl aldehyde, geraniol and linalool, and their acetic esters, camphene, phellandrene and a sesquiterpene, limene, identical with bisabolene.

Lime oil is obtained by mechanical means from the peel of the fresh fruit of *Citrus Limetta* (Risso) (*C. Medica*) (*N.O. Rutaceæ*), and is produced in Italy in December and January. It resembles oil of lemon in odour, but the citral odour is more pronounced: sp.gr. 0·872–0·885; rotation +35° to +40°; refractive index 1·484–1·485. Contains pinene, limonene, dipentene, citral (6–10 p.c.), linalool and its acetic ester, and limettin (m.p. 147°).

Distilled lime oil is an oil of inferior quality obtained by distillation from the peel of the fruits of *Citrus Medica*, var. *acida*, grown in the West Indies, chiefly Montserrat: sp.gr. 0·856–0·868; rotation +34° to +41°; refractive index 1·470–1·471. Contains pinene, limonene, dipentene, cymene, terpineol, and a sesquiterpene, limene (bisabolene).

Myrtle oil is distilled from the leaves of *Myrtus communis* (Linn.) (*N.O. Myrtaceæ*), grown in Spain, Italy, the South of France, and Cyprus. It is a yellowish or greenish oil with a pleasant odour: sp.gr. 0·890–0·915; rotation +10° to +30°. Contains pinene, dipentene, cineol, and a camphor $C_{10}H_{16}O$, b.p. 195°–200°. The fraction, b.p. 160°–180°, is sold as *myrtol*, and contains cineol.

Mustard oil is obtained from the seeds of the black mustard, *Brassica nigra* (Koch) (*N.O. Cruciferæ*) after expressing the fixed oil. The pressed cake is macerated in water at 60°–70° for several hours, when a reaction takes place between the glucoside *sinigrin* (potassium myronate) and the ferment *myrosin* with the production of essential oil of mustard. It is a colourless or pale yellow mobile liquid, with an intensely pungent odour and blistering properties: sp.gr. 1·014–1·032; refractive index 1·525–1·535; optically inactive; distils between 148° and 156°. It consists almost entirely of allyl *iso*thiocyanate $C_3H_5N : C : S$ (95–99 p.c.), with traces of allyl cyanide. Artificial mustard oil is prepared by distilling allyl iodide with an alcoholic solution of potassium thiocyanate.

Nutmeg oil is distilled from the seed of *Myristica fragrans* (Houtt.) (*N.O. Myristicaceæ*). Indigenous to the Molucca, Banda, and Sunda Islands. The yield is from 8 to 15 p.c. Sp.gr.

0·865–0·920; rotation +14° to +28°. Contains pinene, camphene, dipentene, terpineol, myristicol (a mixture of alcohols, terpineol, linalool, borneol, and geraniol), myristicin, and *iso*myristicin, myristic acid, safrol, eugenol, *iso*eugenol, esters of formic, acetic, butyric, and octoic acids.

Oil of mace is practically indistinguishable from it, the oil being almost identical in character and composition. It is derived from the *arillus* of the nutmeg fruit.

Orange oil is obtained by expression from the peel of the fresh fruit. It consists principally of two kinds, the sweet oil from *Citrus Aurantium* (Linn.), and the bitter oil from *C. Bigaradia* (Loisel.) (*N.O. Rutaceæ*), the latter being usually of somewhat higher value. The tree is indigenous to Southern Asia, but largely cultivated in Southern Europe, Northern Africa, and the West Indies. The two oils are only distinguishable by odour. The bitter oil has sp.gr. 0·848–0·853, and rotation +91° to +98°. The sweet oil has sp.gr. 0·846–0·852, and rotation +96° to +99°. *Oil of Mandarin orange* derived from *Citrus Bigaradia*, var. *sinensis*, which is cultivated in China has a density of 0·852–0·859, and an optical rotation of +65° to +75°. *Oil of Tangerine orange* has characters almost identical. Orange oil consists principally of limonene (over 90 p.c.), with small quantities of citral, citronellol, decyl aldehyde, terpineol, linalool, methyl anthranilate, and citraptene.

Orange flower oil (*Neroli oil*) is distilled from the fresh flowers of the bitter and sweet orange, the former being known as '*Bigarade*,' the latter as '*Portugal*.' It is principally distilled in the South of France. The petals are separated from the sepals, covered with water and heated by a coil of steam pipes. The aqueous distillate separated from the oil is sold as orange flower water. It has sp.gr. 0·870–0·880; rotation +0° to +5°; ester content 7–20 p.c. Contains limonene, pinene, dipentene, terpineol, linalool, geraniol, and nerol and their acetic esters, methyl anthranilate and paraffin hydrocarbons.

Orange leaf oil generally known as *Petitgrain oil*, since it was originally obtained from the small immature fruits, is now distilled from the leaves and young shoots of the bitter and sweet orange, the former commanding the higher price. The best oil comes from the South of France, Spain, and Algeria; a slightly inferior quality is exported from Paraguay. The French oil has sp.gr. 0·885–0·900; rotation −5° to +3°; esters calculated as linalyl acetate 50–85 p.c.; soluble in 3 vols. of 70 p.c. alcohol. Contains limonene, linalool, geraniol, nerol, and their acetic esters, a sesquiterpene and stearoptene. The Paraguay oil has sp.gr. 0·884–0·890; rotation 0·0° to +5°; esters calculated as linalyl acetate, 45–65 p.c.; soluble in 1 in 3 vols. 80 p.c. alcohol. Contains pinene, dipentene, camphene, and esters of terpineol and geraniol.

Origanum oil *v. Thyme oil.*

Peach kernel oil *v. Bitter almond oil.*

Palmarosa oil or **Indian geranium oil**, sometimes incorrectly termed *Turkish geranium oil*, is distilled from the grass *Andropogon Schœnanthus* (Benth.) (*Cymbopogon martini*) (*N.O. Gramineæ*), a plant widely distributed in India and found also in tropical Western Africa. The young grass is known by the native name *Motya*, the older grass being termed *Sonfiya*, the former yielding the better oil. It has sp.gr. 0·885–0·895; rotation −2° to +2°; esters 5–11 p.c.; total alcohols calculated as geraniol 75–95 p.c.; soluble in 3 vols. of 70 p.c. alcohol. Contains geraniol, acetic and caproic esters, and traces of citronellol, methyl heptenone, and dipentene. The oil is now sometimes mixed with certain oils rich in geraniol produced from other grasses.

Parsley oil is distilled from the fruit of *Carum Petroselinum* (Benth. and Hook.) (*Petroselinum sativum*) (*N.O. Umbelliferæ*), indigenous to Asia Minor and the Mediterranean countries, cultivated in all moderate climates. It is colourless, yellowish or yellowish-green, partially solid at ordinary temperatures: sp.gr. 1·050–1·100; rotation −5° to −10°. Contains apiol (m.p. 30°, b.p. 294°) and terpenes, probably *l*-pinene. The oil from the root is similar in character, whilst that from the fresh herb has a lighter specific gravity.

Patchouli oil is distilled from the fresh and dried leaves of *Pogostemon Heyneanus* (Benth.) (*P. Patchouly*, Benth.) (*N.O. Labiatæ*), which is cultivated in the Straits Settlements and in the West Indies. The Java oil is probably derived from a different species. It has sp.gr. 0·970–0·995; rotation −50° to −68°; patchouli alcohol, $C_{15}H_{26}O_2$, 50–60 p.c.; soluble in 5 vols. of 90 p.c. alcohol. Contains patchouli alcohol (m.p. 56°), also termed patchouli camphor, cadinene, benzaldehyde, and cinnamic aldehyde.

Pennyroyal oil is obtained from the fresh herb, *Mentha Pulegium* (Linn.) (*N.O. Labiatæ*), and is principally distilled in Spain, Southern France, and Algeria. The oil of American pennyroyal or hedeoma oil is obtained from *Hedeoma pulegioides* (Pers.), which is widely distributed in North America. The two oils are very similar in character; the European oil has sp.gr. 0·930–0·960; rotation +13° to +35°; the American oil has sp.gr. 0·925–0·960; rotation +18° to +22°. Both oils are soluble in 3 vols. of 70 p.c. alcohol and contain pulegone (b.p. 221°–222°) as the chief constituent.

Pepper oil is distilled from the unripe berries of *Piper nigrum* (Linn.) (*N.O. Piperaceæ*), cultivated in Southern India, the Philippines, and the West Indies. It is colourless or yellowish-green, and has sp.gr. 0·870–0·900; rotation −5° to +2°. Consists almost entirely of terpenes and sesquiterpenes, phellandrene being the only constituent actually identified.

Peppermint oil is distilled from the fresh and dried flowering herb *Mentha piperita* (Linn.) (*N.O. Labiatæ*), of which several varieties have been obtained by cultivation. The commercial oil can be classified into three distinct varieties, English, American, and Japanese. The English is of two kinds, 'black' and 'white.' The 'white mint' oil is considered superior in quality. The greater bulk of commercial oil is American, but this is inferior to the English oil. Japanese and Chinese peppermint oil is the chief source of menthol, of which it contains from 70 to 90 p.c. Much of the Japanese oil imported has been partially dementholised and contains only about 40 p.c. of total menthol.

Most oils dissolve in 3–4 vols. of 70 p.c. alcohol, but become turbid with more alcohol unless rectified by redistillation. They contain menthol, and menthyl esters, menthone, pinene,

——	English	American	Japanese
Specific gravity	0·900–0·910	0·900–0·920	0·900–0·910
Rotation	−22° to −33°	−25° to −33°	−30° to −42°
Total menthol	58–66 p.c.	50–60 p.c.	70–90 p.c.
Esters calculated as menthyl acetate	Black, 5–7 p.c. White, 8–15 p.c.	— 8–14 p.c.	— 3–6 p.c.

phellandrene, cineol, acetaldehyde, dimethyl sulphide, and a sesquiterpene. The oils are now largely distilled in the South of France and Italy from plants originally imported from Mitcham (England). For the characters of the oils and other particulars, *see* Perfumery and Essential Oil Record, 1910, 292–300.

Pimento oil (*oil of allspice* or *Jamaica pepper*) is distilled from the unripe fruit of *Pimenta officinalis* (Lindl.) (*N.O. Myrtaceæ*), indigenous to the West Indies; sp.gr. 1·040–1·055; rotation 0° to −4°; phenols 60–75 p.c.; soluble in 3 vols. of 70 p.c. alcohol. Contains eugenol and eugenol methyl ether, cineol, phellandrene, caryophyllene, and palmitic acid.

Pine oils (*Turpentine oil*) (sometimes called spirits of turpentine) is derived from various species of *Pinus* (*N.O. Coniferæ*). The oleo-resin occurs in special resin ducts in the woody portion of the trees. The living tree is 'tapped,' and the oleo-resin or turpentine which exudes is collected. The oleo-resin on distillation with water yields oil of turpentine and the residue is known as *colophony resin.* It is obtained principally in North America, but is also produced largely in Northern Europe and the mountainous districts of Central Europe. American turpentine oil is derived principally from *Pinus palustris* (Mill.) (*P. australis*) and *P. Tæda* (Linn.); the French from *Pinus Pinaster* (Soland), and the Russian from *Pinus sylvestris* (Linn.). The American is chiefly met with in English commerce; the French variety more commonly on the Continent. Russian turpentine is inferior in quality as it has a strong characteristic odour and is not easily deodorised. Swedish turpentine is principally derived from *P. sylvestris*, and closely resembles the Russian product.

——	American	French	Russian
Sp.gr.	0·855–0·877	0·855–0·874	0·855–0·874
Rotation	+1° to +6°	−18° to −40°	+5° to +16°

Most turpentine oils dissolve in 5–8 vols. of 90 p.c. alcohol, but the solubility increases with age owing to the formation of soluble oxidation products. They are soluble in an equal volume of glacial acetic acid. Oil of turpentine is composed almost entirely of hydrocarbons, chiefly pinene, with traces of oxidation products such as formic and acetic acids and resin. Camphene and dipentene are usually present and traces of aldehyde. Turpentine oil readily oxidises to resinous substances on exposure to air and light, and on this property depends its use in paints and varnishes.

Pine needle oils or **Pine leaf oils** are obtained from the fresh leaves of various species of *Pinus.* The chief varieties found in English commerce are those of *Pinus Pumilio* (Haenke) and *Abies sibirica.* The oil from *Pinus Pumilio*, official in the British Pharmacopœia of 1898, is distilled in Hungary and the Austrian Tyrol from the leaves and twigs. It contains little pinene, consisting principally of phellandrene and sylvestrene, whilst cadinene has been found in the higher boiling fractions. Only a small proportion of esters is present.

Oil of Abies sibirica is distilled from the fresh leaves and twigs in Northern Russia and the slopes of the Ural mountains. It has a strong characteristic odour and contains 30–40 p.c. of esters chiefly bornyl acetate. It is more soluble than other pine oils, forming a clear solution in an equal volume of 90 p.c. alcohol.

Oil of Pinus sylvestris (*Fir wool oil*) was official in the 1885 edition of the British Pharmacopœia, but the genuine oil is now practically unobtainable. It consists chiefly of *d*-pinene and contains only a small proportion of esters. *Oil of Abies pectinata* (D.C.) [*A. Alba* (Mill.)], is a fragrant oil distilled principally in Switzerland. It contains limonene as well as pinene and a sesquiterpene. The oil from the cones of the same species, known as *templin oil*, is much lighter in density and has a higher optical rotation. It consists principally of limonene.

Characters of Pine-needle Oils.

——	Specific gravity	Rotation	Esters	Distilling between 155°/165°
P Pumilio . . .	0·863–0·875	−6° to −14°	5–7 p.c.	0–12 p.c.
A. sibirica . . .	0·900–0·920	−32° to −42°	30–40 p.c.	5–10 p.c.
P. sylvestris . . .	0·868–0·925	+5° to + 7°	3–11 p.c.	40–65 p.c.
A. pectinata . . .	0·870–0·875	−20° to −60°	5–12 p.c.	0–10 p.c.
A. pectinata (cones) . .	0·853–0·870	−60° to −75°	0–5 p.c.	5–10 p.c.

Pine tar oils are by-products in the manufacture of charcoal and wood tar by the dry distillation of resinous wood. They have an empyreumatic odour and are usually yellow or light brown in colour. They contain pinene, sylvestrene, and dipentene, together with decomposition products. The crude oil is purified by distillation with milk of lime. German pine-tar oil has a sp.gr. of 0·865–0·870, and an optical rotation of +18 to +22°. About 25 p.c. distils below 165°.

Rose oil (*Otto of roses, Attar of roses*) is obtained by distilling the fresh flowers of *Rosa damascena* (Mill.) (*N.O. Rosaceæ*), which is cultivated principally in Bulgaria and on the slopes of the Balkans, and also in France and Germany. It is largely produced by the Bulgarian peasants in primitive stills. It is a light yellow or slightly greenish oil forming a crystalline mass below 18°; sp.gr. 0·853–0·862 at 30°/15°; rotation −2° to −4°; refractive index at 25°, 1·460–1·465; total alcohols calculated as geraniol 70–75 p.c.; m.p. after solidification 18°–22°. The odorous portion is soluble in 70 p.c. alcohol, but the stearoptene is practically insoluble and can be separated by filtration from the alcoholic solution. The odorous portion consists chiefly of geraniol and citronellol (20–25 p.c.). Traces of phenyl ethyl alcohol, nerol and farnesol are also present. The odourless stearoptene exists to the extent of 10–16 p.c., and consists of two hydrocarbons melting at 22° and 40° respectively, the mixture melting at about 34°. Otto of roses was formerly much adulterated, and is even now to some extent with geraniol and citronellol and oils containing these bodies (Perfumery and Essential Oil Record, 1910, 188 and 217).

Rosemary oil is distilled from the leaves of *Rosmarinus officinalis* (Linn.) (*N.O. Labiatæ*). Indigenous to the Mediterranean countries, principally France, Spain, and Italy. The leaves are collected after the flowering period and are dried for a few days in the sun before distilling. The oil is produced in limited quantity in Great Britain, this variety commanding a very high price. It has sp.gr. 0·900–0·920; rotation +0° to +15° (sometimes lævo-rotatory); total alcohols calculated as borneol 10–18 p.c.; esters calculated as bornyl acetate 2–6 p.c.; soluble in 10 vols. of 80 p.c. alcohol. Contains pinene, camphene, cineol, camphor, borneol, and bornyl acetate.

Rosewood oil (oil of *Bois de Rose, male*) is obtained by the distillation from the wood of *Licaria guianensis* (Aublet) [? *Ocotea caudata* (Mez.)] (*N.O. Lauraceæ*), collected in French Guiana. A similar oil is obtained from the wood of *Protium altissimum* (March.), known as *Bois de Rose femelle* (*see* Perfumery and Essential Oil Record 1910, 32). Rosewood oil has sp.gr. 0·870–0·880; rotation −15° to −17°; soluble in 3 vols. of 70 p.c. alcohol. Contains linalool, geraniol, terpineol, nerol, and traces of methyl heptenone.

Linaloe oil (*Lignaloe oil*) is an oil of similar composition obtained from the wood of *Bursera Delpechiana* (Poiss.), *B. Aloëxylon* (Engl.), and other species. It is principally distilled in Mexico: sp.gr. 0·875–0·895; rotation −5° to −12° (sometimes dextro-rotatory); soluble in 3 vols. of 70 p.c. alcohol. Contains linalool, with geraniol, *d*-terpineol, and methyl heptenone.

Rue oil is distilled from the herb *Ruta graveolens* (Linn.) (*N.O. Rutaceæ*), which is indigenous to Europe. Other species are also cultivated in Algeria, *Ruta* (*bracteosa*) *chalepensis* (Linn.) and *R. montana* (Mill.). It has sp.gr. 0·830–0·840; rotation +0° to +2·30°; m.p. +9° to +10°; soluble in 3 vols. of 70 p.c. alcohol. Consists principally of methylnonyl ketone, with some methylheptylketone. Traces of methyl anthranilate give the fluorescent appearance to the oil.

Sage oil is distilled from the fresh leaves of *Salvia officinalis* (Linn.) (*N.O. Labiatæ*). Indigenous to the Northern Mediterranean countries: sp.gr. 0·915–0·925; rotation +10° to +25°; soluble in 3 vols. of 80 p.c. alcohol. The Spanish oil has a lavender-like odour and contains linalool probably derived from admixture with lavender plants.

Sandal-wood oil is distilled from the wood of *Santalum album* (Linn.) (*N.O. Santalaceæ*). Indigenous to the mountains of India and cultivated under Government control: sp.gr. 0·973–0·985; rotation −13° to −21°; total santalol 90–96 p.c.; soluble in 6 vols. of 70 p.c. alcohol at 20°. Contains santalol, a mixture of two sesquiterpene alcohols $C_{15}H_{24}O$, santalal (an aldehyde), santalene, and santene.

West Indian sandalwood oil, derived from *Amyris balsamifera* (Linn.), is lighter in density (0·960–0·967), and has a rotation of +24° to +29°.

Sassafras oil is distilled from the root of *Sassafras officinale* (Nees.) (*Laurus Sassafras* (Nees.)) (*N.O. Lauraceæ*), a native of North America, Canada, the United States, and Mexico. The best yield of oil is obtained from the root bark: sp.gr. 1·065–1·095; rotation +1° to +4°; soluble in 2 vols. of 90 p.c. alcohol. Contains safrol (80–90 p.c.), pinene, phellandrene, camphor, eugenol, and cadinene. Safrol can be separated by fractional distillation and cooling, but commercial safrol is usually obtained from camphor oil.

Savin oil is distilled from the fresh leaves and twigs of *Juniperus Sabina* (Linn.) (*N.O. Coniferæ*). Distilled in Great Britain and Germany: sp.gr. 0·910–0·930; rotation +40° to +68°; esters calculated as sabinyl acetate 36–47 p.c.; total sabinol 45–55 p.c. Contains sabinol, and sabinyl acetate, pinene, sabinene, furfural, decyl aldehyde, dihydro-cuminol, cadinene. French savin oil is derived from *J. phœnicea* (Linn.) and contains a large percentage of pinene. It is lighter in density (about 0·890), has a much lower rotation (+4° to +5°) and contains only about 10 p.c. of esters and 17 p.c. of total sabinol.

Spearmint oil is distilled from the fresh herb *Mentha viridis* (Linn.) (American) and *Mentha crispa* (Linn.) (German), and probably other species of *Mentha* (*N.O. Labiatæ*): sp.gr. 0·920–0·940; rotation −36° to −48°; soluble in an equal volume of 90 p.c. alcohol, but becoming opalescent on dilution. Contains carvone, phellandrene, limonene, pinene, and traces of valerianic esters. The body having the characteristic odour, according to Elze, is the acetic ester of dihydrocuminol.

Star anise oil *v. Anise oil.*

Tarragon oil or **Estragon oil** is distilled from the flowering herb *Artemisia Dracunculus* (Linn.) (*N.O. Compositæ*). Indigenous to Siberia and cultivated in Europe, used in the manufacture of sauces: sp.gr. 0·890–0·960; rotation +2° to +9°; soluble in 10 vols. of 80 p.c. alcohol. Contains estragol (methyl chavicol), phellandrene, *p*-methoxycinnamic aldehyde, and an olefinic terpene.

Terebene *v. Terpenes.*

Thyme oil. Red Thyme oil is distilled from the fresh flowering herb *Thymus vulgaris* (Linn.) (*N.O. Labiatæ*). It is principally grown in the mountainous parts of Southern France. Spanish thyme oil is probably derived from a species of *Origanum*, as it contains carvacrol but no thymol. Oil of wild thyme from *Thymus serpyllum* contains but a small proportion of phenols. French oil has sp.gr. 0·905–0·930; rotation (after redistillation) 0° to −2°; phenols absorbed by 5 p.c. solution of potash 20–45 p.c.; Spanish oil has sp.gr. 0·930–0·950; phenols absorbed by 5 p.c. solution of potash 40–70 p.c. Thyme oil is soluble in 2 vols. of 80 p.c. alcohol, and contains thymol and carvacrol, cymene, pinene, borneol, and linalool.

Origanum oil is distilled from various species of origanum, the oil imported from Trieste being chiefly derived from *Origanum hirtum* (Link.), that from Asia Minor from *O.* (*smyrnæum*) *Onites* (Linn.), and Cyprus oil from *Origanum Majorana* (Linn.) (*N.O. Labiatæ*).

—	Trieste	Smyrna	Cyprus
Sp.gr. . .	0·940–0·980	0·915–0·945	0·960–0·970
Rotation . .	0° to −1°	−3° to −13°	—
Phenols (absorbed by 5 p.c. solution of potash) .	60–85 p.c.	25–60 p.c.	78–84 p.c.

All are soluble in 3 vols. 70 p.c. alcohol and contain carvacrol and cymene; Smyrna oil contains linalool; Cyprus oil contains origanene and traces of hydroxymethoxycymene.

Verbena oil. True vervain oil is distilled from the leaves of *Verbena triphylla* (L'Hérit.) (*Lippia Citriodora* (H. B. & K.)), which is cultivated for decoration purposes in Spain and the South of France, the oil being distilled only in small quantities: sp.gr. 0·894–0·918; rotation −12° to −16°; contains 21–38 p.c. of citral.

Indian verbena oil or **lemongrass oil** has largely replaced the true verbena oil, as it contains a higher percentage of citral. It is distilled from the grasses *Andropogon citratus* (DC.) and *A. flexuosus* (Nees.). The former is the source of the Ceylon and Straits Settlements oil, the latter of the Malabar and Cochin. *A. citratus* is also cultivated in the West Indies, but the West Indian oil is lighter in density and less soluble than the East Indian variety.

—	East Indian	West Indian
Sp.gr. .	0·895 to 0·905	0·877 to 0·887
Rotation .	+3° to −3°	+2° to −2°
Solubility .	1 in 3 volumes of 70 p.c. alcohol	Not soluble in 90 p.c. alcohol

The chief constituent is citral, of which good oils contain 75–85 p.c. Other constituents are methyl heptenone, limonene, and dipentene. An oil of similar constitution, and containing a still higher percentage of citral, is derived from the leaves of *Backhousia citriodora* (F. Muell.) (*N.O. Myrtaceæ*), a small tree indigenous to Queensland. It has a sp.gr. of 0·895–0·900, is optically inactive, and contains about 95 p.c. of citral.

Wintergreen oil is distilled from the leaves of *Gaultheria procumbens* (Linn.) (*N.O. Ericaceæ*). Indigenous to the United States. The oil is produced by a kind of fermentation from a glucoside *gaultherin* by the action of an enzyme. It has sp.gr. 1·180–1·187; rotation −0°25′ to −1°. Consists almost entirely of methyl salicylate (over 99 p.c.) with traces of an alcohol, ester, ketone, or aldehyde, and a paraffin hydrocarbon melting at 65°. An oil almost identical with the foregoing is obtained from the bark of *Betula lenta* (Linn.), the sweet birch (*N.O. Betulaceæ*). This is now largely sold as wintergreen oil. It differs from true wintergreen oil in being optically inactive. Methyl salicylate is produced synthetically on a large scale, and its detection in oil of wintergreen is very difficult and can only be found by the practised nose.

Wormseed oil. The European oil is distilled from the unexpanded flower buds of *Artemisia maritima* (Linn.) (*N.O. Compositæ*) and other species. Indigenous to Southern Russia and the Levant. Owing to the high price of raw material it is very scarce and has been almost entirely superseded by the American oil. Levant wormseed oil has a sp.gr. of 0·915–0·940, and is lævo-rotatory from −1° to −5°. Contains cineol, dipentene, terpinene, terpineol, and a sesquiterpene.

American wormseed oil is derived from the seeds of *Chenopodium ambrosioides*, var. *anthelminticum*. It has sp.gr. 0·950–0·990; rotation −5° to −10°; saponification about 8·5 (after acetylation about 280). Contains cymene, sylvestrene, camphor, and ascaridol (60–65 p.c.), a body closely allied to cineol, decomposing violently on heating to about 150°. Ascaridol has a density of 1·008.

Ylang Ylang oil is distilled from the flowers of *Cananga odorata* (Hook.) (*N.O. Anonaceæ*). Indigenous to the Malay archipelago and cultivated in the Phillippine Islands.

Cananga oil consists usually of the higher fractions and contains a greater proportion of sesquiterpenes, but in some districts the entire oil is sold as cananga oil. The majority of samples fall within the following limits—

—	Ylang Ylang	Cananga	Manila oil
Sp.gr. .	0·930–0·960	0·910–0·940	0·900–0·945
Rotation	−38° to −45°	−17° to −55°	−22° to −50°
Sapon. No.	95–130	45–100	71–154

Ylang ylang oil forms a clear solution with 1–1½ vols. of 90 p.c. alcohol, becoming turbid on further addition of alcohol. Contains methyl and benzyl acetates and benzoates, linalool, geraniol, eugenol, *iso*eugenol, methyl ether of *p*-cresol, methyl salicylate, methyl anthranilate, and an odourless sesquiterpene alcohol melting at 138°. Cadinene is also present. For other commercial varieties the following characters have been recorded :—

—	Reunion oil	Madagascar	Seychelles
Sp.gr. .	0·939–0·967	0·961–0·981	0·924–0·958
Rotation	−30° to −64°	−50°	−18° to −45°
Sapon. No.	96–98	119	—

J. C. U.

OILS (FIXED) and **FATS.** Oils and fats are distributed throughout the vegetable and animal kingdoms from the lowest organisms up to the most highly organised forms of vegetable and animal life, and are found in almost all tissues and organs. The vegetable oils and fats are deposited in considerable quantities in the seeds, and are associated there with starch, nitrogenous substances, &c., to serve as nourishment to the embryo. Exceptionally, oil has been found in considerable quantities in the rhizomes of *Cyperus esculentus* (Linn.). In the animal organism, oils and fats are mainly enclosed in the cellular tissues of the intestines and in the tissues nearest the outer skin.

The fatty (fixed) oils and fats form a well-defined and homogenous group of substances, passing through all gradations of consistency, from oils which are fluid even below the freezing-point of water, up to the hardest fats which melt at about 50°. Therefore no sharp distinction can be made between fatty oils and fats. Nevertheless, it is convenient to apply the term 'oil' to those glycerides which are fluid below about 20°, and the term 'fat' to those which are solid above this temperature.

The natural oils and fats may, for practical purposes, be looked upon as consisting in the main of mixtures, in varying proportions, of the triglycerides described under GLYCERIN.

No natural oil or fat consists of one simple triglyceride, although some of the vegetable fats derived from the *Myristicaceæ* contain very small quantities only of fatty acids other than myristic. The natural oils and fats must rather be looked upon as mixtures of at least two or three triglycerides, the most important of which would be represented by trilaurin, trimyristin, tripalmitin, tristearin, triolein, trilinolin, trilinolenin, triclupanodonin, and triricinolein. The glycerides of hydnocarpic and chaulmoogric acids are characteristic of the fats of the chaulmoogra group (*q.v.*). Other glycerides occurring in much smaller quantities are glycerides containing butyric acid (in butter fat), caproic, caprylic, capric acids (in butter fat, cocoa-nut oil, palm nut oil), lauric acid (in cocoa-nut oil, palm nut oil, dika fat), and arachidic acid (in arachis oil).

A systematic survey of the most important fatty acids occurring in oils and fats as glycerides is given in the table on p. 744.

In consequence of the discovery of mixed glycerides, the question whether mixed glycerides occur in the natural fats far more frequently than has been assumed hitherto has become a very important one. A good deal of evidence goes to show that the amount of simple triglycerides in such common fats as, *e.g.*, tallow and lard is very small indeed, and that the bulk of the triglycerides consists of mixed glycerides. At present, however, our knowledge is still too limited to justify any definite expression of opinion as to the exact composition of the glycerides in the natural oils and fats (*cf.* also GLYCERIN).

To sum up, oils and fats must not be looked upon as chemical individuals, but rather as representatives of natural species which vary, although within certain narrow limits, according to the climate and soil in which the plants producing them are grown; or, in the case of animal fats, according to the climate, the race, the age of the animal, and especially the food, and also to some extent the idiosyncrasy of the individual.

In nature, apparently, only triglycerides occur. Monoglycerides and diglycerides are, as a rule, not met with in freshly-prepared fats. (The occurrence of the diglyceride of erucic acid in a specimen of crude rape oil is due to the fact that that specimen had become rancid, with the formation of lower glycerides than a triglyceride.)

Monoglycerides and diglycerides (*see also* GLYCERIN) have hitherto been obtained only synthetically. As they have not acquired any practical importance, the reader is referred to the list of monoglycerides and diglycerides collated in Lewkowitsch's Chem. Technology, vol. i. 6.

From the table given on p. 744, it will be gathered that, for practical purposes, a classification of oils and fats can be based on the nature of the fatty acids as measured by their degree of unsaturation. This is best ascertained by determining the magnitude of the iodine absorption of the natural oils and fats, whereby a most important measure of the amount of unsaturated glycerides contained in a given oil or fat, is found. In a classification based on the iodine value the old grouping of oils into *drying oils*, *semi-drying oils*, and *non-drying* oils is implicitly contained.

The apparently antiquated sub-division into vegetable and animal oils and fats did not rest on a scientific basis, until it had been found possible to differentiate chemically between cholesterol and phytosterol (*q.v.*). All evidence goes to show that cholesterol occurs only in oils and fats of animal origin and is characteristic thereof, whereas phytosterol (sitosterol and its congeners) has been found hitherto only in vegetable oils and fats. Based on these two principles, the author has put forward a scheme of classification of the natural oils and fats (Conférence, Bull. Soc. chim. 1909) which is arranged in the following synoptic table:—

I. VEGETABLE OILS AND FATS.

A. *Vegetable Oils.*

1. Drying oils.
2. Semi-drying oils—
   - (*a*) Cottonseed oil group.
   - (*b*) Rape oil group.
3. Non-drying oils—
   - (*a*) Almond oil group.
   - (*b*) Olive oil group.
   - (*c*) Castor oil group.

B.—*Vegetable Fats.*

1. Chaulmoogra oil group.
2. Laurel oil group.
3. Palm oil group.
4. Myristica group.
5. Cacao butter group.
6. Cocoanut oil group.
7. Dika fat group.

II. ANIMAL OILS AND FATS.

A. *Animal Oils.*

1. Marine animal oils—
   - (*a*) Fish oils.
   - (*b*) Liver oils.
   - (*c*) Blubber oils.
2. Terrestrial animal oils—
   - (*a*) Semi-drying oils.
   - (*b*) Non-drying oils.

B.—*Animal Fats.*

1. Drying fats.
2. Semi-drying fats.
3. Non-drying fats—
   - (*a*) Body fats.
   - (*b*) Milk fats.

The tables, pp. 746-748, furnish a list of the most important oils and fats, arranged according

—	Chemical composition	Boiling-point		Melting-point °C.	Characteristic of
		Under mm. pressure	°C.		
I. Acids of the Acetic series, $C_nH_{2n}O_2$—					
Acetic acid . .	$C_2H_4O_2$	760	119	17	Spindle-tree oil, Macassar oil.
Butyric acid . .	$C_4H_8O_2$	760	162·3	−6·5	Butter fat, Macassar oil.
*iso*Valeric acid (?) .	$C_5H_{10}O_2$	760	173·7	−51	Porpoise and dolphin oils.
Caproic acid . .	$C_6H_{12}O_2$	770	202–203	−8	Butter fat, cocoa-nut oil, palm nut oil.
Caprylic acid . .	$C_8H_{16}O_2$	761	236–237	16·5	
Capric acid . .	$C_{10}H_{20}O_2$	760	268–270	31·3	
Lauric acid . .	$C_{12}H_{24}O_2$	100	225	43·6	Laurel oil, cocoa-nut oil.
Myristic acid . .	$C_{14}H_{28}O_2$	100	250·5	53·8	Mace butter, nutmeg butter.
Palmitic acid . .	$C_{16}H_{32}O_2$	100	271·5	62·62	Palm oil, Japan wax, myrtle wax, lard, tallow, etc.
Stearic acid . .	$C_{18}H_{36}O_2$	100	291	69·32	Tallow, cacao butter, etc.
Arachidic acid . .	$C_{20}H_{40}O_2$	—	—	77	Arachis oil.
Behenic acid . .	$C_{22}H_{44}O_2$	60	306	83–84	Ben oil.
Lignoceric acid . .	$C_{24}H_{48}O_2$	—	—	80·5	Arachis oil.
II. Acids of the Acrylic or Oleic series, $C_nH_{2n-2}O_2$—					
Tiglic acid . . .	$C_5H_8O_2$	760	198·5	64·5	Croton oil.
Hypogæic acid . .	$C_{16}H_{30}O_2$	15	236	33–34	Arachis oil.
Oleic acid . . .	$C_{18}H_{84}O_2$	100	285·5–286	6·5	Most oils and fats.
Rapic acid . .	$C_{18}H_{34}O_2$	—	—	—	Rape oils.
Erucic acid . .	$C_{22}H_{42}O_2$	30	281	33–34	Rape oils, fish oils.
III. Acids of the Linolic series, $C_nH_{2n-4}O_2$—					
Linolic acid . .	$C_{18}H_{32}O_2$	14	228	—	Soya bean oil, Maize oil, cotton-seed oil.
Telfairic acid . .	$C_{18}H_{32}O_2$	13	220–225	—	Koëme oil.
Elæomargaric acid .	$C_{18}H_{32}O_2$	—	—	48	Tung oil.
IV. Acids of the Cyclic (Chaulmoogric) series, $C_nH_{2n-4}O_2$—					
Hydnocarpic acid .	$C_{16}H_{28}O_2$	—	—	59–60	Hydnocarpus, Lukrabo, and Chaulmoogra oils.
Chaulmoogric acid .	$C_{18}H_{32}O_2$	20	247–248	68	
V. Acids of the Linolenic series, $C_nH_{2n-6}O_2$—					
Linolenic acid . .	$C_{18}H_{30}O_2$	—	—	—	Linseed oil.
*iso*Linolenic acid .	$C_{18}H_{30}O_2$	—	—	—	
VI. Acids of the Clupanodonic series, $C_nH_{2n-8}O_2$—					
Clupanodonic acid .	$C_{18}H_{28}O_2$	—	—	liquid	Fish, liver, and blubber oils.
VII. Acids of the Ricinoleic series (hydroxylated acids), $C_nH_{2n-2}O_3$—					
Ricinoleic acid . .	$C_{18}H_{34}O_3$	15	250	4–5	Castor oil.
VIII. Dihydroxylated acids of the series $C_nH_{2n}O_4$—					
Dihydroxystearic acid	$C_{18}H_{36}O_4$	—	—	141–143	Castor oil.
IX. Acids of the series $C_nH_{2n-2}O_4$ (dibasic acids)—					
Japanic acid . .	$C_{21}H_{40}O_4$	—	—	117·7–117·9	Japan wax.

to the classification set out in the foregoing table. There are added the botanical and zoological sources, the proportions of oil or fat contained in the seeds or fruits of the plants, the iodine values of the oils and fats, and their principal uses.

The determination of oils and fats in the raw materials of the oil and fat industries is effected in the chemical laboratory by heating the finely divided substance with ether, petroleum ether, or similar solvents. The comminution of hard oil seeds can be effected in a porcelain mortar, which is finally washed out with the solvent so as not to lose any fatty matter which has exuded. It is also feasible to apply an ordinary coffee-grinder, but in this case it is more difficult to avoid loss of fat. In laboratories where such determinations are carried out frequently, special grinding machines are used and loss is obviated by squeezing a large quantity of seeds through the machine. In case the substances contain a considerable amount of moisture, it is best to dry them previously, provided the oil or fat does not suffer an injurious change thereby. If oxidation of the oil or loss of volatile substances is to be expected, the oil or fat may be extracted from the moist substances by means of petroleum boiling below 80°. Ether is most satisfactory for general use, but with this solvent the substance must be dried first. Carbon disulphide and chloroform may also be used, but in this case also it is necessary to dry the substance previous to extraction. The choice of the solvent is by no means immaterial; thus carbon disulphide (which is largely used in France) extracts a larger amount of substances than do ether or petroleum (*cf.* Lewkowitsch, Chem. Technology, [i.] 213).

The most convenient apparatus for the extraction of fat is the one devised by Soxhlet (Szombathy) (see Fig. 1). 10–15 grams of the comminuted substance are filled into a cartridge of filter-paper, easily prepared by rolling filter-paper round a cylindrical piece of wood of suitable size, and folding it up at one end. The cartridge is filled with the substance and transferred to the extractor E. Care must be taken that the syphon tube be not stopped up by the paper case; nor should the cartridge be filled to the top, lest some particles of the substance be washed over by the solvent and carried away. To be quite safe, it will be found advisable to place a plug of (extracted) cotton-wool on the top of the substance, or to close the top by folding the paper over it. The tube N is then fitted by means of a cork to a flask charged with about 50 c.c. of the solvent (petroleum, ether, chloroform, &c.). Another portion of the solvent is carefully poured on to the substance in E, until it commences to run off through the syphon S. Finally, an inverted condenser is fitted to E, and the whole apparatus is placed on a water-bath. In using this form of Soxhlet's extractor there is always some doubt as to the exact time when the extraction is complete, and, as a rule, the operation lasts much longer than necessary, involving both loss of time and solvent. To avoid this, Lewkowitsch has a tap fitted on to the syphon tube, so that some of the solvent can be withdrawn at any time to ascertain the progress of extraction (*see* Fig. 2). If the substance to be extracted has been collected on a filter, the simplest plan is to fold the filter and place it at once in the extractor.

When the extraction is complete, the flask containing the solution is detached from the extractor the solvent is distilled off on the water-bath, and the fat dried in an air-bath at a temperature not exceeding 100°–110°, until the weight remains fairly constant.

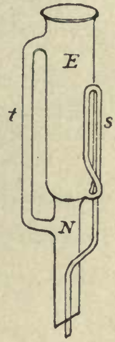


FIG. 1.

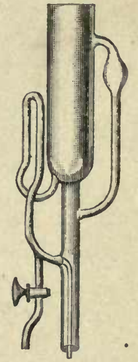


FIG 2.

In case the substance has not been dried completely and ether has been used, it is advisable to extract the residue once more with light petroleum. The drying of the residue is effected by placing the flask in a drying oven, heating to 100°–105°, and turning the contents round the walls of the flask at frequent intervals. If the minute drops of water which collect at the bottom of the oily layer have disappeared, the drying may be considered to be completed. This must be confirmed by re-weighing after further drying for half an hour. In the case of drying oils, it is best to heat the flask in an oil-bath at the temperature of 100°–105°, while a slow current of carbon dioxide or of hydrogen is allowed to pass over the surface of the oil.

TECHNICAL PREPARATION OF OILS AND FATS.

Rendering.—Since oils and fats have served the human race as one of the most important articles of food, the methods of preparing oils and fats may be considered to date back as far as the history of the human race itself. The crudest methods of 'rendering' oils from seeds and fruits, which are still practised at present in Central Africa, in Indo-China, the Malay Archipelago, and the South Sea Islands, consist in allowing the broken fruits to melt by the heat of the sun, when the exuding oil runs off and is collected. The production of palm oil by the natives, as also of the preparation of best cocoanut oil by boiling the fruit kernels with water, are more modern developments of this method, which culminates in the *boiling-out method* practised on the largest scale by 'rendering' animal fats and oils from the tissue, as is done in the preparation of tallow, lard, whale oil, cod-liver oil, &c. The most modern practice in the carrying out of this process, as worked in the enormous packing houses (rendering establishments) in America (tallow, lard, bone fat), and in the modern whale oil and fish oil rendering

I. VEGETABLE OILS AND FATS.

A. Vegetable Oils.

	Oil.	Source	Proportion of oil in seed or fruit	Iodine value	Used in the production of
	1. *Drying Oils.*				
	Perilla . .	Perilla ocymoides	35·8	206·1	Varnishes.
	Linseed . .	Linum usitatissimum	38–40	175–205	Paints, varnishes, linoleum, soft soap.
	Tung (*a*) Chinese . (*b*) Japanese	Aleurites cordata	53	150–163	Paint and varnish.
	Candle nut . .	Aleurites moluccana	62–64	163	Burning oil, soap, paint.
	Hemp seed . .	Cannabis sativa	30–35	148	Paints and varnishes, soft soap.
	Walnut: nut .	Juglans regia	63–65	145	Paints.
	Safflower . .	Carthamus tinctorius	30–32	130–147	Burning oil, varnish ("roghan")
	Poppy seed . .	Papaver somniferum	41–50	123–143	Salad oil, paints, soft soap.
	Sunflower . .	Helianthus annuus	21–23	119–135	Edible oil, soap.
	Soya bean . .	Soja hispida	18	137–141	Edible oil, burning oil, soap.
	Cameline (Ger. sesamé) .	Camelina sativa	31–34	135	Burning oil, soap.
	Madia . .	Madia sativa	32–33	118·5	Soap, burning oil.
	2. *Semi-Drying Oils.*				
(*a*) Cotton-seed oil group	Pumpkin seed .	Cucurbita pepo	47–48	123–130	Edible oil, burning oil.
	Maize: corn .	Zea Mays	6–10	113–125	Edible oil, soap.
	Beech nut . .	Fagus sylvatica	43–45	111–120	Edible oil, burning oil.
	Kapok . .	Bombax pentandrum (Eriodendron anfractuosum)	30–32	116	Edible oil, soap.
	Cotton seed .	Gossypium herbaceum	24–26	108–110	Edible oil, soap.
	Sesamé . .	Sesamum orientale, S. indicum	50–57	103–108	Edible oil, soap.
	Curcas, purging nut	Jatropha curcas	55–57	98–110	Medicine, soap.
	Brazil nut . .	Bertholletia excelsa	73	90–106	Edible oil, soap.
(*b*) Rape oil group	Croton . .	Croton tiglium	53–56	102–104	Medicine.
	Ravison . .	Wild Brassica campestris	33–40	105–117	Lubricants, burning oil.
	Hedge Mustard .	Raphanus Raphanistrum	35–40	105	
	Rape (colza) .	Brassica campestris	33–43	94–102	Lubricant, burning oil.
	Black Mustard .	Brassica nigra (Sinapis nigra)	31–33	116·1	Soap.
	White Mustard .	Brassica alba (Sinapis alba)	85–86	92–103	Soap.
	Radish seed .	Raphanus sativus	45–50	92–112	
	Jamba . .	Brassica campestris var.	24	95	Burning oil, lubricant.
	3. *Non-Drying Oils.*				
(*a*) Almond oil group	Cherry kernel .	Prunus cerasus	35–36	110–114	Edible oil, burning oil, soap.
	Apricot kernel .	Prunus armeniaca	40–45	96–108	Perfumery, medicine.
	Plum kernel .	Prunus domestica Prunus damascæna	25		
	Peach kernel .	Prunus persica	32–35	93–108	Perfumery, medicine.
	Almond . .	Prunus amygdalus	45–55	93–100	Perfumery, medicine.
(*b*) Olive oil group	Arachis (groundnut)	Arachis hypogæa	43–45	83–100	Edible oil, soap.
	Hazel nut . .	Corylus avellana	50–60	83–90	Edible oil, perfumery, lubricant.
	Olive . .	Olea europæa	40–60	79–88	Edible oil, lubricant, burning oil, soap.
	Olive kernel .	Olea europæa	12–15	87	Edible oil, lubricant, burning oil, soap.
	Ben . .	Moringa oleifera	35–36	82	Edible oil, perfumery, lubricant.
(*c*) Castor oil group	Grape seed .	Vitis vinifera	10–20	96	Edible oil, burning oil.
	Castor . .	Ricinus communis	46–53	83–86	Medicine, soap, Turkey red oil, lubricant.

B. Vegetable Fats.

	Fat.	Source	Proportion of oil in seed or fruit	Iodine value	Used in the production of
	Laurel oil group—				
	Laurel oil	Laurus nobilis	24–26	68–80	Medicine.
Palm oil group	Mowrah seed oil	Bassia latifolia	50–55	63	Edible fat, soap, candles.
	Mahua butter	Illipe latifolia			
	Mowrah butter	Bassia longifolia	50–55	58–63	Edible fat, soap, candles.
	Illipe butter				
	Macassar oil Kusum oil	Schleichera trijuga	70·5	48–69	Medicine.
	Palm oil	Elaeis guineensis, E. melanococca	16–44	53	Candles, soap.
Myristica group	Mace butter Nutmeg butter	Myristica officinalis	38–40	40–52	Medicine, perfumery.
	Phulwara butter	Bassia butyracea	50–52	42	Edible fat.
	Shea butter (Galam butter)	Bassia Parkii	49–52	56	Edible fat, soap, candles.
Cacao butter group	Mkányi fat	Stearodendron Stuhlmannii	67	41·9	Soap, candles.
	Malabar tallow	Vateria indica		37–40	Edible fat.
	Cacao butter	Theobrama cacao	44–50	32–41	Chocolate.
	Chinese vegetable tallow	Stillingia sebifera (Croton seb.)	22	28–32	Soap, candles.
	Kokum butter (Goa butter)	Garcinia indica	49	33	Edible fat.
	Borneo tallow	Shorea stenoptera, Hopea aspera	45–50	15–31	Edible fat, candles.
Cocoa-nut oil group	Mocaya oil	Cocos sclerocarpa	60–70	24	Edible fat, soap.
	Maripa fat	Palma (?) Maripa	—	17	,, ,,
	Palm kernel oil Palm nut oil	Elaeis guineensis E. melanococca	45–50	13–14	,, ,,
	Cocoa-nut oil	Cocos nucifera, C. butyracea	20–25	8–9	Edible fat, soap, candles.
Dika fat group	Dika oil (oba oil, wild mango oil)	Irvingia gabonensis	60–65	5·2	Edible fat.
	Japan wax	Rhus succedanea, R. vernicifera	25	4–10	Polishes.
	Myrtle wax	Myrica cerifera, M. carolinensis	20–25	2–4	Soap, candles (?).

II. ANIMAL OILS AND FATS.

A. Animal Oils.

Oil	Source	Iodine value	Principal use
1. *Marine Animal Oils.*			
(*a*) Fish oils—			
Menhaden	Alosa menhaden	140–173	Currying leather; soap making.
Sardine	Clupea sardinus	161–193	,, ,, ,,
Japanese sardine	Clupanodon melanosticta	187	,, ,, ,,
Salmon	Salmo salar	161	Currying leather.
Herring	Clupea harengus	124–142	,, ,,
Stickleback	Gasterosterus trachurus	162	,, ,,
Sturgeon	Accipenser sturio	125·3	,, ,,
Sprat	Clupea sprattus, Cuv.	122–142	,, ,,
(*b*) Liver oils—			
Cod liver	Gadus morrhua	167	Medicine, currying leather.
Skate liver	Squatina vulgaris	157·3	,, ,, ,,
Tunny liver	Thynnus vulgaris	191·1	,, ,, ,,
Shark (arctic)	Scymnus borealis	115	Currying leather.
Coal fish	Gadus merlangus (virens)	161·1	,, ,,
Hake liver	Merluccius commun. (vulgaris)	—	,, ,,
Ray liver	Raja clavata (batis)	—	,, ,,
Ling liver	Molva vulgaris	132–151	,, ,,

II. ANIMAL OILS AND FATS—*continued.*

A. Animal Oils.

Oil	Source	Iodine value	Principal use
(*c*) Blubber oils—			
Seal . .	Phoca vitulina	137–147	Burning, currying leather.
Whale . .	Balæna mysticetus	121–136	Burning, soap-making, fibre dressing, currying leather.
Dolphin, black fish			
Body oil .	Delphinus globiceps	99–126	Lubricating oil for delicate machinery.
Jaw oil .		33	
Porpoise—			
Body oil .	Delphinus phocæna	119	
Jaw oil .			
	2. Terrestrial Animal Oils.		
Non-Drying oils—			
Sheep's foot .	Ovis aries	74	Lubricating.
Horses' foot .	Equus caballus	74–90	„
Neat's foot .	Bos taurus	67–73	Lubricating, leather.
Egg . .	Gallus domesticus	68–82	Leather dressing.

B. Animal Fats.

	Fat	Source	Iodine value	Principal use
		1. Drying Fats.		
	Ice bear . .	Ursus maritimus	147	Pharmacy.
	Rattlesnake .	Crotalus durissus	106	Pharmacy.
		2. Semi-drying Fats.		
	Blackcock .	Tetrao urogallus	121·1	
	Hare . . .	Lepus timidus	102·2	
	Rabbit, wild .	Lepus cuniculus	99·8	
	Rabbit, tame .	Lepus cuniculus	67·6	
	Wild duck . .	Anas boschas	84·6	
	Domestic duck .	Anas boschas	58·5	
	Horses' fat . .	Equus caballus	75–85	Edible fat, soap.
		3. Non-drying Fats.		
Body fats	Horse marrow fat	Equus caballus	77–81	Food, soap.
	Domestic goose .	Anser cinereus		Food.
	Wild goose . .	Anser ferus	99·6	
	Lard . . .	Sus scrofa	66	Food, soap.
	Hog, wild . .	Sus scrofa	76·6	
	Beef, marrow .	Bos taurus	55	Pomades
	Bone . . .	Bos; Ovis	46–56	Soap, candles.
	Tallow, beef .	Bos taurus	38–46	Food, soap, candles, lubricants.
	Tallow, mutton .	Ovis aries	35–46	Food, soap, candles, lubricants.
Milk fat	Butter . .	Bos taurus	26–38	Food.

works, consists essentially in cutting up the fatty tissues into small fragments, which are transferred into vessels containing water, wherein the comminuted mass is heated by steam, either under ordinary pressure in open vessels or under higher pressure in digesters. The fat gradually exudes and collects on the top of the water whilst the membranous matter ('greaves') falls to the bottom. The fat is then drawn off from above the aqueous (gluey) layer, and strained through sieves or filters. The 'greaves' are placed in hair or woollen bags and submitted to hydraulic pressure, whereby a further portion of oil or fat is obtained. In the case of those animal fats which are intended for edible purposes, such as lard or suet for margarine, the greatest cleanliness must, of course, be observed, and the temperature must be kept as low as possible in order to obtain a perfectly 'sweet' and pure material.

Pressing.—The preparation of oils and fats from small oleaginous seeds, such as linseed and rape seed, was practised originally by crushing the seeds and grinding between stones, as is still done in India. A more modern development, still in vogue in Manchuria in the production of soya bean oil, consists in bruising the seeds and reducing them under an edge-stone, heating the meal in an open pan, and pressing out the oil in a wedge-press, the wedges being driven home by hammers. The screw-press used in vineyards served as a model for the construction of the primitive olive-press. The several stages through which the industry of oil presses developed from these early beginnings of machinery to the Dutch wedge-press, until it reached the most complete form of modern oil-pressing plant, cannot be detailed here, and the reader is therefore referred for a rapid survey to Lewkowitsch's Chemical Technology, [ii.] 1–15. It must suffice here to state that the most modern presses in vogue at present are the *Marseilles press*, the *Anglo-American press*, and the *cage press* (clodding-press), which have reached their present completeness through the combination of the inventions of the hydraulic-press by Joseph Bramah (1795), and of the accumulator by William George (later Lord) Armstrong (1843). It is due to the early application of these inventions in this country, that England secured the supremacy in the oil-crushing trade in the latter half of the last century and has been able to retain it, notwithstanding severe foreign competition.

The sequence of operations in treating oil seeds, oil nuts, &c., for the separation of the oils they contain is, at the present time, as follows: As a preliminary operation the oil seeds and nuts are freed from dust, sand, and other impurities by sifting in an inclined revolving cylinder or sieving machine, covered with woven wire, having meshes varying according to the size and nature of the seed operated upon. This preliminary purification is of the greatest importance, especially for the preparation of *edible oils and fats.* In the case of those seeds amongst which are found pieces of iron (hammer heads and nails, amongst palm kernels, &c.), the seeds are passed over magnetic separators, which retain the pieces of iron. The seeds and nuts are then decorticated (when required), the shells removed, and the kernels ('meats') converted into a pulpy mass or meal (in older establishments by crushing and grinding between stones in edge-runners) on passing through a hopper over rollers consisting of (five) chilled-iron or steel cylinders mounted vertically like the bowls of a calendar. These rollers are finely grooved so that the seed is cut up whilst passing in succession between the first and second rollers in the series, then between the second and the third, and so on to the last, when the grains are sufficiently bruised, crushed, and ground. The distance between the rollers can be easily regulated so that the seed leaving the bottom roller has the desired fineness. The comminuted mass, forming a more or less coarse meal, is either expressed in this state or subjected to a preliminary heating, according to the quality of the product to be manufactured. For the preparation of edible oils and fats the meal is expressed in the cold, after having been packed into bags and placed in hydraulic presses under a pressure of 300 atmospheres or more. The cakes are allowed to remain under pressure for about 7 minutes. The oil exuding in the *cold* dissolves the smallest amount of colouring matter, &c., and hence has suffered least in its quality. Oils so obtained are known in commerce as 'cold-drawn oils,' 'cold-pressed oils,' 'salad oils,' 'virgin oils.'

By pressing in the cold, obviously only part of the oil or fat is recovered. A further quantity is obtained by expressing the seed meal at a somewhat elevated temperature, reached by warming the comminuted seeds or fruits either immediately after they leave the five-roller mill, or after the 'cold-drawn oil' has been taken off. Of course, the cold-pressed cakes must be first disintegrated, which may be done under an edge-runner. The same operation may be repeated once more. Thus oils of the 'second expression' and of the 'third expression' are obtained.

In the case of oleaginous seeds of low value (cotton-seed, linseed) it is of importance to express in one operation the largest possible quantity of oil. Hence the bruised seed is, after leaving the five-roller mill, generally warmed at once in a steam-jacketed kettle fitted with a mixing gear, by passing steam into the jacket, and sending at the same time some steam through a rose, fixed inside the kettle, into the mass while it is being agitated. This practice is a survival of the older method of moistening the seed with a little water, while the seeds were bruised under edge-runners, so as to lower the temperature and facilitate the bursting of the cells. The warm meal is then delivered through measuring boxes into closed press-bags ('scourtins' of the 'Marseilles' press), or through measuring boxes, combined with an automatic moulding machine, into cloths open at two sides (Anglo-American press), so that the preliminary pressed cakes can be put at once into the hydraulic press. In the latest constructions of cage presses, the use of bags is entirely dispensed with, a measured quantity of seed falling direct into the circular-press cage and being separated from the material forming the next cake by a circular plate of sheet iron.

The method of expressing is exclusively employed wherever the pressed cakes are used as cattle food. These cakes retain a notable amount of oil or fat—from 5 to 10 p.c.—which must, however, not be considered as lost, inasmuch as the fat constitutes a most valuable and, indeed, even necessary constituent of cattle food.

Extraction by solvents. In those cases where the full yield, or approximately full yield, of the oil contained in the seeds is aimed at, the comminuted seeds are extracted with volatile solvents, such as petroleum hydrocarbons, boiling below 120°, and carbon disulphide. As these solvents are highly inflammable, an endeavour is made at present to extract by means of the non-inflammable carbon tetrachloride and other chloro derivatives of ethane (such as dichloro-ethylene $C_2H_2Cl_2$, trichloro-ethylene C_2HCl_3, perchloro-ethylene C_2Cl_4, tetrachloro-ethane $C_2H_2Cl_4$, and pentachloro-ethane C_2HCl_5). At present the high price of these solvents still militates against their general employment, in addition to some other drawbacks in their use.

The apparatus employed on a large scale

depends on the temperature at which the extraction is carried out. In the main two types of extracting apparatus may be differentiated, viz. for extraction in the cold and for extraction in the hot. The seed is prepared in a similar manner as for pressing, except that it is not reduced to a fine meal, so as not to impede the percolation of the solvent through the mass. In the case of *cold extraction* the seed is placed in a series of closed vessels, through which the solvent percolates by displacement, on the 'counter-current' system. A battery of vessels is so arranged that one vessel can always be made the last of the series to discharge finished meal and to be recharged with fresh meal, so that the process is practically a continuous one. The solution of the extracted oil or fat is then transferred to a steam-heated still, where the solvent is driven off and recovered by condensing the vapours in a cooling coil, to be used again. The last remnant of volatile solvent in the oil is driven off by a current of open steam blown through the oil in the warm state. The extracting process *in the hot* is carried out in an apparatus, the principle of which is exemplified by the well-known Soxhlet extractor. The comminuted seed is placed on trays or baskets inside a vessel connected with an upright refrigerator, and is surrounded there by the volatile solvent. On heating the solvent with steam through a coil or jacket, the vapours rise through and around the meal. They pass into the refrigerator, where they are condensed and fall back as a liquid through the meal, percolating it on their way downwards, and reaching the bottom of the vessel as a more or less saturated solution of oil in the solvent. The solvent is again evaporated, leaving the oil at the bottom of the vessel until the extraction is deemed finished. The solution of fat is then run off into a still, as described already, and the last traces of solvent are driven out. The solvent is recovered and used again.

The meal left after extraction is not suitable for cattle food, and no extracted meal can be sold in this country for feeding purposes. On the Continent, however, frequent endeavours are being made to sell (and even recommend under specious 'scientific' pretensions) extracted meal for feeding purposes, and although Agricultural Associations in many cases stipulate that no extracted meal should be accepted by farmers, yet a considerable amount of extracted meal finds its way, chiefly on the Continent, into 'compound cakes.'

With regard to the merits and demerits of the last two mentioned processes—expression and extraction—the adoption of either must largely depend on local conditions and the objects for which the products are intended. Wherever the cake is the main product, expression will commend itself as the most advantageous process. Where, however, the fatty material forms the main product, as in the case of palm kernel oil, or sesamé and cocoa-nut oils from damaged seeds (which would no longer form proper cattle food), the process of extraction will be preferred, especially when the price of oil is high. In some cases the combination of the two processes commends itself, as in the production of olive oil. The fruits are expressed, and after the edible qualities and best classes of oils for technical purposes have been taken off by expression, the remaining pulp is extracted by means of solvents. This process is known under the name of the mixed process (*huilerie mixte*) [*v.* OLIVE OIL].

Refining and *bleaching.* The oils and fats prepared by any of the methods described above are, if obtained from perfectly fresh ('sweet') material, and in their fresh state, practically neutral. If care be exercised in the process of rendering animal oils and fats, or expressing vegetable oils in the cold, the products are, as a rule, sufficiently pure to be delivered to the consumer, after a preliminary settling has allowed any mucilaginous matter, such as animal or vegetable fibres or other impurities, as also traces of moisture, to separate out. This spontaneous clarification was at one time the only method in vogue. This process is now shortened by filtering oils through filter presses, or otherwise brightening them, *e.g.* by blowing with air. In many cases these methods still suffice for the production of commercial oils and fats.

In special cases, such as the preparation of edible oils and fats, a further improvement in colour, and at the same time greater purity is obtained by filtering the oils over charcoal, or over natural absorbent earths, such as fuller's earth. Where this process does not suffice, as in the case of cocoanut oil or palm kernel oil, a preliminary purification in a current of steam must be resorted to before the final purification, described above, is carried out.

Oils, intended for table use, which deposit 'stearine' in winter, must be freed from such solid fats. This is done by allowing the oil to cool down to a low temperature and pressing the cold oil through cloths in a press, when a limpid oil exudes, which remains proof against cold. Such oil is termed 'winter oil.' Thus whereas most olive oils are naturally non-congealing oils, the Tunisian and Algerian olive oils deposit so much 'stearine' that they must be 'demargarinated.' Similar methods are employed in the production of lard oil, edible cotton-seed oil, &c.

For *refining* oils and fats intended for edible purposes only the foregoing methods, which may be summarised under the name of *physical methods*, can be used; the only chemicals permissible are alkalis or alkaline earths to remove any free fatty acids present. Treatment with other chemicals renders the oils and fats unfit for consumption. Therefore all bleaching and refining processes involving other means than those enumerated can only be employed for technically used oils and fats, such as lubricating oils, burning oils, paint oils, soap-making oils, &c.

Bleaching with the aid of chemicals requires great circumspection. There is no universal method of oil-refining applicable to any and every oil or fat. Not only must each kind of oil or fat be considered as a special problem, but frequently even varieties of one and the same oil or fat are apt to cause the same difficulties as would a new individual. In many cases purification by means of sulphuric acid, invented and patented by Charles Gower in 1792 (frequently ascribed to Thénard), is still usefully applied. It consists in treating the oil with a small percentage of a more or less concentrated sulphuric acid, according to the nature of the oil or fat. The acid not only takes up water, but it acts on the suspended impurities, carbonising them to some extent, and thus causing them to coagulate and fall down in the form of a flocculent mass, which carries with it mechanically other impurities which have not been acted upon. This method is chiefly used in the refining of linseed and rape oils.

Purification by means of strong caustic soda was first recommended as a general process by Louis C. Arthur Barreswil, his suggestion being to heat the oil and add 2–3 p.c. of caustic soda. In most cases the purification consisted in removing the free fatty acids from rancid oils and fats, the caustic soda forming a soap with the fatty acids, which would either rise as a scum and lift up impurities with it, or fall to the bottom and carry them down. This process is a useful one in the case of cotton-seed oil. As a rule, however, it is very precarious, since emulsions are formed which in many cases altogether prevent the separation of oil. After the treatment with sulphuric acid or caustic soda, the oils must be washed to remove the last traces of chemicals. The water is then allowed to settle out, and the oils are finally filtered.

The number of chemicals which have been proposed from time to time for the purification of oils and fats is almost legion, and so long as the nature of oils and fats was little understood, a secret trade in oil-purifying chemicals flourished. With our present knowledge most of these chemicals may be removed into the limbo of useless things.

The general methods of bleaching, besides those mentioned already as physical methods (viz. filtration over charcoal or absorbent earth), are chiefly methods based on treatment with oxygen or by chlorine. The methods of bleaching by oxygen include all those which aim at the bleaching by exposure to the air and to sunlight (as in the case of artists' linseed oil), or where oxygen or ozone is introduced in the form of gas or is evolved by chemicals, such as manganese dioxide, potassium dichromate, or potassium permanganate and sulphuric acid. In the process of bleaching by means of chlorine either bleaching powder or dichromates and hydrochloric acid are used. It must again be emphasised that no general rule can be laid down as to which process should be employed in each given case. There is still a wide field open for the application of proper processes for the removal of impurities and colouring matters without, however, running the risk of attacking the oil or fat itself.

Hence the attention of inventors has been directed during the last few years to the exploitation of this subject and a considerable number of processes and chemicals have been suggested. Thus bleaching by means of ultra-violet rays has, through the introduction of the 'uviol lamp,' gained favour and the bleaching of linseed oil by these means has been patented. It is stated that other oils also can be bleached with the aid of ultra-violet rays ('uviol oils').

Peroxides (sodium peroxide, calcium peroxide, and barium peroxide), persalts (such as perborates, persulphates, percarbonates of sodium or potassium), organic peroxides (benzoyl peroxide, acetyl peroxide, acetone peroxide), further sodium and calcium hydrosulphites, basic zinc formaldehyde-sulphoxylate and other similar preparations have been suggested and have also been used in practice occasionally. A number of these preparations are sold under fancy names, but notwithstanding a number of laudatory articles persistently launched into the technical press, by interested parties, no favourable statement can be made as to their permanent usefulness or superiority over the reagents named above. Most of these strongly acting chemicals produce a temporary effect, but frequently the colour 'reverts.' In other cases they introduce such complications into the routine of the oil refiners and of soap and candle manufacturers that it is impossible to recommend them without very serious qualification.

Even after such purification as has been described above, small quantities of non-glyceridic substances remain dissolved. Some of these must be considered as entirely foreign (adventitious) substances, *e.g.* traces of colouring matters, chromogenetic substances (producing the colour reactions which are characteristic of some oils and fats), ethereal oils, resinous matters, sulphur compounds, and cyanogenetic glucosides.

Other substances are constant concomitants of the natural products, and must therefore be looked upon, to some extent at least, as constituents thereof. The most important of these are phytosterol and cholesterol, inasmuch as the presence or the absence of one or other enables us to recognise a specimen as a vegetable or animal oil or fat. Of less importance are aliphatic alcohols (such as myricyl or ceryl alcohol) and lecithin, although the latter is of very great importance from a physiological point of view (*see* GLYCERIN).

Hydrocarbons, which have been hitherto considered as of little importance, occur more frequently in natural oils and fats than has been ascertained hitherto. More attention is now being paid to their occurrence, as they will probably furnish a means of identifying individual oils and fats.

In their liquid state oils and fats penetrate easily into the pores of dry substances; if dropped on paper they leave a translucent spot—grease spot—which cannot be removed by washing with water and subsequent drying (difference from glycerol spots).

A curious effect, caused by the presence of the minutest quantities of oils and fats, has been described by Lightfoot. Camphor, crushed between layers of paper without having been touched with the fingers, rotates when thrown on to water, but a trace of oil or fat on the surface of the water causes the rotation to cease immediately; it is sufficient to touch the water with a needle which has been passed previously through the hair.

The *specific gravity* of oils and fats varies between the limits 0·910 and 0·975 at 15·5°. The specific gravity alone only exceptionally furnishes a means of identifying an individual oil. Hence the 'oleometers' which were formerly credited with the power of detecting individual oils are now practically abandoned. Castor oil alone can be identified by its exceptionally high specific gravity.

The *solidifying point* of those oils which are fluid at the ordinary temperature range from a few degrees above zero down to −28° C. (linseed oil). (For melting and solidifying points of individual oils and fats, *cf.* tables at the end of this article.)

Although at first sight little importance should be ascribed to the melting and solidifying points, inasmuch as from some oils there separate out on standing glycerides containing solid acids (in practice frequently termed ‘ stearine ’ or ‘ margarine ’), they are, from a technical point of view, of importance as they are a measure of the consistence and furnish reliable guidance in the preparation of ‘ demargarinated edible oils ’ or ‘ racked ’ fish and cod-liver oils. For the manufacture of such demargarinated oils, the natural oils are exposed to a low temperature. The solid glycerides then separate out as a deposit and the clear limpid oil can be drawn off as an upper layer after sufficient time has been allowed for subsidence. When the solid glycerides separate out in a crystalline form, this slow and cumbersome process can be shortened by cooling (refrigerating) the oils artificially and filtering the liquid portion from the solid at a low temperature. The limpid oils thus obtained are sold in commerce as ‘ winter oils.’

Demargarinating is employed on a large scale in the case of cotton-seed oil, whale oil, tallow, and some Algerian and Tunisian olive oils.

The *refractive index* of the natural oils and fats varies within certain limits which, though narrow, are sufficiently characteristic, if observed through accurate optical instruments, to allow a differentiation of the individual oils and fats to a certain extent. This will be further explained below under *Analysis*, but it may be pointed out here that exaggerated importance has frequently been attached to the interpretation of the results of refractometric observation.

The majority of oils and fats have practically no action on the *plane of polarised light*, the small deviations observed in sensitive polariscopes being chiefly due to adventitious substances, such as cholesterol or phytosterol or resinous or volatile ethereal substances, as in the case of sesamé oil, cocoa-nut oil, cod-liver oil.

There are, however, several oils which are distinguished by notable rotations; this is more particularly the case with the oils belonging to the Chaulmoogra group, and it is thus possible by means of the polariscope alone to identify an oil as belonging to this class, as has been done by the author in the case of ‘ cardamom fat ’ (*see Chaulmoogra oil group*). Notable rotations are also afforded by castor oil and stillingia oil.

Solubility.—Natural oils and fats may be considered as completely insoluble in pure water. On shaking vigorously with large quantities of water, minute quantities are dissolved, as is evidenced by allowing the emulsions formed at first to become clear by standing and shaking out the clear aqueous layer with ether.

Oils and fats dissolve in their turn small quantities of water, which can be expelled by warming at 100°. From the foregoing it follows that the emulsifying power of water as regards oils and fats is practically *nil*. It can, however, be increased to a very notable extent by addition of small quantities of soap and a number of other substances (*see* Lewkowitsch, Chem. Tech. [iii.] 88, *Emulsified Oils and Fats*).

With the exception of castor oil, oils and fats dissolve but very sparingly in *cold alcohol*. Boiling alcohol, however, dissolves somewhat larger quantities, especially of those oils and fats which contain glycerides of the lower fatty acids; but on cooling, nearly all the dissolved substance separates out. The solubility is considerably increased by the presence of free fatty acids; if the amount of the latter be large, exceeding about 30 p.c., even cold alcohol will readily effect dissolution.

Oils and fats dissolve very readily in ether, carbon disulphide, chloroform, carbon tetrachloride, trichlorethylene (and its congeners), benzene, paraffin oils, and light petroleum. Castor oil, however, forms an exception as regards the two last-mentioned solvents. Triacetin is insoluble in carbon disulphide and in petroleum ether.

Oils and fats dissolve *sulphur* and *phosphorus* at the ordinary temperature to a slight extent. Certain pharmaceutical preparations, notably phosphorised oils, are thus prepared.

The *smell* and *taste* of oils and fats, although frequently characteristic of the individual oils and fats, is due to the presence of certain foreign matters. Thus in the case of fats belonging to the Myristica group the presence of an ethereal oil imparts the taste of mace. In the case of cocoanut oil the peculiar taste appears to be due to the presence of some ethereal ketones (occurring also in the essential oil of rue). It may be accepted that in their purified state oils and fats are entirely devoid of free fatty acids, and are practically odourless and tasteless. Hence absolutely neutral oils have an insipid taste, and what is considered as a peculiarly characteristic taste is due to minute traces of foreign substances or to small quantities of free fatty acids.

When freshly rendered, animal fats contain but very small quantities of *free fatty acids*. Oils and fats of vegetable origin, however, even in their fresh state, contain appreciable amounts of free fatty acids. This may be due to the fact that in all seeds there are present enzymes which hydrolyse glycerides, the acid necessary for inducing the hydrolysis being supplied in the form of carbonic acid, which is always present in seeds.

Oils and fats do not suffer any loss when heated at temperatures of 150°–180°. However, oils and fats containing notable quantities of free volatile fatty acids, such as rancid butter fat, and cocoanut oil, lose in weight, no doubt through volatilisation of free fatty acids; it is not certain that glycerides of the lower fatty acids volatilise as well.

Provided prolonged contact with air is avoided, most oils and fats can be heated to a temperature of about 250° without undergoing a chemical change. (Some oils and fats become paler in consequence of the destruction of dissolved colouring matters, *e.g.* linseed oil.) On being heated above 250°, up to 300°, some oils, especially the drying oils, undergo a change which may be described as due to polymerisation. Thus linseed oil is converted into a thick oil, having a considerably higher specific gravity than that of ordinary linseed oil. On this reaction is based the manufacture of *Polymerised Oils. Linseed oil* is converted by heating above 250° into 'varnishes' (not to be confounded with oil-varnishes containing linseed oil, gums, and oil of turpentine), which, according to their specific gravity, are graded in commerce as 'thin varnish' (sp.gr. 0·966), 'medium varnish' (sp.gr. 0·972), 'strong varnish' (sp.gr. 0·974), 'extra strong varnish' (sp.gr. 0·978). These oils find application in lithographic printing and in the preparation of printer's ink, also as 'bird-lime,' and in the manufacture of plastic masses. Hence these oils are also known in the trade as '*lithographic varnishes.*' *Tung oil* is converted by heating to 250° into a jelly-like mass, 'polymerised tung oil,' used in the preparation of oil varnishes and even in the manufacture of linoleum. *Polymerised Safflower oil* is prepared in a similar manner from safflower. In India this product has been prepared by the natives for many centuries, and is known as 'Roghan' ('Afridi wax'). *Castor oil* especially lends itself to the preparation of polymerised oil, owing to the chemical constitution of *ricinoleic acid* (of which it contains considerable quantities), by prolonged heating, as is practised, *e.g.*, in the preparation of cognac oil, when a spongy, very bulky indiarubber-like mass is obtained (for which a solvent has not yet been found). The polymerisation can be accelerated in some cases by the addition of 'condensing agents,' such as concentrated sulphuric acid, aluminium chloride, and zinc chloride.

When oils and fats are heated beyond 250°, decomposition sets in, with the formation of volatile products, the most prominent of which is *acroleïn*. The intense odour of acroleïn, which all fats emit when heated above 300°, is one of the most characteristic reactions, enabling one to distinguish rapidly fatty oils and fats from mineral and ethereal oils. Amongst the volatile products obtained on heating oils and fats to high temperatures are found, besides volatile acids and sebacic acid, hydrocarbons of the ethane, ethylene, and aromatic series (and perhaps also naphthenes), the quantity of which is considerably increased when the destructive distillation takes place under pressure. This fact lends strong support to the theory that the natural petroleum hydrocarbons owe their origin to the destruction of oils and fats. The vegetable fats generally offer much greater resistance to their conversion into hydrocarbons under pressure than do animal oils and fats. If an optically active fat is distilled destructively, the hydrocarbons formed exhibit optical activity (Lewkowitsch, Ber. 1907, 4161). Before gas-making from coal was generally adopted, illuminating gas was frequently prepared from fatty oils. In this connection it may be interesting to remember that Faraday discovered benzene in condensed gas made from whale oil.

As these changes are most important, special attention must be paid to the influence which *light, air,* and *moisture* exert, both separately and conjointly.

Effect of light.—The action of light alone, air and moisture being excluded, has hitherto not been studied thoroughly. It is well known that oils and fats acquire a paler colour under the influence of insolation, some oils even becoming colourless. The application of insolation to industrial purposes is well exemplified by the method of bleaching linseed oil, cod-liver oil, and olive oil under glass or in glass bottles. Since pure glycerides are themselves colourless, the light can only affect the foreign substances dissolved in them. This is further proved by the fact that insolated cotton seed oil does not reduce silver nitrate so readily as does cottonseed oil kept in the dark, and that exposure to light destroys those minute traces of chromogenetic substances which give rise to colour reactions that have for a long time been erroneously considered as characteristic (*v. infra*). It would appear that the specific action of light is due especially to the ultra-violet rays (*see* above under *Bleaching*).

Effect of air.—When studying the effect of air we must clearly discriminate between the influence of the ordinary atmosphere—which necessarily includes the action of oxygen, moisture, and light (diffused daylight, direct sunlight)—and the influence of *dry* air, to the exclusion of moisture and light. The effect of the atmosphere on oils and fats varies in a very marked degree with the chemical composition of the glycerides. As a general rule, it may be stated that the greater the proportion of unsaturated fatty acids in the glycerides of oils and fats, the greater is their power to absorb oxygen. The chemical change is most marked in the case of drying oils; it becomes gradually less pronounced with the decrease of the power of absorbing iodine, as we pass through the classes of semi-drying oils and non-drying oils down to the solid fats. Marine animal oils occupy a position similar to that of drying oils. The oxygen absorption power of the various oils and fats will be considered below in the section *Analysis*. Drying oils thicken at first and form an elastic skin on the surface. If exposed in sufficiently thin layers, as, for instance, if spread on wood or glass, they are finally converted into a transparent, yellowish, flexible substance, insoluble in water, alcohol, and also, to a very great extent, in ether. While this energetic oxidation takes place, heat is developed to such a degree that if the drying take place in presence of organic substances in a fine state of division, offering a large surface to the atmosphere (cotton waste, woollen rags), spontaneous combustion will ensue. The non-drying oils remain more or less unchanged. The semi-drying oils occupy an intermediate position. The gradations between the various classes are, however, by no means so distinct as to warrant the drawing of hard and fast dividing lines between the three classes.

The action of air is intensified by spreading oils and fats over finely divided metals (lead powder, copper powder), the metals acting as accelerators or catalysts. This reaction is used for analytical purposes in the determination of the oxygen absorption power of oils (*v. infra*).

Dry air, to the exclusion of moisture and light, has no action on oils and fats, at the ordinary temperature. They will therefore remain unchanged for practically an indefinite length of time, if kept protected from moisture and light. Since it is very difficult to exclude the last traces of moisture when storing oils and fats, such moisture as gains access to the oils and fats will exercise a slight action in the manner described in the following paragraph, that is to say, small amounts of fatty acids will be formed, but rancidity need not set in.

Effect of moisture.—The effect of moisture (always present in the atmosphere) is a far-reaching one. In order fully to understand its effect, it is necessary to consider the action of water on oils and fats.

At temperatures up to about 150° water does not attack glycerides, but if the temperature be raised to 200° or more, the triglycerides are finally decomposed (hydrolysed) into their proximate components, glycerol and fatty acids, whilst the elements of water are assimilated. This action appears to have been observed first by Appert in 1823.

The hydrolysis thus produced at high temperatures is greatly accelerated if the action of the water is assisted by suitable chemical agents (catalysts). If such agents are present, it is possible to reduce the temperature. Thus, by the assistance of concentrated sulphuric acid, the chemical change may be effected at a temperature of about 120°. The temperature required for the chemical change may be further reduced to about 100° by employing strong hydrochloric acid. A still further reduction of temperature can be effected by the introduction of strong bases in alcoholic solution (*see Saponification*). Finally, the change may be brought about by water even at the ordinary temperature, if naturally occurring ferments, such as lipase, or steapsin, are intimately intermixed with the oils and fats. Fat-hydrolysing enzymes seem to occur in most, if not in all, oleaginous seeds, and no doubt play an important part in the utilisation of the fatty reserve products stored in the seeds. During the germination of the seeds, hydrolysis takes place, and free fatty acids are liberated; hence, it appears very likely that the presence of small quantities of free fatty acids, which are always found in even the freshest vegetable oils and fats, is due to the slight action of these enzymes on the glycerides stored in the seeds. The absence of suitable conditions in ungerminated seeds would appear to lead to limiting very sensibly the progress of hydrolysis. Such conditions are the presence of sufficient water and of small amounts of a mineral acid (carbonic acid, *v. supra*), or of a strong fatty acid (such as acetic acid). If water acidified with small quantities of such acids be churned up with oils and fats, and suitable enzymes be introduced into the mixture, hydrolysis of the glycerides takes place gradually at first, but rises, at the optimum temperature, to a considerable extent within a comparatively short time (*see Saponification*). Thus the ferment contained in castor seed is capable of effecting practically complete hydrolysis in the course of a few days. Similarly acting ferments, such as 'catalase,' may reasonably be assumed to be contained in commercial animal fats to a smaller or greater extent, according to the care exercised in the separation of the animal tissue from the rendered fat.

Accepting, then, as a fact the occurrence of small quantities of fat-hydrolysing enzymes in those commercial oils and fats which have not been heated to such temperatures that inhibition of the enzymic action must set in, we shall be able to understand those changes which oils and fats undergo on exposure to the atmosphere. As is well known, they acquire thereby a disagreeable smell and an acrid taste; and the presence of free, non-volatile fatty acids, as also of small quantities of volatile acids, can be observed. We comprise these changes under the term 'rancidity,' and we express this by stating that the oils and fats have become 'rancid.'

The effect of light, air, and moisture can now be explained as follows: In the presence of sufficient moisture and acid, enzymes are enabled to accelerate hydrolysis so that a certain proportion of the glycerides may give rise to the production of diglycerides (and monoglycerides) and free fatty acids within a comparatively short time (a few days or a few weeks according to the conditions). Hence the first postulate is that free fatty acids should make their appearance.

It is well known that oils and fats, if kept fully protected from light, air, and moisture, retain indefinitely their state of neutrality, whereas if they are not carefully preserved, moist air easily gains access (as in imperfectly corked bottles, barrels, &c.), and free fatty acids, of the same composition as those which are combined with glycerol in the neutral fat, are produced. The quantity of enzymes in filtered commercial oils and fats being very small, the amount of hydrolysis effected in such oils and fats will be restricted; hence the proportion of free fatty acids in commerical oils and fats does not, as a rule, exceed a few per cent. If, however, oils and fats be allowed to remain in contact with the organic matter from which they have been obtained, such as the marc of fruits (as in the case of olive oil, palm oil, and cocoa-nut oil), or animal tissues (as in the case of 'rough fat,' blubber, fish livers), or casein, &c. (as in the case of butter), the hydrolysis of the glycerides increases somewhat rapidly and may reach very high proportions. Thus the so-called bagasse olive oils (*i.e.* oils expressed from exposed olive marc) contain as much as 70 p.c. of free fatty acids. Palm oil may even undergo complete hydrolysis, and hence be found to consist almost exclusively of fatty acids. In all these cases we can satisfactorily explain the formation of a high proportion of fatty acids by the conjoint action of water and enzymes. It appears, therefore, unnecessary to invoke the action of air and light in order to explain the presence of free fatty acids.

The author, therefore, ascribes the primary cause of rancidity, namely, the formation of free fatty acids, to the action of moisture in the presence of soluble ferments which act as catalysts or accelerators. The occurrence of small quantities of free fatty acids even in refined oils and fats (edible oils and fats), would thus be explained. Yet these oils and fats are by no means rancid. Indeed, the presence of the free fatty acids imparts a slight, not unpleasant, flavour; for it is well known that completely neutral oils and fats have an insipid taste.

Hence, rancidity is not due, as is still widely believed, to the presence of free fatty acids alone; in other words, rancidity must not be considered as coterminous with acidity. The frequent confounding of these two terms is caused by the fact that acid oils and fats are frequently rancid as well. It is only when oxygen and light gain access to the acid fats that the conditions favouring the setting in of rancidity are provided. Rancidity is rather due to the direct oxidation of free fatty acids by the oxygen of the air, assisted and intensified by the exposure to light. Oxygen and light must act simultaneously, either of these agents alone being unable to produce rancidity; hence, the greater the surface offered to the atmosphere, the more rapidly will they be able to exercise their influence.

Oils (liquid fats) turn rancid more readily than solid fats. This agrees with the fact that liquid fats are much more easily hydrolysed in the fermentative process (*see Saponification*) than are solid fats, such as tallow. Whether fats containing glycerides of the lower fatty acids (butter fat, cocoa-nut oil), are more liable to become rancid than the fats containing glycerides of the higher fatty acids (cacao butter, tallow, &c.) has not yet been decided experimentally. It may, however, be taken as a general rule, that the higher the proportion of insoluble saturated fatty acids, and the lower the percentage of unsaturated glycerides in the fat, the less will be its liability to turn rancid. This rule, however, appears to break down in the case of cocoa-nut oil and of Japan wax, which differ greatly in the composition of their constituent glycerides.

Whilst it may then be taken as proven that rancidity is due to the simultaneous action of moisture, oxygen, and light, very little is known as to the actual chemical change which the liberated free fatty acids undergo. The observation that rancid fats contain free fatty acids had been made before 1814, and both steam distillation and extraction with alcohol were proposed for their removal. The opinion has also been frequently expressed that the bodies characteristic of rancid fats are aldehydes (oenanthaldehyde) and similar substances. Hence the usual reagents employed for the detection of aldehydes have been suggested as a chemical mean of differentiating rancid fats from acid fats.

In the present state of our knowledge we are still unable to ascertain rancidity by chemical means alone; nor does there appear to be any need for a chemical test, as we may rely on the taste and smell as the best means of ascertaining whether an oil or fat is rancid or not.

Some isolated observations regarding the chemical changes suffered by rancid fats are given in a table, published by Lewkowitsch (Analyst, 1899, 327).

Action of oxygen. If air, or better still oxygen, be blown through fatty oils at the temperature of boiling water, oxidation takes place. So much heat is thereby evolved that the oxidation process continues without further heating. On this reaction is based the industry of 'blown oils.'

Blown Oils.

The most notable change produced by the action of oxygen is an increase in density (hence they are also termed 'thickened oils'). The oils thus obtained simulate castor oil in their density and viscosity, but differ from it in that they are soluble in light petroleum. Hence, these oils are known in the trade also as 'soluble castor oils.' The similarity to castor oil, as also the high acetyl values of the blown oils, led to the opinion that glycerides of hydroxylated acids are formed, but the fatty acids actually produced differ from the castor oil fatty acids and form a special class of fatty acids, comprised by the author under the term 'oxidised acids.' Fatty oils belonging to the class of semi-drying oils lend themselves specially to the manufacture of 'blown oils.' Thus in commerce there are obtainable: blown maize oil, blown cotton seed oil, blown rape oil, and blown castor oil. The specific gravity of these oils is increased by the formation of oxidised acids and may reach, according to the time of treatment with air, as high values as 0·96 and above. The chemistry of the oxidised oils has been investigated by Lewkowitsch (*see* Chem. Tech. [iii.] 134). Blown oils are also prepared from fish liver and blubber oils, and are used in the leather industries as also in the production of compound lubricating oils. In the case of drying oils the oxidation process proceeds much further, finally yielding jelly-like or even solid elastic masses. Thus linseed oil dries on exposure to the atmosphere in a thin film to an elastic, thin skin. Blown soya bean oil also yields a viscous somewhat elastic mass.

Boiled Oils.

Extensive use is made of this action in the industries of boiled oils, paint oils, and varnishes. The boiled oils were up to a few decades ago prepared exclusively by 'heating' linseed oil, as also other drying oils, with a small quantity of suitable metallic oxides or metallic salts—driers, siccatives (*see* DRIERS and LINSEED OIL)—over free fire to temperatures varying from 210° to 260°.

It had been found that linseed oil, after heating with lead oxide, absorbed oxygen more rapidly than did linseed oil not so prepared, and whereas raw linseed oil requires about 3 days for drying to an elastic skin, the drying process is so much accelerated by the treatment with lead oxide over free fire, that linseed oil so prepared will dry even within 6–8 hours to an elastic skin.

What reaction takes place during the process of boiling is not yet fully known. A slight decomposition of the glycerides undoubtedly occurs, as is proved by the evolution of acroleïn vapours during the boiling; but such decomposition of the linseed oil is very limited, as the 'boiled oil,' like the polymerised linseed oils (lithographic varnish), still yields almost its full amount of glycerol. Moreover, practical experience has proved that boiled oils must be made from glycerides, since 'boiled oils' cannot be obtained from linseed oil fatty acids, or from ethyl esters of the mixed linseed oil fatty acids.

The process of boiling with 'driers' appears to be an empirical way of producing metal salts (lead salts or manganese salts) of the fatty acids of the boiled oils, partial saponification of the glycerides taking place at the high temperature to which the oils were subjected while being 'boiled.' These lead (or manganese) salts of the fatty acids are able to act as oxygen carriers in the process of 'drying,' when the boiled oils are exposed to the atmosphere either in their original state or in admixture with pigments, gum-resins, &c. This would lead to the explanation that the driers act as catalysts, a small quantity only being required to accelerate the oxidation, so that the oils finally yield a skin. These views find support in the modern methods of preparing 'boiled oils.'

Thus at present the bulk of the 'boiled oils' is obtained by heating linseed oil with driers to a temperature of about 150° only. The process is carried out by introducing the oil into a cylindrical vessel provided with a heating coil and agitating gear, so as to produce an intimate intermixture between oil and drier, while they are heated to the desired temperature.

According to the quality and the amount of drier added, and the length of time during which the oil is heated ('boiled'), *pale* or *dark* oils are produced. The former are known in commerce as 'pale-boiled oils,' the latter as 'double-boiled oils.' The temperature can be reduced even to 120° by merely dissolving 'liquid driers' (solutions of lead linoleate, &c., in linseed oil), and assisting the operation, if required, by a current of air.

These boiled oils have the property of absorbing oxygen from the air at a much more rapid rate than does raw linseed oil, and the time required for the formation of a skin is thereby much shortened.

The chemical change which takes place when a vegetable oil 'dries' to a solid elastic skin, is but very imperfectly understood. The final product appears, however, to be the same, whether raw linseed oil be allowed to absorb oxygen from the atmosphere slowly, or whether the 'drying' be accelerated by previously converting the oil into 'boiled' oil, or the raw linseed oil be treated in a current of oxygen or ozone at a somewhat elevated temperature, after having been intermixed with driers. Mulder's opinion, that in the first stage the glyceridic constituent of the oil is oxidised and that the liberated fatty acids take up oxygen and are converted into the anhydride of 'hydroxylinoleic' acid (*i.e.* the anhydride of hydroxylated linseed oil fatty acids), a neutral substance, insoluble in ether, termed by him 'linoxyn,' must be rejected as erroneous, for this view postulates that hydrolysis of the glycerides precedes oxidation. It has been pointed out already that the solid skin is not formed when the mixed fatty acids are exposed to the atmosphere. Moreover, Bauer and Hazura have shown that, at any rate in the first stage of oxidation, the glyceridic constituent of the linseed oil remains intact, and that the oil is converted by exposure in thin layers into a substance simulating in its properties Mulder's 'linoxyn,' but still representing a glyceride. This substance was assumed by Bauer and Hazura to be hydroxylinolein (*i.e.* a mixture of hydroxylinolin and hydroxylinolenin).

Fahrion applied Engler and Weissberg's autoxidation theory to this problem, and in the light of this theory he regards the linseed oil as an 'acceptor,' and the driers, especially lead and manganese, which are readily converted into peroxides, as autoxidisers or catalysers. He further argues that some facts seem to show that the drying process may also be considered as a molecular autoxycatalysis, and that driers can therefore only be looked upon as pseudo-catalysers (pseudo-autoxidisers), they causing the addition of hydroxyl groups, and leading to the formation of a secondary autoxidiser. The latter in its turn would take up oxygen in its molecular form, and become converted into a hydroperoxide of a metal and hydrogen peroxide.

Genthe, in an elaborate physico-chemical study of the drying of linseed oil, has shown by a series of experiments that the drying process would appear to represent a special case of autocatalysis, inasmuch as his results correspond approximately to numbers obtained by means of the equation $dx/dt=k(m+x)\ (a-x)$ (the equation propounded by Ostwald for autocatalytic reactions). The substance which acts as the auto-catalyst could, however, not be isolated, and the assumption is made that it has the character of a peroxide. The so-called 'blown boiled oils' would, therefore, be linseed oils, in which peroxides are pre-formed, and the accelerating action which old oil of turpentine possesses would be due to the high proportion of peroxide it contains. (It must, however, not be overlooked, that the peroxide has not yet been isolated.) The 'driers' would thus have to be considered as pseudo-catalysts, their function being to accelerate the drying process by assisting in the formation of autocatalysers ('peroxides').

Boiled oils are not (yet) oxidised oils, but do become oxidised when exposed to the atmosphere, forming the well-known skin which paints (that is intimate mixtures of boiled oil and pigments) form on the painted objects.

The oxidation of linseed oil can be much accelerated by blowing linseed oil in the same manner as is done in the preparation of blown oils (*see* above). This process is carried out in the manufacture of *linoleum*, when boiled linseed oil is allowed to run over 'scrim' (a light cotton fabric) hanging down from the ceiling of a high building, the temperature of which is kept at about 100° F. A portion of oil solidifies on the fabric; the oil which drains off is again pumped up and allowed to run down until the layers of the semi-solid mass have reached (after several weeks) the thickness of about half an inch. The solidified oil obtained by this method is termed 'scrim oil.'

Another method consists in passing a current of oxygen gas through linseed oil intermixed with a drier and heated by steam in jacketed pans. When the maximum amount of oxygen has been absorbed, the mass forms a thick viscous fluid, which will still flow while hot, but on cooling solidifies to a substance similar to the 'scrim oil.' During the 'blowing' partial hydrolysis and oxidation of the glycerol formed takes place, as notable quantities of acroleïn vapours escape. The semi-solid oil so obtained has not the same elastic properties which the 'scrim oil' possesses. (Both processes were invented by F. Walton, in 1860 and 1863 respectively.) The solid linseed oil is used in the manufacture of linoleum.

In a third process, known as the Taylor-Parnacott method, the linseed oil is thickened at a high temperature in a current of air.

The *non-drying oils* are less readily attacked by oxygen, and solid fats only suffer a change if heated to a high temperature.

Action of ozone.—Ozone has no action on the glycerides of saturated fatty acids. The glycerides of unsaturated fatty acids are, however, easily acted on by ozone, each pair of doubly-linked carbon atoms absorbing 1 molecule of ozone.

According to Harries, 'perozonides' appear to be formed first, which are easily converted into stable ozonides (*see* OLEIC ACID).

Action of hydrogen. Hydrogen gas under ordinary conditions or under pressure, or even if evolved in *statu nascendi*, either electrolytically or by means of sodium amalgam, has no action on the glycerides of higher unsaturated fatty acids.

Sabatier and Senderens, however, furnished by their method of reducing organic substances by means of hydrogen in the presence of finely divided metals, especially of finely divided nickel, an easy means of converting the glycerides of unsaturated fatty acids into practically completely saturated glycerides. Thus whale oil, cotton-seed oil, sesamé oil, &c., can be reduced to hard tallow-like substances which practically absorb no iodine. The same effect can be obtained by using colloidal palladium (Paal and Roth) or simply finely divided palladium. A somewhat considerable number of patents has been taken in this direction, all of them claiming modifications of the fundamental process of Sabatier and Senderens.

Action of chlorine.—Chlorine acts on oils and fats with evolution of hydrochloric acid, glycerides of chlorinated fatty acids being formed. At the same time chloro addition products are obtained. Hitherto it has not been possible to moderate the action of chlorine to such an extent that chloro addition products be obtained exclusively. Attempts are being made at present to find applications for chlorinated oils and fats in the arts.

Action of bromine.—Bromine acts in a manner similar to chlorine, although much less violently, so that it is possible to limit the reaction in the case of unsaturated glycerides so far, that bromo addition products only are obtained. Hence it is possible to obtain on a practical scale brominated oils and fats. Such products are recommended for pharmaceutical purposes. Thus bromine compounds of sesamé oil are sold as 'bromipin.'

Action of iodine. Iodine is only slowly absorbed when mixed with oils or fats, but it does not yield substitution products. The assimilating power of oils or fats for iodine varies with the chemical constitution of their glycerides and also with the temperature, but never reaches that theoretical amount, which is indicated by the iodine value of oils and fats (*see* above). Iodised oils and fats have also been introduced into pharmacy. Thus 'iodipin' is a derivative of sesamé oil, containing about 25 p.c. of iodine.

Complete saturation of the unsaturated glycerides with halogens can be effected in the cold, if an alcoholic solution of iodine and mercuric chloride, or a solution of iodine monochloride or iodine monobromide in glacial acetic acid, is allowed to act on a dilute solution of oils or fats. The glycerides of the unsaturated acids absorb in that case 1 molecule of iodine chloride, or iodine monobromide, for each pair of doubly-linked carbon atoms, with the formation of saturated compounds. On this action is based one of the most important analytical operations practised in the examination of oils and fats, viz. the determination of the iodine value (*v. infra*).

Chloro-iodo, as also iodo-bromo fats and oils prepared by the above-described reaction are being introduced (or attempted to be introduced) into pharmacy.

Action of sulphur chloride.—Sulphur chloride acts energetically on fats. The reaction appears to consist in an absorption of the elements of sulphur chloride, much as iodine chloride is absorbed by the unsaturated carbon atoms (*see* above). The action of sulphur chloride would, therefore, appear to consist in the conversion of unsaturated (fatty acids or their) glycerides into saturated compounds.

In the two tables shown on page 758 a systematic examination made by Lewkowitsch (of the products obtained by the action of sulphur chloride) has been collated in a synoptic manner.

The sulphur chloride reaction finds technical application in the manufacture of rubber substitutes (*see Vulcanised oils*, below).

Action of sulphur.—Sulphur has no chemical action on oils and fats in the cold. At higher temperatures, however, from 120°-160°, all oils (since they contain glycerides of unsaturated fatty acids), notably linseed oil, castor oil, rape oil, cotton-seed oil, and marine animal oils, assimilate sulphur, and it would appear that the sulphur is absorbed much in the same manner as oxygen is absorbed by oils. On cooling, the sulphur does not separate out; on saponifying the sulphurised oils in the cold, sulphurised fatty acids are obtained whilst very little sulphuretted hydrogen is evolved. On heating the sulphurised fatty acids to 130°-200°, however, sulphuretted hydrogen escapes in large quantities, and substitution of hydrogen in the molecule of the fatty substance by sulphur seems to take place. The action of sulphur on oils is made use of in the manufacture of vulcanised oils.

Vulcanised Oils.

Vulcanised oils, 'rubber substitutes,' are prepared by a process simulating the vulcanising of india-rubber, namely, either by treating oils with sulphur at a somewhat elevated temperature (comparable to the 'hot cure' of vulcanising india-rubber), or by treatment with sulphur chloride in the cold (corresponding to the 'cold cure' in the vulcanising of india-rubber). Hence the term 'vulcanised oils' is applied to these products.

According to the process used, the vulcanised oils are differentiated in the trade as 'brown' (black) and 'white substitutes' respectively.

The ‘white substitutes’ contain, therefore, a considerable proportion of chlorine, which is, of course, absent from the ‘brown’ (black) substitutes; thus it is possible easily to distinguish by chemical means between the two classes of rubber substitutes.

The white substitutes form a yellowish, elastic, crumbly substance of oily smell and neutral reaction; the brown (black) substitutes occur in commerce either as sticky lumps or as a coarsely ground powder.

Oils and Fats treated with Sulphur Chloride; 5 grams of Fat, 2 c.c. of Sulphur Chloride, and 2 c.c. of Carbon Disulphide.

A. *Products completely soluble in Carbon disulphide.*

Class of oil	Kind of oil	—
Vegetable fats	Mowrah seed oil	Mass does not thicken
	Palm oil	
	Palm nut oil	
	Cocoa nut oil	
Animal fats .	Lard	
	Butter fat	
	Beef tallow	
	Mutton tallow	

B. *Products not completely soluble in Carbon Disulphide.*

Class of oil	Kind of oil	Solidifies after minutes		Soluble in carbon disulphide
		In the cold	On the water-bath	
				p.c.
Drying oils	Linseed	10	2	14·4
	Tung	1½	—	—
	Hemp seed	11	—	9·2
	Poppy seed	21	—	10·6
Fish oils	Japan fish	9	—	12·4
Liver oils	Cod liver, pure	15	—	4·4
	,, ,, rancid	1½	—	6·4
Blubber oils	Seal	11	—	4·4
	Whale	13	—	3·0
Semi-drying oils	Cotton seed	20	4	24·0
	Sesamé	21	—	18·4
	Colza	23	—	2·8
	Rape	12	2	4·2
	Croton	18	—	25·4
Non-drying oils	Peach	26	—	4·8
	Almond, sweet	27	—	4·0
	Almond, bitter	28	—	3·4
	Arachis	30	—	6·0
	Olive	22	4	4·2
	Castor	½	at once	3·8
	Sheep's foot	36	—	6·0
	Horses' foot	20	—	13·6
	Neat's foot	23	—	9·4
	Lard	10	—	15·0
	Tallow	12	—	29·8

To manufacture the white substitutes a suitable oil, especially rape oil, castor oil, soya bean oil, maize (corn) oil (also sesamé or arachis oil), is dissolved in carbon tetrachloride, in a wooden, earthenware, or enamelled iron vessel. While the oil is agitated, sulphur chloride is run in, the agitation being continued until the mass has solidified. The reaction is accompanied by evolution of hydrogen chloride.

The brown substitutes are manufactured by heating oils with sulphur at 160°. In the United States considerable quantities of brown substitutes are made from maize (corn) oil by heating 50 parts of oil at 240°, and mixing with it about 20 parts of molten sulphur.

Action of nitric acid. Concentrated nitric acid attacks oils and fats, acting on them violently, with copious evolution of red fumes. Hot dilute nitric acid oxidises oils and fats gradually. *Fuming nitric acid*, in presence of concentrated sulphuric acid, reacts with linseed oil and castor oil to form ‘nitrated’ oils, the nature of which has not yet been investigated, although they have found technical application.

Nitrated Oils.

The nitrated oils are viscid liquids, heavier than water; thus the product obtained from linseed oil has the sp.gr. 1·112, that from castor oil 1·127. Nitrated castor oil is insoluble in carbon disulphide. The composition of these substances is not yet known; they contain 4–5 p.c. of nitrogen. Samples examined by the author had high saponification values, varying from 278·5 to 286·5. The most prominent property of these products is that of forming homogeneous compounds with nitro-cellulose. Thus a mixture of 1 part of nitrated castor oil with 9 parts of nitro-cellulose yields a product resembling ebonite. Solutions of these compounds in acetone have been proposed as varnishes, as a basis for paint, and for enamelling leather. By heating ‘nitrated oils’ at 130°, or by oxidising them with lead peroxide, rubber-like substances are obtained.

Action of nitrous acid. On treatment with nitrous acid the non-drying oils become solid, or acquire the consistence of butter, according to the proportion of triolein (trierucin) they contain, triolein (trierucin) being converted into the solid isomeride trielaïdin (tribrassidin). Drying and marine animal oils, on the other hand, remain liquid under the same treatment.

The different behaviour of the drying and marine animal oils is explained by the fact that while ‘oleic’ (erucic) acid is converted by nitrous acid into a solid isomeride, elaïdic (brassidic) acid, linolic, linolenic, and clupanodonic acids remain liquid under the same conditions. Hence the non-drying oils yield solid masses, whereas the semi-drying and the drying and marine animal oils give more or less liquid products, according to the predominance of the glycerides of oleic acid. The fact that fuming nitric acid has the property of thickening olive and almond oils appears to have been observed first by Boyle in 1661. Poutet, in 1819, proposed this reaction, known as the *elaïdin* test, for the detection of adulterants in olive oil. The test is carried out in the following manner (viz. in the modification suggested by Archbutt); 18 grams of mercury are placed in a dry stoppered 50-c.c. cylinder, and 15·6 c.c. of nitric acid, sp.gr. 1·42, are added from a burette. The nitrous acid is entirely absorbed with production of a green colouration; as long as the reagent retains its green colour, it is fit for use. Eight grams of the reagent are shaken up with 96 grams of the oil in a wide-mouthed stoppered-bottle, placed in water at the required temperature, and again shaken at intervals of 10 minutes during 2 hours.

In the early history of oil analysis, before the present scientific (quantitative) methods (*v. infra*) were known, this test afforded some guidance. It was even attempted to base a classification of the oils on it, but such a classification must lead to inconclusive results. Although this test was somewhat extensively practised here as also in France, it may be said to have been abandoned in *this* country, as the results indicated by the elaïdin test are in every respect much less valuable than those furnished by the iodine test. Nevertheless, the elaïdin test is still being used, notably in France, in the examination of olive oils. In the comparative examination of almond oil and its congeners this test may afford some little information of a discriminative nature. In order to obtain trustworthy results, it is indispensable to institute side by side with the oil under examination, under exactly the same conditions, tests with standard oils of known purity.

Action of concentrated sulphuric acid. If oils, which, of course, contain glycerides of unsaturated fatty acids, be mixed with the acid very gradually, and at a low temperature, glycerides of a complex constitution are formed. The formation of these products is indicated by a notable rise of temperature. (The antiquated 'Maumené test' is based on the measurement of the rise of temperature (*see* Lewkowitsch, Chem. Techn. of Oils, &c. [i.] 384).) Thus, on treating olive oil with concentrated sulphuric acid a compound was obtained which may be regarded (Geitel) as a mixed glyceride of oleic acid, stearic acid, hydrogen sulphate, and hydroxystearic acid, having the formula—

$$C_3H_5[O{\cdot}C_{18}H_{33}O][O{\cdot}C_{18}H_{34}(SO_4H)O][O{\cdot}C_{18}H_{34}(OH)O].$$

This product is very unstable in the presence of water. On boiling with water it is rapidly decomposed into compounds which form a complete emulsion with water and fats; on agitating the emulsion with steam, complete hydrolysis to glycerol and fatty acids is brought about (*see Saponification*). This reaction is employed on a large scale in the manufacture of Turkey-red oils.

Turkey-red Oil.

Turkey-red oil is a fatty substance used in the preparation of the cotton fibre for dyeing and printing Turkey-red. The part which the Turkey-red oil plays is not fully understood; opinions differ as to whether it exercises a physical or a chemical action. The advocates of the former explanation assume that the oil protects the lake formed on the fibre, much as boiled linseed oil serves to protect a painted surface. The supporters of the chemical theory hold that the Turkey-red oil combines with alumina and finally with the colouring matter to form a compound lake. In those cases, however, where chemical combination with formation of a lake is excluded on account of the chemical constitution of the colouring matter, the physical theory appears to commend itself. Hence Turkey-red oil is not a mordant proper, but acts as a fixing agent in so far as it imparts to the dyed fabric a better and superior lustre, which does not belong to the unoiled fibre. The sulphonated oils would appear to the author to be absorbed by the fibre in the same manner as glycerol (from soft soaps) is fixed on the fibre on washing woollen goods.

Before the process of sulphonating castor oil was discovered (1875), rancid olive oil and sulphonated oils (such as sulphonated olive oil) were used as Turkey-red oils. At present Turkey-red oil is prepared by allowing concentrated sulphuric acid to run slowly into castor oil, with constant stirring, taking care that the temperature of 35° is not exceeded. If necessary, the mass must be cooled, for secondary reactions take place at temperatures above 35° with liberation of sulphurous acid. The product is then mixed with a small quantity of water and the dilute acid allowed to settle out as a lower layer. This is drawn off and the oil washed with a solution of Glauber's salt, until the washings are only slightly acid. Finally ammonia is added, until a sample gives a clear solution with a small quantity of water. Some manufacturers use soda instead of ammonia, or a mixture of ammonia and soda. Since the sulphonated oil is not completely neutralised by alkali, the resultant product still possesses a strong acid reaction.

The portion of sulphonated castor oil soluble in water contains principally ricinoleo-sulphuric acid, which is easily hydrolysed to some extent by boiling with dilute acids into sulphuric acid and ricinoleic acid, whereas another portion is converted into inner anhydrides of ricinoleic acid. The portion of castor Turkey-red oil insoluble in water consists chiefly of free ricinoleic acid and small quantities of neutral (unacted-on) oil, and also of anhydrides of ricinoleic acid (*cf.* also Lewkowitsch, Chem. Tech. [iii.] 155 *et seq.*).

At a temperature exceeding 100° *concentrated sulphuric acid* reacts energetically with all oils and fats, partly carbonising them and hydrolysing them, whereby glycerol and sulpho compounds of fatty acids are formed. On steaming, the latter are decomposed into sulphuric acid and fatty acids. On this reaction is based the 'acid saponification' process employed in the candle industry (*see* SAPONIFICATION).

Dilute sulphuric acid, even at temperatures of 100°, does not act on oils and fats (Lewkowitsch).

A dilute solution of sulpho-aromatic compounds (Twitchell's reagent) readily effects hydrolysis of the glycerides (*see* SAPONIFICATION).

Action of hydrochloric acid. Hydrochloric acid exercises a very slow action at the ordinary temperature; at higher temperatures it behaves as a catalytic agent, and accelerates considerably the hydrolysis of oils and fats. Obviously, hydrochloric acid does not take part in the chemical change, but merely accelerates the hydrolysis primarily brought about by water (Lewkowitsch, J. Soc. Chem. Ind. 1903, 67). If a thorough intermixture as in an emulsion could be effected between fat and water, hydrolysis would proceed much more rapidly than was observed in Lewkowitsch's experiments, for it has been shown by him experimentally that the catalytic action of hydrochloric acid takes place even at the ordinary temperature in course of time.

Action of caustic alkalis and alkaline earths. Caustic alkalis and alkaline earths, if treated with oils and fats in the presence of water, act in the first instance as catalysts bringing about rapid hydrolysis of the oils and fats. The free fatty acids formed combine with the caustic alkalis and alkaline earths, yielding as a secondary product soaps of the alkaline metals and the alkaline earths. On this reaction are based the great industries of soap- and candle-making (*see* SAPONIFICATION and SOAP).

Action of ammonia and aromatic bases. Ammonia hydrolyses oils and fats to some extent if acting under pressure (*see* SAPONIFICATION). Alcoholic ammonia, on prolonged standing in the cold with oils and fats, yields amides.

Aromatic bases, such as aniline, &c., on being heated under pressure at 210°, react similarly with oils and fats. In the case of aniline, the reaction was stated to take place according to the following equation—

$$C_3H_5(OR)_3+3C_6H_5{\cdot}NH_2=C_3H_5(OH)_3+3C_6H_5{\cdot}NHR.$$

But it has been shown that this reaction is unworkable on a practical scale.

In the case of hydroxylamine, hydroxamic derivatives of fatty acids are obtained, together with glycerol, as is exemplified by the following equation—

$$C_3H_5(OR)_3+3NH_2OH=C_3H_5(OH)_3+3R(NOH)OH.$$

SYSTEMATIC EXAMINATION OF OILS AND FATS.

The simplest problem in the examination of oils and fats is to identify a given oil or fat. As the natural oils and fats represent a complicated mixture of not only simple triglycerides, but also of mixed triglycerides, it is impossible, in the present state of our knowledge, to indicate a definite course of analysis, applicable to all circumstances, such as is the case in inorganic quantitative and qualitative analysis. Yet, by adopting a systematic plan of examination, it is possible, in the majority of cases, to identify a given sample of one individual oil or fat and to ascertain whether it is a pure or adulterated specimen. In the latter case, the nature of the adulterant can generally be ascertained. The methods described below permit also to identify a mixture of two or more oils and fats and to ascertain the presence and recognise the nature of the constituents of the mixture, at least qualitatively. Frequently, it is even possible to determine quantitatively the proportion in which the component parts have been mixed. The greater the number of component oils and fats in a mixture, the more difficult becomes the examination, but if the analyst proceeds logically and combines the methods described below in a suitable manner, it will be possible in many cases to ascertain the composition of a complicated mixture with such accuracy as suffices for technical purposes.

If it be borne in mind that adulteration has almost become a fine art, and that it is being practised with the full armour of scientific knowledge by experts who are frequently some years ahead of the knowledge possessed by the analytical chemist, it will readily be understood that the analyst must select special methods and tests and adapt them to each case.

A systematic examination will deal, in the first instance, with the natural oils and fats themselves. The methods applied to this purpose may be broadly divided into physical and chemical methods.

Since all natural oils and fats contain as a common constituent the radicle glycerol, or in other words, since all oils and fats yield glycerol on saponification, the difference of the several glycerides can only be conditioned by, or due to, the difference of the fatty acids contained in the glycerides. Hence it follows that in the second place the examination of the fatty acids themselves will prove of great importance. A section is, therefore, devoted specially to the *examination of the fatty acids.*

The identification of an oil or fat as a *vegetable* or *animal* oil or fat rests, as explained above, on the occurrence of phytosterol or cholesterol in vegetable or animal oils respectively. Hence the examination of the 'unsaponifiable' furnishes an excellent means to differentiate between vegetable and animal oils. From this point of view alone, the examination of the unsaponifiable matter becomes a valuable aid in the systematic course of examination. Obviously, if a mixture of vegetable and animal oils be given, a mixture of phytosterol and cholesterol will be obtained, the resolution of which into its components may be required in many cases. The examination of the 'unsaponifiable' becomes, furthermore, most important in those cases in which adulteration has taken place with unsaponifiable oils.

One of the most important problems required to be solved by analysis is to ascertain whether a sample is pure or sophisticated with hydrocarbons. Thus the examination of the unsaponifiable matter, provided it exceed 1 or at most 2 p.c. of an oil or fat, furnishes an important clue as to adulteration. It will, therefore, be most convenient to subdivide this section under the following three heads :—

I. Examination of Oils and Fats.
II. Examination of Fatty Acids.
III. Examination of the Unsaponifiable Matter.

Correct interpretation of indications afforded by the following tests and strict logical reasoning enable us, in the majority of cases, to narrow down, by a process of elimination, the range of possible constituents of a mixture to such an extent that the practised analyst will but rarely be confronted with the impossibility of arriving at approximate accuracy at least. In order to facilitate the interpretation of the results obtained with the aid of the following methods, the characteristic values of the most important oils and fats are arranged in a practically natural system in the tables collated at the end of this article. With the aid of these tables, it will not be difficult to identify a single individual. If, in the course of a commercial analysis, the limits of our present knowledge have been reached, the application of methods that have not yet been used for the case under consideration will suggest itself. This happens not infrequently in the examination of technical products.

For a number of examples, giving a clue as to how complicated mixtures may be examined, the reader is referred to Lewkowitsch's Chem. Techn. [i.] 509.

I. Examination of Oils and Fats.

The methods described under this head may be broadly divided into physical and chemical methods. With the physical methods may be incorporated suitably the so-called organoleptic methods, comprising odour, taste, colour, and consistence.

Examination by physical methods.

Odour and *taste* are especially characteristic of the oils of marine animals. In the case of solid fats, the *red colour* indicates preliminarily raw palm oil. The *consistence* at ordinary temperature gives a rapid indication as to whether the specimen belongs to oils or fats. In most cases, however, these organoleptic methods afford some help to the expert only. In the case of edible oils and fats, odour and taste must be considered as very important criteria, as rancidity is most readily recognised by taste and by taste alone, the chemical methods recommended by some writers for this purpose being superfluous. The following physical methods are of importance :—

Specific gravity. The specific gravity of the liquid oils is best determined by means of a pyknometer or a hydrostatic balance. In the case of solid fats, the specific gravity is most readily taken at a temperature at which the fat is liquid. Suitable temperatures are 40° in the case of fats liquid at that temperature. In other cases, the temperature of boiling water is usually resorted to. In the tables given at the end of this article, the specific gravities have been added. Speaking generally, it may be stated that the specific gravity number does not afford such important information as has been allotted to it at a time before the quantitative methods have been worked out. Still, castor oil would be recognised at once by its exceptionally high specific gravity.

Melting and solidifying points. Fats do not melt so sharply as is the case with chemically pure substances. Hence fats, if examined in a capillary tube, melt within several degrees, the fats softening at first, then melting at the edge of the substance, becoming transparent at the same time until they are melted completely. Therefore, some uncertainty obtains as to which temperature should be regarded as the melting-point. Some observers denote as melting-point that temperature, at which the fat which has been allowed to solidify in a small tube open at both ends, softens sufficiently to be driven up by the hydrostatic pressure of water. Others again denote that temperature as the melting-point at which the fat drops off the mercury bulb of a thermometer, which has previously been dipped into the melted fat and allowed to cool. Hence, it is imperatively necessary to state in each case by what method the melting-point has been determined. It is, therefore, customary in commerce to agree between buyer and seller as to the method. It is important to note that the freshly melted sample does not indicate the true melting-point, which is only ascertainable after the sample has been kept for 24 hours. In the case of cacao butter, even an interval of two or more days is required. The melting-points of most fats are given in the tables at the end of this article. It may be pointed out that, as a rule, it is preferable to determine the solidifying point of the *fatty acids* prepared from the oils and fats (*v. infra*).

Refractive index.—The determination of the refractive index—which can be carried out in a very simple and rapid manner, thanks to the construction of the oleorefractometer by Amagat and Jean, and especially that of the butyrorefractometer by Zeiss—forms one of the simplest preliminary tests in the examination of oils and fats, and especially in the examination of butterfat and lard. Owing to the ease and rapidity with which this 'characteristic' can be determined, the previously raised objections against observations with the aid of an ordinary refractometer have given place to a widely held over-estimation of the importance of this test. The observer should, therefore, be warned against placing too much importance on the indications of the refractometer and, as stated already, should only consider it as a preliminary test, the indications of which must be supported and corroborated by other methods (*cp.* Lewkowitsch, Chem. Tech. [i.] 245, 247 ; [ii.] 682).

Thus, in the case of butterfat, a glance at a sample in the refractometer may decide whether the specimen is grossly adulterated or not. But if the number be only slightly abnormal, or even if so-called 'normal numbers' have been found, the purity of the specimen is not yet proven, as it is easy, *e.g.*, to prepare specimens of margarine containing cocoa-nut oil which show the same refraction as a normal butter fat. Even if abnormal numbers have been obtained, this would not prove adulteration. It would be entirely erroneous to look upon the refractometric method as permitting the identification of an oil or fat. Equally erroneous would be the attempt to deduce quantitative interpretations as to the proportions of an adulterant from the deviation from normal numbers. The refractive indices of most oils are contained in the tables at the end of this article. By comparing these numbers with the iodine values, it will be gathered that there is a certain, although by no means definite, correlation between the refractive indices and the iodine values. For the description of refractometers, see Lewkowitsch, Chem. Techn. [i.] 247, and art. REFRACTOMETER.

Rotatory power. The determination of the rotatory power has not been practised extensively in the examination of oils and fats for the reasons stated above. Since, however, oils belonging to the 'Chaulmoogra group' can be identified readily —and indeed have been the means of identifying the 'Cardamom oil'—(see CHAULMOOGRA OIL GROUP) the polarimetric method is destined to find a wider application.

Solubility test. Almost all oils and fats are easily soluble in the usual organic solvents, hence the solubility test has little importance. Only castor oil is distinguished from all other natural oils and fats by its ready solubility in alcohol.

Examination by Chemical Methods.

The most important chemical methods employed in the examination of oils and fats have for their object the determination of certain numerical values which depend on the nature of the fatty acids occurring in the oils and fats.

These numbers represent only a measure of the amounts of the several fatty acids or fatty acid groups present in the oils and fats, without, however, expressing their absolute quantity. Hence these methods have been suitably termed 'quantitative reactions.' In addition to these quantitative reactions there are also at the disposal of the analyst a number of 'qualitative reactions.'

(a) *Quantitative Methods.*

The numerical values which are ascertained by means of quantitative methods are divided by the author into two classes.

(*a*) 'Characteristics,' *i.e.* those numbers which depend entirely on the specific nature of an oil or fat and hence assist most materially in identifying a given oil or fat.

(*b*) 'Variables,' *i.e.* those numbers which allow us to judge of the quality of a given oil or fat. These numbers naturally vary with the state of purity, rancidity, age, etc., of a given specimen.

The *characteristics* will be considered under the following heads.

(1) Saponification Value.
(2) Iodine Value.
(3) Reichert (Reichert-Meissl or Reichert-Wollny) Value.

The *variables* will comprise :—

(1) Acid Value.
(2) Amount of Glycerol, expressed in per cent.
(3) Amount of Unsaponifiable Matter, expressed in per cent.

Midway between these two classes stands the 'acetyl value' which, in some cases, must be considered a 'characteristic,' whereas in other cases it is a 'variable.'

(A) **Characteristics.**

1. *Saponification Value.*

The saponification value indicates the number of milligrams of potassium hydroxide required for the complete saponification of one gram of an oil or fat; in other words, it represents the amount of potassium hydroxide, expressed in tenths per cent., requisite to neutralise the total fatty acids in one gram of an oil or fat.

The saponification value is determined as follows :—Weigh off accurately, in a flask holding 150–200 c.c., 1·5 to 2 grams of the purified and filtered sample. Next run into the flask 25 c.c. of an approximately semi-normal alcoholic solution of caustic potash, measuring it off by means of a pipette. It is not necessary to add exactly 25 c.c., but care must be taken that for each determination precisely the same volume is used. Then attach a long cooling tube or an inverted condenser to the flask, and heat on the boiling water-bath for half an hour so that the alcohol is kept simmering; in order to accelerate saponification, the contents should be mixed by imparting to the flask a rotary motion. When the saponification is deemed to be complete, allow to cool a little, add 1 c.c. of a 1 p.c. phenolphthalein solution and titrate back the excess of potash with semi-normal hydrochloric acid. In case too much alcohol has been volatilised, it is advisable to add some alcohol (previously neutralised) or to add normal acid at first and to complete the titration with semi-normal acid.

It is necessary to make a blank test by treating the same amount of alcoholic potash in exactly the same manner as is done with the sample.

Example.—Weighed off 1·532 grams of olive oil, and saponified with 25 c.c. of alcoholic potash solution. Required for titrating back, 12·0 c.c. semi-normal acid; further, required for the blank test, 22·5 c.c. of the same acid. Therefore a quantity of caustic potash, corresponding to $\frac{(22{\cdot}5-12{\cdot}0)0{\cdot}0561}{2}$ grams = 294·5 milligrams KOH was employed for saponification. Hence, used for 1 gram of fat $\frac{294{\cdot}5}{1{\cdot}532}$ milligrams KOH = 192·2 milligrams KOH. The saponification value of the sample of olive oil is, therefore, 192·2.

The saponification values of neutral glycerides (esters of fatty acids) vary, of course, with the nature of the fatty acids; the lower the molecular weight of the fatty acids (or, what amounts to the same, of the esters), the more potash will be required to neutralise the fatty acids of 1 gram of oil or fat, or, in other words, the higher will be the saponification value. To illustrate this more clearly, the saponification values of some pure triglycerides are subjoined in the table on next page.

It will be gathered from the numbers given in the tables at the end of this article that the saponification values of the majority of natural oils and fats lie in the neighbourhood of 193 to 195. In the case of unknown samples, wide deviations from this number in either direction will at once enable the analyst to single out individual oils or fats. Thus, oils belonging to the rape oil group are characterised by a considerably lower saponification value, viz. about 175. The lower saponification values of these oils find their explanation in the large proportion of erucin they contain. In the case of castor oil, the lower value is due to the presence of hydroxylated fatty acids.

On the other hand, large deviations in the opposite direction enable us to single out a number of oils and fats and hence render their recognition a comparatively easy task. Thus the high saponification value of the fluid portion of dolphin and porpoise oils are indicative of a high proportion of lower fatty acids. A prominent example of a fat having a characteristically high saponification value is butter fat; hence by the saponification value alone, butter fat can be differentiated from margarine. High saponification values are also characteristic of fats consisting preponderantly of glycerides of myristic acid, and especially of the members of the cocoa-nut oil and dika fat groups.

If mineral oils or other unsaponifiable substances are intermixed with the fatty substances, then, naturally, the indications furnished by the saponification values alone, if accepted without any further investigation, would be entirely misleading, since the unsaponifiable matter depresses the saponification value. Thus, to take an example, an oil having the saponification value 193, if adulterated with 10 p.c. of mineral oil, would show a saponification value of about

SAPONIFICATION VALUES OF TRIGLYCERIDES.

Triglycerides	Formula	Molecular weight	Saponification value
Simple Triglycerides—			
Acetin	$C_3H_5(O{\cdot}C_2H_3O)_3$	218	772·0
Butyrin	$C_3H_5(O{\cdot}C_4H_7O)_3$	302	557·3
Valerin	$C_3H_5(O{\cdot}C_5H_9O)_3$	344	489·2
Caproin	$C_3H_5(O{\cdot}C_6H_{11}O)_3$	386	436·1
Caprylin	$C_3H_5(O{\cdot}C_8H_{15}O)_3$	470	358·1
Caprin	$C_3H_5(O{\cdot}C_{10}H_{19}O)_3$	554	303·7
Laurin	$C_3H_5(O{\cdot}C_{12}H_{23}O)_3$	638	263·8
Myristin	$C_3H_5(O{\cdot}C_{14}H_{27}O)_3$	722	233·1
Palmitin	$C_3H_5(O{\cdot}C_{16}H_{31}O)_3$	806	208·8
Stearin	$C_3H_5(O{\cdot}C_{18}H_{35}O)_3$	890	189·1
Olein	$C_3H_5(O{\cdot}C_{18}H_{33}O)_3$	884	190·4
Linolin	$C_3H_5(O{\cdot}C_{18}H_{31}O)_3$	878	191·7
Hydnocarpin	$C_3H_5(O{\cdot}C_{16}H_{27}O)_3$	794	211·9
Chaulmoogrin	$C_3H_5(O{\cdot}C_{18}H_{31}O)_3$	878	191·7
Linolenin	$C_3H_5(O{\cdot}C_{18}H_{29}O)_3$	872	193·0
Clupanodonin	$C_3H_5(O{\cdot}C_{18}H_{27}O)_3$	866	194·3
Ricinolein	$C_3H_5(O{\cdot}C_{18}H_{33}O_2)_3$	932	180·6
Arachin	$C_3H_5(O{\cdot}C_{20}H_{39}O)_3$	974	172·7
Erucin	$C_3H_5(O{\cdot}C_{22}H_{41}O)_3$	1052	160·0
Cerotin	$C_3H_5(O{\cdot}C_{26}H_{51}O)_3$	1226	137·3
Melissin	$C_3H_5(O{\cdot}C_{30}H_{59}O)_3$	1394	120·7
Mixed Triglycerides—			
Oleodipalmitin (Dipalmitoölein)	$C_3H_5(O{\cdot}C_{16}H_{31}O)_2(O{\cdot}C_{18}H_{33}O)$	832	202·3
Stearodipalmitin (Dipalmitostearin)	$C_3H_5(O{\cdot}C_{16}H_{31}O)_2(O{\cdot}C_{18}H_{35}O)$	834	201·8
Oleopalmitostearin (Stearopalmitoölein)	$C_3H_5(O{\cdot}C_{16}H_{31}O)(O{\cdot}C_{18}H_{33}O)(O{\cdot}C_{18}H_{35}O)$	860	195·7
Palmitodistearin (Distearopalmitin)	$C_3H_5(O{\cdot}C_{18}H_{35}O)_2(O{\cdot}C_{16}H_{31}O)$	862	195·2
Oleodistearin	$C_3H_5(O{\cdot}C_{18}H_{33}O)(O{\cdot}C_{18}H_{35}O)_2$	888	189·5
Dioleostearin	$C_3H_5(O{\cdot}C_{18}H_{33}O)_2(O{\cdot}C_{18}H_{35}O)$	886	189·9

175, and might, therefore, be mistaken for a rape oil if no further tests were applied.

If colophony (rosin) be dissolved in the fatty substance, the saponification value will remain unaffected, provided rosin of about the same saponification value be used. With a rosin of a lower saponification value than that of the oil or fat, the saponification value of the mixture would, of course, be somewhat depressed.

2. *Iodine Value.*

The iodine value indicates the percentage of iodine chloride absorbed by an oil or fat, expressed in terms of iodine. Theoretically, the acids belonging to the oleic and ricinoleic series should absorb two atoms of chlorine or iodine, or one molecule of iodochloride. Hence the glycerides of these acids should absorb six atoms of chlorine or iodine, or three molecules of iodochloride. Similarly, the acids of the linolic series should assimilate four atoms of halogens or two molecules of iodochloride; whereas the members of the chaulmoogric series would assimilate only two atoms of halogens or one molecule of iodochloride, on account of the cyclic arrangement of some carbon atoms; the members of the linolenic series six atoms of halogens or three molecules of iodochloride, and the members of the clupanodonic series eight atoms of halogens or four molecules of iodochloride.

These rules apply, however, only to doubly-linked carbon atoms. Trebly-linked pairs of carbon atoms, the occurrence of which in fatty acids (and hence in natural oils and fats) has not yet been definitely ascertained, do not absorb the theoretical amount of halogens.

The determination of the iodine value has been introduced into fat analysis by von Huebl and is carried out either in the manner indicated originally by Huebl or in the modification proposed by Wijs. The author's experience leads him to recommend the latter modification as more convenient and reliable. Since, however, Wijs' method has not yet been accepted as generally as it deserves, both methods will be described here.

Huebl's method.—From 0·15–0·18 gram of a drying or a marine animal oil, 0·2–0·3 gram of a semi-drying oil, 0·3–0·4 gram of a non-drying oil, or 0·8–1·0 gram of a solid fat, are weighed off accurately, and placed in a bottle of 500–800 c.c. capacity provided with a well-ground stopper. The weighing off is best done in a small weighing bottle, the cork of which is fitted with a finely drawn out tube so that a certain number of drops of an oil or of a previously melted fat can be easily taken out with the aid of an india-rubber tube fixed on the top. The fat is dissolved in 10 c.c. of chloroform, or carbon tetrachloride, and 25 c.c. of an 'iodine solution' are run in from a pipette. (This iodine solution is prepared by dissolving 25 grams of pure iodine on the one hand, and 30 grams of mercuric chloride on the other hand, in 500 c.c. of 95 p.c. of alcohol. Both solutions are kept separate and the quantity required for an experiment must have been prepared 24 hours before by mixing equal volumes of the two solutions. The mixture must not be used immediately after preparation, since the solution of iodochloride rapidly changes its titre after preparation. Although even after 24 hours' standing, the mixture still slowly changes its titre, it remains sufficiently constant during an experiment.) The pipette is always emptied in the same manner: this is best done by allowing it to drain until two or three drops have run out. In order to prevent loss of iodine by volatilisation, it is advisable to moisten the stopper with potassium iodide solution. The solvent and the iodine solution should give a clear solution on shaking, otherwise more solvent must be added. The bottle is then allowed to stand in a dark place. Should the deep brown colour of the solution disappear after a short time, another 25 c.c. of the iodine solution must be run in, an excess of iodine being essential for the reaction to become complete. The solution, after two hours, must still exhibit a deep brown colour. Most of the iodine is absorbed during the first two hours. The reaction then slows down; it cannot be considered complete in less than six to eight hours in the case of solid fats and non-drying oils, and twelve to eighteen hours in the case of drying oils and fish oils. Semi-drying oils require 8 to 10 hours. After standing for the requisite number of hours, from 15 to 20 c.c. of a 10 p.c. potassium iodide solution are run in, the liquid is well shaken and then diluted with 400 c.c. of water. The appearance of a red precipitate of mercuric iodide at this stage would indicate that an insufficient amount of potassium iodide had been employed, therefore more must be added. The excess of free iodine, part of which will be in the aqueous solution, whereas the remainder is dissolved in the solvent, is titrated with a standardised thiosulphate solution by running the latter into the bottle until, after repeated agitation, both the aqueous and the chloroform (carbon tetrachloride) layers are but faintly coloured. A few drops of a starch solution are next added and the titration is then brought to an end. Immediately before or after this titration, 25 c.c. of the original iodine solution are standardised in exactly the same manner. The difference between the two results corresponds to absorbed halogen, and is calculated in terms of iodine to units per cent. of the sample. The number thus found is termed the iodine value.

Example.—Weighed off 0·3394 gram of lard, dissolved in 10 c.c. of carbon tetrachloride, added 25 c.c. of iodine solution, which required in a blank experiment 60·9 c.c. of thiosulphate solution, 16·45 c.c. of which were equivalent to 0·2 gram of iodine. For titrating back the excess of iodine in the experiment, there were required 39·6 c.c. of thiosulphate solution. Hence, the absorbed iodine corresponds to 60·9–39·6=21·3 c.c. of thiosulphate solution.

Since 16·45 c.c. of thiosulphate solution are equivalent to 0·2 gram of iodine, 21·3 c.c. correspond to $\frac{0{\cdot}2\times 21{\cdot}3}{16{\cdot}45}=0{\cdot}2589$ gram of iodine. Hence 0·3394 gram of lard absorb 0·2589 gram of iodine, or 100 grams absorb $\frac{0{\cdot}2589\times 100}{0{\cdot}3394}=76{\cdot}28$ grams of iodine. The iodine value of the lard is, therefore, 76·28.

(With regard to the theory of the complicated chemical reactions occurring in Huebl's solution, *v.* Lewkowitsch, Chem. Techn. [i.] 316.)

Wijs' method. The solution required for Wijs' method is prepared by dissolving separately 7·9 grams (the theoretical figure is 7·9617) of iodine trichloride and 8·7 grams (the theoretical figure is 8·6670) of iodine in glacial acetic acid on the water-bath, taking care that the solutions do not absorb moisture. The two solutions are then poured into a 1000 c.c. flask, and the flask is filled up to the mark with glacial acetic acid.

A cheaper way of preparing the solution is to dissolve 13 grams of iodine in a litre of glacial acetic acid, then to determine accurately its content of iodine, and to pass washed and dried chlorine gas through the solution until the titre of the original iodine solution is doubled. A little experience will readily show when this point is reached, as a very distinct change of colour takes place when all the iodine has been converted into iodine monochloride.

The glacial acetic acid must be pure, and should be tested by heating with potassium dichromate and concentrated sulphuric acid; even after prolonged standing a green tinge should not be noticeable.

The iodine value is determined in exactly the same manner as described above for the Huebl solution. It is, however, preferable to use carbon tetrachloride since chloroform frequently contains alcohol. Wijs' iodine solution can be used immediately after preparation and possesses the great advantage over Huebl's solution in that it keeps its strength unchanged for a considerable length of time. Hence, in ordinary work, a blank test is not required in each case, and the determination of the iodine value can be carried out almost as rapidly as the determination of the saponification value. Wijs' solution has the further advantage that in the case of fats and non-drying oils the absorption of iodochloride is complete after half an hour, in the case of semi-drying oils after about 1 hour, and in the case of drying oils and marine animal oils in from 2 to 6 hours, according to the unsaturation of the glycerides.

The iodine value is one of the most important characteristics in the analysis of oils and fats, as this number permits us to classify the oils and fats in a practically natural system. This will be gathered from an inspection of the tables given at the end of this article.

If a given sample of oil or fat contains the glycerides of one unsaturated fatty acid of known composition in admixture with glycerides of saturated fatty acids, it is possible to calculate the absolute amount of the glyceride of that unsaturated fatty acid. In cases of this kind, the following table will be found useful. It will also guide the analyst as to the direction which further research should take in the case of samples of unknown composition, when, of course, the proportion of glycerides of unsaturated fatty acids cannot be calculated from the iodine value alone.

IODINE VALUES OF UNSATURATED FATTY ACIDS AND OF THEIR TRIGLYCERIDES (Lewkowitsch).

Acid.	Formula.	Iodine value of	
		Fatty acid.	Triglyceride.
Tiglic	$C_5H_8O_2$ $C_{12}H_{22}O_2$ $C_{14}H_{26}O_2$	254·00 128·28 112·39	225·44 120·57 106·42
Hypogaeic Physetoleic	$C_{16}H_{30}O_2$	100·00	95·25
Hydnocarpic	$C_{16}H_{28}O_2$	100·79	95·97
Oleic Rapic	$C_{18}H_{34}O_2$	90·07	86·20
Erucic	$C_{22}H_{42}O_2$	75·15	72·43
Linolic Tariric	$C_{18}H_{32}O_2$	181·42	173·58
Chaulmoogric	$C_{18}H_{32}O_2$	90·71	86·79
Linolenic *iso*Linolenic	$C_{18}H_{30}O_2$	274·10	262·15
Clupanodonic	$C_{18}H_{28}O_2$	368·11	351·96
Ricinoleic	$C_{18}H_{34}O_3$	85·23	81·76
Mixed Triglycerides—			
Myristopalmitoölein	—	—	31·59
Oleodipalmitin	—	—	30·53
Oleopalmitostearin	—	—	29·53
Oleodistearin	—	—	28·60
Dioleostearin	—	—	58·00

3. *Reichert* (*Reichert-Meissl, Reichert-Wollny*) *Value.*

The Reichert (or Reichert-Meissl) value indicates the number of cubic centimetres of decinormal potash or soda solution requisite for the neutralisation of that portion of the soluble volatile fatty acids which is obtained from 2·5 (or 5) grams of an oil or fat by the Reichert distillation process.

Reichert, who originated this method, used 2·5 grams of fat. Meissl, as also Wollny, proposed 5 grams, which is now generally employed. It must, however, be pointed out that the Reichert-Wollny value is not twice the Reichert value, but mostly 2·2 of the Reichert value. Since Wollny's process has been adopted by a Joint Committee of the Government Laboratory and the Society of Public Analysts as the standard method for the determination of the soluble volatile fatty acids in margarine and butter the Reichert-Wollny process alone will be described.

Reichert-Wollny process. Five grams of liquefied fat are introduced into a 300 c.c. flask, of the form shown in Fig. 3 (length of neck 7–8 cms., width of neck 2 cms.). Two c.c. of a caustic soda solution, prepared by dissolving 98 p.c. sodium hydroxide in an equal weight of water—protected from the action of atmospheric carbon acid—and 10 c.c. of (about 99 p.c.) alcohol are added, and the mixture is heated for 15 minutes under a reflux condenser, connected with the flask by a **T**-piece, in a bath containing boiling water. The alcohol is evaporated off by heating the flask on the water-bath for about half an hour, or until the soap is dry. One hundred c.c. of hot water, which has been kept boiling for at least 10 minutes (to drive out all dissolved carbonic acid, the retention of which would vitiate the result), are added, and the flask is heated until the soap is dissolved. Forty c.c. of normal sulphuric acid and three or four fragments of pumice or broken pipe-stems are added, and the flask is at once connected with a condenser by means of a glass tube, 7 mm. wide, and 15 cms. from the top of the cork to the bend. At a distance of 5 cms. above the cork is a bulb 5 cms. in diameter. The flask is supported on a circular piece of asbestos, 12 cms. in diameter, having a hole in the centre 5 cms. in diameter, and is first heated by a very small flame, to fuse the insoluble fatty acids, but the heat must not be so great as to cause the liquid to boil; when fusion is complete the heat is increased, 110 c.c. are distilled off into a graduated flask, the distillation lasting about 30 minutes (from 28 to 32 minutes); the distillate is shaken, 100 c.c. are filtered off, transferred to a beaker, 0·5 c.c. of phenolphthalein solution (1 gram in 100 c.c. alcohol) is added, and the filtrate is titrated with decinormal soda or baryta solution. In precisely the same manner (with the same reagents), a blank test should be made, and the amount of decinormal alkali required to neutralise the distillate ascertained. This should not exceed 0·3 c.c. The volume of decinormal solution of alkali used, less the figure obtained in the blank experiment, is multiplied by 1·1. The number so found is the Reichert-Wollny value.

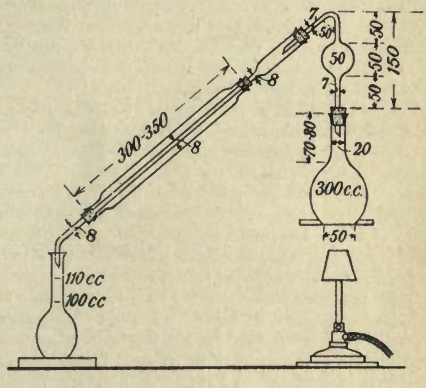


FIG. 3.

The Reichert-Meissl value (see tables at the end of this article) is practically identical with the Reichert-Wollny value. The Reichert-Meissl value of the majority of oils and fats, that is of those the saponification value of which is less than 200, is below 0·5. All oils and fats, the saponification value of which exceeds 200, are characterised by Reichert-Wollny values exceeding 1·0. The Reichert-Meissl value furnishes important indications regarding the nature of an oil or fat; thus butter fat is most prominently characterised by its high Reichert-Meissl value of about 27 to 29; the fats belonging to the cocoa-nut oil group by Reichert-Wollny values of 5 to 8, and dolphin and porpoise oils by Reichert-Meissl values varying from 47 to 120 (see tables at the end of this article).

Leffmann and Beam proposed the method of saponification with a concentrated solution of caustic soda in glycerol. This process is convenient owing to its rapidity, and has therefore been introduced by Polenske in the examination of butter fats, suspected of being adulterated with cocoa-nut oil. The method is carried out as follows: 5 grams of butter fat are placed in a 300 c.c. flask and heated with 20 c.c. of a solution of caustic soda in glycerol (prepared by dissolving 100 grams of caustic soda in an equal weight of water and mixing 20 c.c. of this solution with 180 c.c. of pure concentrated glycerol) over a naked flame for 2–3 minutes, until the water has evaporated off and the liquid has become clear. The values obtained by Leffmann and Beam's method are practically identical with those furnished by the Reichert-Wollny process, as the author can testify from his own experience.

It must be distinctly understood that by the Reichert method only a portion of the volatile fatty acids is recovered in the distillation process. The volatile fatty acids passing over consist, in the case of butter fat, preponderantly of butyric acid with which caproic, caprylic, and capric acids are admixed. In the case of cocoa-nut and palm-nut oils, butyric acid is absent, caproic and caprylic acids preponderating in the distillate. By filtering the distillate, caproic, caprylic, and capric acids are removed to the largest extent and are thus not accounted for in the Reichert-Wollny value.

Both Müntz and Coudon in France and Polenske in Germany extended the Reichert process by introducing a method for the approximate determination of the *insoluble* volatile fatty acids which pass over in the Reichert distillation process. Thus, after the Reichert-Meissl value has been determined, subsequently a second important value, affording a measure of the *insoluble volatile acids*, can be ascertained.

In the determination of this new value, the greatest attention must be paid to minute details and especially to the form of apparatus employed. Whereas Müntz and Coudon's apparatus is confined to France, Polenske's method has found application in this country, especially for the reason that this method closely followed the Reichert-Wollny process, and is in fact carried out in conjunction with it and in one and the same apparatus. As this method affords the best means of detecting cocoa-nut and palm-kernel oils in butter fat and in margarine, the process deserves the attention of the analyst.

Polenske saponifies 5 grams of filtered (butter) fat, by the Leffmann-Beam process, with 20 grams of glycerol and 2 c.c. of caustic soda solution (prepared from equal parts of sodium hydroxide and water) in a 300 c.c. flask by heating over a free flame. The solution is allowed to cool below 100°, 90 c.c. of water are added, and the mass dissolved by warming on the water-bath to about 50°. The solution must be clear and almost colourless. In case a brown solution be obtained, the test must be rejected. Fifty c.c. of dilute sulphuric acid (containing 25 c.c. of pure concentrated sulphuric acid in 1000 c.c.) and some *powdered* pumice are added to the hot soap solution; the flask is then immediately attached to the condenser. The apparatus to be employed must correspond in all details to the dimensions given in Fig. 4. The heat must be so regulated that within 19 to 20 minutes 110 c.c. are distilled off; the cooling water must be supplied at such a rate that the distillate does not drop into the 110 c.c. flask at a higher temperature than 20° to 23°. As soon as 110 c.c. have distilled over, the distillation is interrupted, the flask is removed, and is replaced by a 20 c.c. measuring cylinder.

The distillate, which must not be shaken up, is immersed almost completely in water at 15°. After about 5 minutes the neck of the flask is slightly tapped, so that the oily drops floating on the surface may adhere to the walls of the flask. After a further 10 minutes, the consistence of the insoluble acids is noted, with a view to ascertaining whether they form a solid (semi-solid) mass or oily drops. The contents of the flask are then mixed by turning the corked flask four or five times upside down, avoiding, however, violent shaking. 100 c.c. are filtered off through a filter of 8 cms. diameter, and titrated with decinormal caustic potash, as is done in the determination of the Reichert-Meissl value. In order to remove the soluble acids completely, the insoluble volatile acids on the filter are washed three times in succession with 15 c.c. of water, which have been passed severally through the tube of the condenser, the 20 c.c. measuring cylinder, and the 110 c.c. flask. These wash-waters are thrown away. In order to collect the insoluble volatile acids adhering to the tube of the condenser, the measuring cylinder, and the 110 c.c. flask, these vessels are rinsed three times in succession with 15 c.c. of neutralised 90 p.c. alcohol, and the alcoholic washes poured through the filter, each quantity being allowed to drain before a fresh wash is poured on the filter. The alcoholic filtrate is then titrated with decinormal alkali. The figure thus obtained has been termed 'new butter value' or 'Polenske value,' but the author prefers the term *titration number of insoluble volatile acids*, a term which has been adopted in France and Belgium. The titration value of the insoluble volatile acids lies in the case of butter fats as a rule between 2 and 4, in the case of cocoa-nut oil between 15 and 20, and in the case of palm-kernel oil between 10 and 12. (For a full discussion of this 'value,' see Lewkowitsch's Chem. Techn. [ii.] 695.)

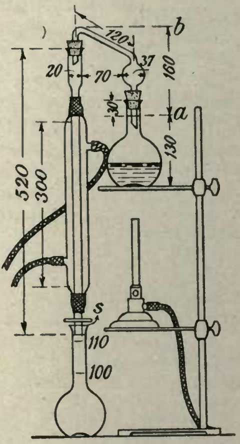


Fig. 4.

Acetyl Value.

The acetyl value indicates the number of milligrams of caustic potash (KOH) required for the neutralisation of the acetic acid obtained on saponifying one gram of an acetylated oil or fat.

The determination of the acetyl value of oils and fats is based on the principle that glycerides containing hydroxylated fatty acids assimilate, on being heated with acetic anhydride, one or more acetyl groups, according to whether the fatty acids contain one or more alcoholic hydroxyl groups. The chemical change consists in the replacing of the hydrogen atom of the alcoholic hydroxyl group or groups by the radicle of acetic acid, as explained by the following equations :—

$$C_3H_5[O{\cdot}C_{18}H_{32}O(OH)]_3+3(C_2H_3O)_2O$$

Ricinolein. Acetic anhydride.

$$=C_3H_5[O{\cdot}C_{18}H_{32}O(O{\cdot}C_2H_3O)]_3+3C_2H_4O_2$$

Acetyl ricinolein. Acetic acid.

$$C_3H_5[O{\cdot}C_{18}H_{31}O(OH)_4]_3+6(C_2H_3O)_2O$$

Sativin. Acetic anhydride.

$$=C_3H_5[O{\cdot}C_{18}H_{31}O{\cdot}(O{\cdot}C_2H_3O)_4]_3+6H_2O$$

Tetra-acetyl sativin.

The determination of the acetyl value (first proposed by Benedikt) is carried out in the form given to it by Lewkowitsch : 10 grams, or any other convenient quantity, are boiled with twice the amount of acetic anhydride for 2 hours in a round-bottomed flask attached to an inverted condenser. The solution is then transferred to a beaker of about 1 litre capacity, mixed with 500 to 600 c.c. of boiling water and heated for half an hour, while a slow current of carbon dioxide is passed into the liquid through a finely drawn-out tube reaching nearly to the bottom of the beaker ; this is done to prevent bumping. The mixture is then allowed to separate into two layers, the water is siphoned off, and the oily layer again boiled out in the same manner three successive times. The last trace of acetic acid is thus removed ; this is ascertained by testing with litmus paper. Prolonged washing beyond the required limit causes slight dissociation of the acetyl product. This would lead to too low an acetyl value. The acetylated product is then filtered through a dry filter-paper, and dried in an oven to remove water.

About 5 grams of the acetylated product are then saponified by boiling with alcoholic potash, as is done in the determination of the saponification value. If the 'distillation process' be adopted, it is not necessary to work with an accurately measured quantity of standardised alcoholic potash. In case the 'filtration process' be used, the alcoholic potash must be measured exactly. (It is advisable to use in either case a known volume of standard alkali, as one is then enabled to determine the saponification value of the acetylated oil or fat.) Next the alcohol is evaporated off and the soap dissolved in water. From this stage onwards, the determination is carried out either by (*a*) the distillation process, or (*b*) the filtration process.

(*a*) *Distillation process.*—Add dilute sulphuric acid (1 : 10), more than is required to saturate the potash used, and distil the liquid in a current of steam : 600–700 c.c. of water are distilled off. As a rule, this will be quite sufficient, and the last 100 c.c. will be found to require no more than 0·1 c.c. of decinormal alkali. Then titrate the distillate with decinormal potash, using phenolphthalein as an indicator, multiply the number of c.c. by 5·61, and divide by the weight of substance taken. This gives the *acetyl value.*

(*b*) *Filtration process.*—Add to the soap solution a quantity of standardised sulphuric acid, exactly corresponding to the amount of alcoholic potash employed, and warm gently, whereupon the fatty acids will readily collect on the top as an oily layer. (If the saponification value has been determined, it is, of course, necessary to take into account the volume of acid used for titrating back the excess of potash.) Filter off the liberated acids, wash with boiling water until the washings are no longer acid, and titrate the filtrate with decinormal alkali. The acetyl value is calculated in the manner shown above (*a*).

Both methods give identical results ; the latter requires less time and will, therefore, be found more convenient. The distilled water used in determining this value by either the distillation or filtration process must be carefully freed from carbonic acid by previous boiling, as otherwise serious errors ensue.

Pure triglycerides containing no hydroxylated acids have no acetyl value ; pure glycerides of hydroxylated fatty acids yield acetyl numbers which are in complete agreement with theory. In these cases, the acetyl value is a 'characteristic.' In the case of triglycerides containing, in addition to hydroxylated fatty acids, soluble acids as well, the acetyl value determined as described above would, of course, include soluble acids. The 'apparent' acetyl value obtained in such a case must, therefore, be diminished by the amount of alkali required for the saturation of the soluble fatty acids in order to obtain the *true* acetyl value. The amount of alkali required for the saturation of the soluble volatile acids must be ascertained by a blank test. Since acetyl values are also furnished by mono-glycerides and diglycerides (occurring in oils and fats having notable acid values), by free alcohols (such as phytosterol), and oxidised acids, and since all these substances occur in varying amounts in natural oils and fats, especially in those which have been exposed to the atmosphere and have become rancid, the acetyl value must, in these cases, be considered a 'variable.'

B. Variables.

1. *Acid Value.*

The acid value indicates the number of milligrams of potassium hydroxide required to saturate the free fatty acids in one gram of an oil or fat ; or, in other words, it gives the amount of potassium hydroxide, expressed in tenths per cent., necessary to neutralise the free fatty acids in an oil or fat. This value is therefore a measure of the free fatty acids in an oil or fat.

For the determination of the acid value of an oil or fat, about 5 grams of a sample (if available) are mixed with neutral or neutralised alcohol (purified methylated spirit) and titrated with aqueous or alcoholic caustic potash or caustic soda, using phenolphthalein as an indicator.

Example.—Weighed off 3·254 grams of tallow. Required for neutralising the free fatty acids 3·5 c.c. of decinormal caustic potash (or soda) or 3·5×5·61 milligrams KOH. The amount of KOH required for 1 gram of tallow, *i.e.* its acid value, is therefore

$$A=\frac{3{\cdot}5\times5{\cdot}61}{3{\cdot}254}=6{\cdot}03$$

The acid value is frequently expressed in per cent. of oleic acid. Since the molecular weight of oleic acid, 282, is approximately five times 56·1 (the molecular weight of KOH), and the acid value expresses the amount of KOH in tenths per cent., a rapid and in most cases sufficiently accurate method of converting the acid value into per cent. of oleic acid is to multiply the former by 0·5. In the case of cocoa-nut oil and palm-kernel oil fatty acids, this procedure would not be applicable, as their mean molecular weight lies, as a rule, between 210–220.

2. *Glycerol.*

If natural oils and fats represented neutral triglycerides, it would be possible to calculate the amount of glycerol obtainable on saponification from the following equation:

$$C_3H_5(OR)_3+3KOH=C_3H_8O_3+3KOR.$$

In the case of pure triglycerides, the proportion of glycerol obtainable being a 'characteristic' (see GLYCERIN), the quantity of glycerol yielded by an oil or fat can be calculated from the saponification value. In the case of natural oils and fats, a calculation of this kind will lead to erroneous results, not only on account of the (small) quantity of 'unsaponifiable matter' that is always present, but chiefly on account of the free fatty acids and mono- and di-glycerides which occur in natural oils and fats in variable quantities. Therefore, in the case of natural oils and fats, the percentage number of glycerol must be looked upon as a 'variable.'

This 'variable' stands in that general relation to the acid value that the higher the acid value, the smaller the yield of glycerol.

In order to determine the proportion of glycerol which an oil or fat yields on saponification, it is best to apply the 'acetin process' (*see* GLYCERIN) after a 'crude glycerin' has been prepared in the following manner:—

Twenty grams of the oil or fat are saponified (as described under *Saponification value*) with alcoholic potash, and the alcohol is driven off on a water-bath. The resulting soap is decomposed with sulphuric acid and the liberated fatty acids are filtered off. The filtrate is neutralised with an excess of barium carbonate and boiled down on the water-bath until most of the water has been driven off. The residue is exhausted with a mixture of ether and alcohol, the ether-alcohol driven off, for the most part, by gently heating on the water-bath, and the residue then left is dried in a desiccator and weighed. It is not necessary to dry until constant weight is obtained, as the actual glycerol present is determined in the crude product by the acetin method.

3. *Determination of the Unsaponifiable Matter.*

The author comprises under the term 'unsaponifiable matter' all those substances that are insoluble in water, or do not combine with caustic alkalis to form soluble soaps. Most oils and fats contain, in their natural state, small quantities of unsaponifiable matter which consists to a great extent either of phytosterol in the case of vegetable oils and fats, or of cholesterol in the case of animal oils and fats. Other alcohols and hydrocarbons represent the smaller part of the 'unsaponifiable matter.'

Preparatory to the determination of the unsaponifiable matter, the oil or fat must be saponified as described above under *Saponification value.* In many cases it will, therefore, be found convenient to combine the determination of the saponification value with that of the unsaponifiable matter. But the amount of oil or fat taken should not be less than 5 grams. The unsaponifiable matter is determined as follows:—

Saponify 5 grams of the sample with 25 c.c. of double normal alcoholic potash in a flask under a reflux condenser and evaporate off the bulk of the alcohol. The residual soap is dissolved in 50 c.c. of hot water, and transferred to a separating funnel of about 200 c.c. capacity, using about 20–30 c.c. of water for rinsing the dish. After cooling, add 30–50 c.c. of ether and shake the solution thoroughly. Addition of a little alcohol will accelerate the separation. The soap solution is then run off into another separating funnel and is again exhausted with fresh ether. As a rule, two extractions will suffice; it is, however, safer to extract a third time. The ethereal solutions are united, washed with a small quantity of water to free them from any dissolved soap, and transferred to a tared flask. The ether is distilled off on the water-bath, and the residue dried at 100° and weighed.

In the case of most oils and fats ether should be preferred to light petroleum (which is largely used on the Continent). In order to counteract the property of light petroleum to dissolve alkaline soaps, the petroleum layer holding the unsaponifiable matter in solution should be washed with 50 p.c. alcohol instead of with water.

The above method must not be used in the case of oils and fats which have admixed with them vegetable or animal waxes, as the alkali salts of the fatty acids are not readily soluble in water nor even in dilute alcohol. In such cases, it is best to neutralise the soap solution with acetic acid, using phenolphthalein as an indicator, and to precipitate with barium chloride or lead acetate. The residue is then washed, dried, mixed with sand and extracted in a Soxhlet apparatus with petroleum boiling below 80°. If it be desirable to ascertain whether cholesterol or phytosterol or both, or animal or vegetable waxes or mineral oils, &c., be present, the unsaponifiable matter should be prepared in sufficient quantity to admit of further examination (*see* below *Examination of the Unsaponifiable Matter*).

(b) *Qualitative Methods.*

A large number of qualitative methods which were formerly in vogue, such as the elaïdin test, the sulphur chloride test, the thermal reactions with sulphuric acid (Maumené test), bromine or sulphur chloride, have been practically superseded by the determination of the iodine value. Inasmuch as the latter yields the same information in a more reliable and less ambiguous fashion than the tests enumerated, they need not be described here. (For a description of these methods, *see* Lewkowitsch, vol. I, chap. vii.) More important are the qualitative methods described below, inasmuch as they frequently furnish important data for the recognition of some oils and especially as they are usable for the valuation thereof. In cases where the quantitative methods do not supply full information the qualitative methods may be applied with advantage. The following qualitative methods are described here :—

(1) Oxygen absorption test.
(2) Bromide tests.
(3) Colour tests.

(1) Oxygen Absorption Test.

The absorption of oxygen from the atmosphere has a very important bearing on the liability of oils to cause spontaneous combustion when spread in a finely divided state on fibrous organic substances (*see* WOOL OILS). It is also of very great importance in the industries of paint oils, boiled oils, and varnishes.

It has been pointed out already that the iodine absorption of oils and fats stands in close relationship to the absorption of oxygen, and that the latter property, being a measure of the drying power of oils, was formerly used for purposes of classification. It has also been explained that the classification based on the iodine value includes the sub-division of oils into drying, semi-drying, and non-drying oils.

If a convenient method were known for the accurate determination of the oxygen which is absorbed during the drying process, it would be possible to class the determination of the drying power, or, as it might be termed, the 'oxygen value,' amongst the quantitative tests.

Determinations by earlier observers were made in a very unsystematic fashion, insufficient regard having been paid to such important factors as temperature, influence of light, moisture of the atmosphere, thickness of layer exposed, age of the oil, &c.

Since the drying of an oil requires a protracted length of time, attempts were made to accelerate the process of drying by mixing with the oils finely divided lead (Livache) or finely divided copper (Huebl; Lippert). Livache's lead powder is prepared by precipitating a lead salt with zinc, washing the precipitate rapidly in succession with water, alcohol, and ether, and finally drying *in vacuô.* The test is carried out as follows : Spread about 1 gram of lead (or copper) powder, weighed off accurately on a somewhat large watchglass, in a thin layer, and allow to fall on to it from a pipette 0·6 to 0·7 grams (not more) of the oil to be tested, placing each drop separately on the lead (or copper) powder, taking care that the drops do not run into one another. Then allow the watchglass to stand at the ordinary temperature exposed to light.

In this process, linseed oil reaches the maximum absorption within a few days, whereas under ordinary conditions the same result is only arrived at after a much longer time has elapsed. Livache states that drying oils absorb the maximum quantity of oxygen after 18 hours, or, in some cases, after three days, whereas non-drying oils do not gain in weight before the lapse of four or five days. Weger condemns Livache's process, and recommends that larger quantities of lead should be used, so that for 0·2 grams of oil there should be taken at least 2 grams of lead powder. But even in that case the results were not found to be satisfactory.

Lippert, as also Weger, undertook a systematic study of the drying power of oils, by exposing them in very thin layers on glass plates to the action of the atmosphere. It was found that glass could not be replaced by any other material lighter in weight; thus celluloid, gelatin, and even ebonite were found useless. Sheets of mica, although useful for the work, are too easily damaged, and even sheets of thin metals have the drawback of being too easily creased. Necessary precautions in this test are: that the glass be perfectly clean, free from dust, and that the oil be spread with the greatest possible care in an evenly thin layer. If the layer is of uneven thickness, increase of weight might occur at one place, whilst simultaneously in a thinner layer loss of weight might take place. A series of experiments showed that the thinner the layer of oil exposed, the more rapidly is oxygen absorbed at the commencement of the experiment, but after 24 hours an equilibrium seems to be established. The thicker the layer the smaller is the increase, but if the layer is too thin, unreliable results will be obtained. The best conditions seem to be reached by spreading the oil so that about 0·0005 gram is used per square cm. of a glass plate.

The process is an extremely tedious one, and depends on the accuracy with which decimilligrams can be ascertained. Besides, the method does not yield absolute values, and can only be used as a guide in comparative tests. It must, however, depend on the given circumstances whether this process should be applied. For if it is merely a question of discriminating between drying, semi-drying, and non-drying oils, the iodine value will not only be the most convenient sorting test, but will, at the same time, furnish quantitative results. It should be noted, however, that the iodine value must not be accepted as tantamount to defining the drying power. To take a striking example, fish and liver oils absorb approximately as much iodine as do the best drying oils, and yet they are greatly inferior to the latter as regards oxygen absorption power. Furthermore, fish and liver oils differ most materially from the 'drying oils,' in that they do not form a skin as does linseed oil.

Fish and liver oils are best differentiated from the drying oils by the bromide test.

(2) Bromide Test.

On the strength of Hazura's investigations of the bromine derivatives of the unsaturated fatty acids, Hehner and Mitchell devised a process, best applied in the following manner, which embodies some modifications worked out in the author's laboratory : Dissolve 1 to 2 grams of oil in 40 c.c. of ether, to which a few c.c. of glacial acetic acid have been added, cool the solution in a corked flask to 5°, and add bromine drop by drop until the brown coloration remains permanent. If the temperature were allowed to rise too high, evolution of hydrogen bromide would become noticeable ; in that case, the experiment must be repeated. After standing for 3 hours at a temperature of 5°, the liquid is passed through a filter, and the precipitate is washed four times in succession, using each time 10 c.c. of chilled ether. The residue is finally dried in a water-oven to constant weight. In the following table a number of experiments are collated which have been carried out by Hehner and Mitchell, by the author and by his assistants Walker, Warburton, and Stadler.

Kind of Oil	Yield of insoluble bromides from glycerides per cent.	Observer
Linseed (iodine value 181)	23·14; 23·52	Walker and Warburton
Linseed (iodine value 186·4)	24·17	Lewkowitsch
Linseed (iodine value 190·4)	37·72	,,
Linseed	23·86–25·8	Hehner and Mitchell
Tung	nil	,, ,,
,, I.	nil	Walker and Warburton
,, II.	0·38; 0·39	,, ,,
Candle nut	8·21; 7·28	,, ,,
Walnut	1·42–1·9	Hehner and Mitchell
Safflower	0·65–1·65	Walker and Warburton
Poppy seed	nil	Hehner and Mitchell
Soya bean oil	5·0	Lewkowitsch
Maize	nil	Hehner and Mitchell
Cotton seed	nil	,, ,,
,, ,, cooled	nil	Lewkowitsch
Rape oil	3·0	Stadler
Brazil nut	nil	Hehner and Mitchell
Almond	nil	,, ,,
Olive	nil	,, ,,
Japan fish	21·14; 22·07	Walker and Warburton
Fish, deodorised	49·01; 52·28	,, ,,
Cod liver	42·9	Hehner and Mitchell
,, ,,	35·33; 33·76	Walker and Warburton
,, Newfoundland	32·68; 30·62	,, ,,
Shark liver	22·0	Hehner and Mitchell
,, ,,	21·22; 19·08	Walker and Warburton
Seal	27·54; 27·92	,, ,,
Whale	25·0	Hehner and Mitchell
,, old sample	15·54; 16·14	Walker and Warburton
,, fresh sample	20·1–22·6	Lewkowitsch
Sperm	2·61; 2·42	Walker and Warburton

In the author's opinion, derived from very extensive practice with this method, it is preferable to apply the 'bromide test' to the isolated fatty acids (*see* below).

(3) Colour Tests.

A very large number of colour reactions have been proposed from time to time, and are still being proposed, for the recognition of individual oils.

Colour reactions were chiefly resorted to for lack of better methods; they have been superseded in the majority of cases by the 'quantitative reactions.' It should be borne in mind that many colour reactions quoted in older text-books, and perpetuated even in more modern treatises, were not always obtained with typical samples, little or no regard having been paid to their source, their mode of purification, their age, and all that variety of circumstances which influence the colour produced by the reagents. In consequence of progress made in technical processes, a large number of impurities, which were in fact the very substances that gave origin to the colours supposed to be characteristic of the oils or fats, have ceased to occur in commercial samples.

A colour reaction can only be considered of some value if it be produced by a well-defined substance, occurring naturally in an oil or fat, and characteristic of it to such an extent that the sample may be identified by that reaction. Obviously, these characteristic substances which only occur in minute quantities should not be easily removable in the course of the usual manufacturing processes.

An extensive inquiry made by the author (J. Soc. Chem. Ind. 1894, 617, and Chem. Techn. [i.] 398-400) into the colour reactions, has led him to conclude that only the following tests can be considered:—

Baudouin's test.—This test, originally proposed by Camoin, is indicative of sesamé oil, inasmuch as a substance which occurs in this oil gives with hydrochloric acid and sugar a characteristic red colouration. Since cane sugar yields lævulose and furfural, Villavecchia and Fabris proposed to carry out this test in the following manner, which can be thoroughly recommended:—

Place 0·1 c.c. of a 2 p.c. alcoholic furfural solution in a test-tube, add 10 c.c. of the oil to be tested, and 10 c.c. of hydrochloric acid of sp.gr. 1·19; shake the mixture for half a minute and allow to settle. In the presence of sesamé oil, even if it be less than 1 p.c., the aqueous layer will acquire a distinct crimson colour. In the absence of sesamé oil, the lower layer is either colourless, or has at most (as in the case of a very rancid though pure olive oil) a dirty yellow colour. The great sensitiveness of this reaction has led to the compulsory ear-marking of margarine, in several continental countries, by the legally prescribed addition of 5–10 p.c. of sesamé oil to margarine. In case an oil or fat has already been coloured with a colouring matter furnishing a red colouration with hydrochloric acid alone (which not unfrequently occurs in the case of margarine coloured with 'butter colour'), the colouring matter must be previously removed by frequent shaking out with concentrated hydrochloric acid. In many cases, however, the colouring matter contained in the sesamé oil is destroyed at the same time.

Halphen's Colour Test.—This test indicates cotton-seed oil and is carried out in the following manner: 1 to 3 c.c. of the oil is dissolved in an equal volume of amyl alcohol; to this is added 1 to 3 c.c. of carbon disulphide holding in solution 1 p.c. of sulphur (flowers). The test-tube containing the mixture is then immersed in boiling water, and kept therein for some time. The carbon disulphide evaporates off; in the presence of cotton-seed oil a deep red colouration appears in the course of 5 to 15 minutes. This colour reaction is most characteristic; it is possible to detect thereby 5 p.c., and even less, of cotton-seed oil admixed with other oils and fats, *e.g.* olive oil or lard. In case the proportion of cotton-seed oil is very small, the test-tube must be kept in the water-bath for 20 to 30 minutes, or preferably in a salt-bath at 105°. Mixtures of olive and arachis oils containing 1 p.c. of cotton-seed oil, gave, in the author's laboratory, distinct colourations after 25 to 30 minutes. Over-estimation of this test must, however, be guarded against as, on the one hand, cotton-seed oil, which has been heated at 180°–250°, no longer yields the red colouration. On the other hand, it must be remembered that on feeding cows and pigs with cotton-seed cake, the chromogenetic substance passes into the milk fat of cows and into the lard. It must, also, be noted that no quantitative interpretation should be based upon the depth of the red colouration obtained, even if the presence of cotton-seed oil has been placed beyond doubt.

It should further be noted that kapok oil and baobab oil give the same colour reaction, the last-named oil with even greater intensity than cotton-seed oil.

Becchi's Colour Test.—This test is much less reliable than Halphen's test and is only described here because it is still largely used in the South of Europe (France, Italy). It is safest, if Becchi's test must be applied, to use it in the form suggested by Tortelli and Ruggeri: Five grams of the liquid fatty acids of the suspected sample are dissolved in 10 c.c. of alcohol, and 1 c.c. of a 5 p.c. silver nitrate solution is added; the sample is then heated on a water-bath at 70°–80°. Cotton-seed oil acids reduce the silver immediately, whereas the fatty acids of olive oil and other oils remain clear for some time. Even cotton-seed oils—which have been heated at 250° for 10 and 20 minutes respectively—can be recognised when present in as low a proportion as 10 p.c. in olive oil, on allowing the liquid acids of the mixed oil to stand in the hot water-bath for several hours.

Nitric Acid Test.—This test may be used in many cases for the preliminary identification of cotton-seed oil. The test is best carried out with nitric acid of 1·375 sp.gr. (Lewkowitsch). A few c.c. of the sample are shaken energetically with an equal measure of nitric acid of the specified gravity 1·375, and the sample is allowed to stand for some time, up to 24 hours. Cotton seed oil gives a coffee-brown colouration which is characteristic of this oil to such an extent that admixtures of 10–12 p.c. of cotton-seed oil with olive oil can be detected in certain cases. But even here circumspection is necessary, as the coffee-brown colouration given by some specimens of cotton-seed oil is not characteristic of all cotton-seed oils. Of importance is the observation made by the author, viz. that a specimen of heated cotton-seed oil which no longer gives the Halphen test still gives a brown colouration with nitric acid, and also that the fatty acids from heated cotton-seed oil showed the colouration distinctly.

It may be repeated that the last three colour tests, which are employed for the detection of cotton-seed oil, should only be used with the greatest circumspection. In any case they can only serve as preliminary or confirmatory tests.

Liebermann-Storch Reaction.—This colour test is exceedingly reliable for the detection of rosin oils: 1 to 2 c.c. of the sample under examination are shaken, in a test-tube, with acetic anhydride at a gentle heat; after cooling, the acetic anhydride layer is drawn off by means of a pipette, and tested by adding one drop of sulphuric acid of 1·53 sp.gr. (This acid contains 62·53 p.c. of SO_4H_2; it is prepared by mixing 34·7 c.c. of concentrated sulphuric acid with 35·7 c.c. of water.) If rosin oil is present, a fine violet (fugitive) colour is immediately produced. If less than 1 to 2 c.c. are available, the test can be done on a watch-glass, by stirring the liquid with acetic anhydride and allowing a drop of sulphuric acid to run down the side. It should be borne in mind that cholesterol gives a similar colour reaction.

Sulphuric acid test.—All sulphuric acid colour reactions described in the older literature of this subject are unreliable with the exception of the test for liver oils. This is best carried out in the following manner:—1 drop of oil is dissolved in 20 drops of carbon disulphide and 1 drop of concentrated sulphuric acid is added. In the presence of liver oils, a beautiful violet-blue colour appears at once, changing afterwards into red and brown. The colouration is not only caused by the presence of cholesterol but also by some 'lipochromes' which are extracted from the liver in the course of preparing the oils.

II. Examination of Fatty Acids.

In case the preceding methods, described under A and B, have not furnished sufficient information for the identification of a specimen, it becomes necessary to examine the free fatty acids.

If great accuracy is required it is not permissible to examine the fatty acids as obtained by the decomposition of the soap solution—resulting on saponification of the oils and fats—as the separated fatty acids naturally retain the unsaponifiable matter. Rather is it necessary to remove the unsaponifiable matter previous to the decomposition of the soap solution by the methods described above.

A list of the natural fatty acids likely to be met with in the examination has been set out in the table, p. 744. It will be found convenient to have the few indications given above amplified by the following notes.

I. ACIDS OF THE ACETIC SERIES: $C_nH_{2n}O_2$.

These acids contain a normal chain and are best characterised for analytical purposes by their property of not absorbing any iodine, *i.e.* their iodine value is *nil*. The lowest members of the series are miscible with water in every proportion. The solubility in water decreases rapidly with the increase of the number of carbon atoms in the molecule. Capric acid is practically insoluble in cold water, somewhat more soluble in hot water. Lauric acid is very slightly soluble in boiling water. The higher acids are practically insoluble in water.

Taking solubility in water as a basis of classification we may, for analytical purposes, subdivide these fatty acids into *soluble* and *insoluble* fatty acids. The acids up to caprylic acid are termed *soluble* fatty acids; the higher fatty acids, from myristic acid upwards, are the *insoluble* fatty acids. Capric and lauric acids occupy, also as regards solubility, an intermediate position. The lead salts of the higher fatty acids, commencing with palmitic acid, are insoluble in ether.

Acetic Acid *v.* vol. i. p. 7.

Butyric Acid *v.* vol. i. p. 591.

*iso***Valeric Acid** *v.* VALERIC ACID.

Caproic acid, $C_6H_{12}O_2$, discovered by Chevreul in 1818, is not miscible with water, although it is, to some extent, soluble in it; sp. gr. at 20°/4° is 0·924; $n_D^{20}=1{\cdot}41635$; its odour is like that of sweat: 100 c.c. of water dissolve 0·822 gram at 15°.

Methyl ester, sp.gr. 0·9309 at 0°; b.p. under 760 mm. pressure, 149·6°; under 15 mm. pressure, 52°–53°.

Ethyl ester, sp.gr. 0·8890 at 0°; sp.gr. 0·8732 at 20°; sp.gr. 0·8594 at 40°; b.p. 165·5°–166° under 735·8 mm. pressure.

Caprylic acid, $C_8H_{16}O_2$, discovered by Lerch (1844) in butter fat: sp.gr. 0·9270 at 0° and 0·9100 at 20°/40°; n^{20}_{D}1·42825. One part dissolves in 400 parts of boiling water; the dissolved acid separates out almost completely on cooling: 100 c.c. of water at 15° hold in solution 0·079 gram of acid. The acid has an intense odour of sweat. It also occurs in the oils belonging to the cocoa-nut oil group.

Methyl ester, sp.gr. 0·8942 at 0°; sp.gr. 0·887 at 18°; solidifying point −40° to −41°; b.p. 192°–194° under 760 mm.; 95° under 25 mm., 83° under 15 mm. pressure.

Ethyl ester, sp.gr. 0·8842 at 0°; 0·8730 at 16°; solidifying point, −47° to −48°; b.p. 207°–208°.

Capric acid, $C_{10}H_{20}O_2$, like the foregoing two acids, is characteristic of the milk fats and the oils of the cocoa-nut group. It occurs in wool yolk as potassium salt. The acid crystallises in fine needles, sp.gr. 0·930 at 37°; 0·8858 at 40; n^{40}_{D}1·42855. It is almost insoluble in cold water; one part dissolves in about 1000 parts of boiling water. The acid has a goat-like smell, which becomes more distinct at the temperature of its melting-point.

Methyl ester, boils at 223°–224° under 760 mm. and at 114° under 15 mm., solidifies at −18°.

Ethyl ester, sp.gr. 0·862; b.p. 243°–245°.

Lauric acid, $C_{12}H_{24}O_2$, is characteristic of the oils of the cocoa-nut oil and dika fat groups. At the ordinary temperature the acid is solid, and crystallises from alcohol in needles. It is the first acid of the acetic series that cannot be distilled at ordinary pressure without undergoing (slight) decomposition: sp.gr. 0·883 at 20°/4°; 0·875 at 43·6°/4; 0·8642 at 60°/4°; n^{60}_{D} 1·42665; n^{76}_{D} 1·4236. Lauric acid is slightly soluble in large quantities of boiling water; on distilling its aqueous solution, it passes over to an appreciable extent with the vapours. The laurates of the alkali-metals differ from the corresponding salts of the higher fatty acids in that they require large quantities of salt for ‘salting out’ (*v.* SAPONIFICATION).

Methyl ester, b.p. 141° under 15 mm.; 148° under 18 mm.; m.p. +5°.

Ethyl ester, sp.gr. 0·8671 at 19°; solidifying point −10°; b.p. 269° under ordinary pressure.

Myristic acid, $C_{14}H_{28}O_2$, is characteristic of all the fats belonging to the *Myristica* group (*see* MYRISTICA FATS). It was discovered by Playfair in nutmeg butter. It is also stated to occur as cetyl myristate in spermaceti and, in combination with unknown alcohols, in wool wax. The acid crystallises in laminæ; sp.gr. 0·8622 at 53·8°/4°; 0·8584 at 60°/4°; n^{60}_{D} 1·43075; $n^{76·5}_{D}$ 1·4248; is completely insoluble in water; when boiled with water, about 7·7 p.c. is carried over with the vapour; it dissolves with difficulty in cold alcohol and ether.

Methyl ester, b.p. 167°–168° under 15 mm. pressure; m.p. 18°.

Ethyl ester, boils at 295° under ordinary pressure, and *in vacuô* at 102° or 124°; solidifies at 10·5°–11·5°; sparingly soluble in alcohol or ether, more readily soluble in light petroleum.

Palmitic acid, $C_{16}H_{32}O_2$, occurs in most vegetable and animal fats; and notably in large quantities in palm oil (from which it was first isolated in a pure state by Fremy); in Chinese vegetable tallow, Japan wax, and myrtle wax. It occurs also in spermaceti and in opium wax as ceryl palmitate, in beeswax as myricyl palmitate.

Palmitic acid has been prepared artificially on a large scale by melting oleic acid with caustic alkali, hydrogen being evolved; in addition to palmitic acid smaller quantities of oxalic and acetic acids are formed. This process has been abandoned as impracticable.

Palmitic acid forms tufts of finely crystalline needles; the melted acid solidifies on cooling to a nacreous, scaly, crystalline mass. It boils between 339° and 356° with slight decomposition; distils unchanged under a pressure of 100 mm. at 271·5°; under a pressure of 15 mm. at 215°, and *in vacuô* at 138°–139°. On a large scale it is distilled with the aid of superheated steam; sp.gr. 0·8527 at 62°/4°; 0·8412 at 80°/4°; $n^{74·5}_{D}$ 1·4284; n^{80}_{D} 1·42693. It is not readily soluble in cold alcohol; 100 c.c. of methylated alcohol (sp.gr. 0·8183) dissolve at 0° from 1·2 to 1·3 grams; 100 c.c. of 95 p.c. (by volume) alcohol hold in solution at 0°, 0·56 gram; 100 parts of absolute alcohol dissolve, at 19·5°, 9·32 parts. It dissolves very easily in boiling alcohol; light petroleum does not dissolve it very readily.

The metallic salts of palmitic acid resemble very closely those of stearic acid (*v. infra*), but they possess a somewhat greater solubility. Palmitic acid is determined quantitatively in palmitates by precipitating their solutions with hydrochloric acid, washing the precipitate with water, dissolving it in absolute alcohol or ether, evaporating to dryness, and finally drying in a desiccator over sulphuric acid.

Methyl ester, b.p. 196° under 15 mm. pressure; m.p. 28°.

Ethyl ester, b.p. 122° *in vacuô*; m.p. 24·2°.

Stearic acid, $C_{18}H_{36}O_2$, occurs very abundantly in many vegetable and animal fats, especially in the hard ones, such as cacao butter, shea butter, and tallow. The higher the melting-point of a fat, the higher is, as a rule, the proportion of stearic acid it contains. Stearic acid can be obtained synthetically by the reduction of less saturated acids, containing an open chain of 18 carbon atoms (oleic, linolic, linolenic, clupanodonic) by means of hydrogen in the presence of a suitable catalyst, such as nickel or palladium. It forms white, nacreous laminæ, melting at 69·32° to a perfectly colourless liquid which, on cooling, solidifies at 69·3° to a crystalline translucent mass; boils under ordinary pressure at about 360° with slight decomposition; *in vacuô* it distils unchanged. On a large scale it is distilled in a current of superheated steam without any decomposition. Under 100 mm. pressure it boils at 291°, under 15 mm. at 232°, and *in vacuô* at 154·5°–155·5°: sp.gr. 0·8454 at 69·2°/4°, 0·8386 at 80°/4°. At 11° its sp.gr. equals that of water; at more elevated temperatures it floats on water, as it expands more quickly than the latter: n^{80}_{D} 1·43003.

Like palmitic acid it possesses neither smell nor taste; it is greasy to the touch and produces a grease-spot on paper. Insoluble in water; in hot alcohol it dissolves easily; it is less soluble in absolute alcohol than palmitic acid, one part of stearic acid requiring 40 parts of alcohol. 100 c.c. of alcohol, sp.gr. 0·818 (at 15·5°) hold in solution at 0° 0·0814 gram, if the solution be prepared with about 3 grams of stearic acid, but owing to supersaturation, the dissolved amounts fluctuate considerably, depending on the amount of stearic acid used. Thus, with 7 grams of stearic acid, varying quantities of dissolved stearic acid from 0·0810 rising up to 0·1082, have been found (Lewkowitsch). Stearic acid dissolves easily in ether.

Potassium stearate $KC_{18}H_{35}O_2$, forms crystals having a greasy lustre; dissolves in 6·6 parts of boiling alcohol. On diluting the hot aqueous solution with a large proportion of water, pearly laminæ of an acid stearate,

$$KC_{18}H_{35}O_2.C_{18}H_{36}O_2,$$

separate. The salt is insoluble in ether, light petroleum, carbon disulphide, and chloroform. (Difference from potassium oleate.)

Sodium stearate, $NaC_{18}H_{35}O_2$, closely resembles the potassium salt. In the crystalline state it forms lustrous laminæ.

Ammonium stearate, $(NH_4)C_{18}H_{35}O_2$, loses part of its ammonia on being warmed in aqueous solution, and is converted into the acid salt. The same change takes place when the ammonia soap is allowed to stand over concentrated sulphuric acid in a desiccator.

Calcium, strontium, and barium stearates form crystalline precipitates, practically insoluble in alcohol. The insoluble salts are, to some extent, hydrolysed on washing with water. Thus barium stearate gives up to the water barium oxide, and free stearic acid (which can be extracted with alcohol) remains behind with the undissociated residue. The *magnesium* salt crystallises in microscopical laminæ; it is nearly insoluble in cold alcohol, but sufficiently soluble in boiling alcohol to allow it to be crystallised from its solution. The *lead* salt melts at 115°–116° without undergoing decomposition; it is very sparingly soluble in ether (difference from oleic acid), and still less in light petroleum. 50 c.c. of absolute ether dissolve 0·0074 gram of lead stearate. In hot benzene, lead stearate dissolves, but separates almost completely on cooling to 8°–12°. In absolute alcohol, lead stearate is very sparingly soluble. Stearic acid cannot be determined quantitatively by weighing its calcium or barium salts, a method which has been proposed repeatedly.

Methyl ester, b.p. 214°–215°; m.p. 38°.

Ethyl ester, boils *in vacuô* at 139° or 154°; it melts at 36·7°.

Arachidic acid, $C_{20}H_{40}O_2$, discovered by Goessmann (1854), occurs in notable quantities in arachis oil; it has also been found in butter fat. It crystallises in small lustrous scales, sparingly soluble in cold alcohol; dissolves easily in boiling alcohol. 100 parts of 90 p.c. alcohol dissolve at 15°, 0·022 parts, and at 20°, 0·045 parts of arachidic acid. It dissolves readily in ether, chloroform, light petroleum, or benzene.

Methyl ester, m.p. 54·5°.

Ethyl ester, b.p. 284°–286° under 100 mm. pressure; m.p. 50°.

Behenic acid, $C_{22}H_{44}O_2$, melts at 80°–82° and solidifies at 79°–76°. Synthetical behenic acid from erucic acid melts at 83°–84° and solidifies at 79°–77°. It boils under 60 mm. pressure at 306° and crystallises in needles; it is less soluble in alcohol than in ether. 100 parts of alcohol dissolve at 17°, 0·102 gram; 100 parts of ether, at 16°, 0·1922 gram.

Ethyl ester, m.p. 48°–49°.

Lignoceric acid, $C_{24}H_{48}O_2$, occurs in arachis oil, in association with arachidic acid; crystallises from alcohol in white flocks of silky lustre, which become scaly and show nacreous lustre when pressed between filter-paper; sparingly soluble in cold alcohol, dissolves readily in benzene, ether, or carbon disulphide.

Methyl ester, m.p. 56·5°–57°.

Ethyl ester, m.p. 55°; distils without undergoing decomposition at 305°–310° under a pressure of 15–20 mm.

II. ACIDS OF THE ACRYLIC OR OLEIC SERIES, $C_nH_{2n-2}O_2$.

These acids absorb two atoms of halogen from Huebl's or Wijs' iodine solution. By means of hydrogen, in the presence of a catalyst, they are readily reduced to the corresponding acids of the acetic series. By oxidation with a dilute solution of potassium permanganate in alkaline solution, the unsaturated acids are converted into the corresponding saturated hydroxylated acids (*v. infra*). On melting with caustic alkalis, they are broken up into lower acids; thus oleic acid yields palmitic, acetic, and other acids. During this reaction, a migration of the double linkage takes place. Some of the higher acids, notably oleic and erucic acids, are changed into crystallisable isomerides when treated with a small quantity of nitrous acid at the ordinary temperature, or with sulphurous acid or bisulphites at high temperatures and under pressure.

The unsaturated acids are more readily soluble in alcohol than the saturated acids having the same number of carbon atoms. The lead salts of these acids are readily soluble in ether, with the exception of erucic acid which dissolves with difficulty only in cold ether.

Ozone is readily assimilated by oleic acids, forming perozonides, which are easily converted into the more soluble ozonides (*see* Lewkowitsch, Chem. Techn. [i.] 142).

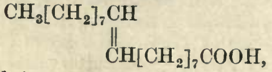
The action of concentrated sulphuric acid or anhydrous zinc chloride on the higher members of this series is a very complicated one (*v. infra* and also SAPONIFICATION).

Tiglic acid, $C_5H_8O_2$ (an isomeride of angelic acid), occurs in croton oil; crystallises in triclinic columns, melting at 64·5°, and boiling at 198·5° under ordinary pressure; sp.gr. 0·9641 at 76°.

Hypogaeic acid, $C_{16}H_{30}O_2$, occurs naturally in arachis oil. It has been prepared synthetically from stearolic acid and crystallises in needles melting at 33°–34°, boiling at 236° under a pressure of 15 mm., and at 230° under a pressure of 10 mm. By nitrous acid it is converted into *gaïdic acid*.

Oleic acids. Theory predicts a number of different 'oleic acids,' according to the position which the doubly linked carbon atoms occupy in the molecule, quite apart from stereo-isomerides obtained by the action of nitrous acid on the several 'oleic acids.' Here only the more important members of this group can be described.

(*a*) **Ordinary Oleic acid**



$$\begin{array}{l}\mathrm{CH_3[CH_2]_7CH}\\ \qquad\quad\|\\ \qquad\quad\mathrm{CH[CH_2]_7COOH,}\end{array}$$

is found in most vegetable and animal fats, especially in the liquid ones, in combination with glycerol. Pure oleic acid is best prepared from tallow (which practically does not contain any less saturated acids than oleic acid), by saponifying with caustic potash, precipitating the soap solution with lead acetate, and extracting the dried lead salt with ether. The dissolved lead salt is decomposed by hydrochloric acid under ether, the liberated acid dissolved in ammonia, and the solution precipitated by barium chloride. The barium salt is dried, dissolved in hot alcohol, and the hot solution allowed to crystallise. The crystallised salt is decomposed either by strong mineral acid or by tartaric acid. The acid so prepared still contains some palmitic and stearic acids, owing to the solubility of the lead salts of the solid acids in the ethereal solution of lead oleate.

Pure oleic acid is a colourless liquid free from odour. It crystallises in the form of needles, solidifying at 4°, and melting at 6·5°; an allotropic form melts at 16°. Sp.gr. 0·898 at 14°; or 0·8908 at 11·8°/4, 0·898 at 15°, 0·895 at 20°, 0·889 at 30°, 0·875 at 50°, 0·854 at 78·4°.

On distilling oleic acid under ordinary pressure, it is partially broken up into water, and into carbonic, acetic, caprylic, and capric acids; at the same time, sebacic acid and hydrocarbons are formed. In a current of superheated steam, however, it passes over unchanged at a temperature of about 250°. This is, indeed, the method by which oleic acid is prepared on a manufacturing scale in candle-works. It is insoluble in water, dissolves readily in cold alcohol, even if the alcohol be somewhat dilute. On adding large quantities of water to the alcoholic solution, the acid is thrown out.

Nitrous acid at the ordinary temperature converts oleic acid into elaïdic acid. The same change takes place when the acid is treated with sodium bisulphite under pressure at 175°–180°, or with sulphurous acid, under pressure, at 200°. The change, however, is not complete, as the reaction is a reversible one.

On blowing air through oleic acid at 120° for 2, 4, 6, and 10 hours, the author obtained respectively 0·62, 2·6, 3·5, and 6 p.c. of 'oxidised' acids, insoluble in light petroleum (*v. infra*); the specific gravities of the products rose in the same order from 0·8980 to 0·9098, 0·9121, 0·9123, and 0·9238 respectively. Similarly, on digesting oleic acid with sulphur at a temperature between 130° and 150°, sulphur is absorbed, without evolution of sulphuretted hydrogen; apparently an addition-product is formed. At higher temperatures, from 200°–300°, sulphuretted hydrogen is evolved.

Oleic acid dissolves in concentrated sulphuric acid in the cold, and forms stearic-acid-hydrogen sulphate, $C_{18}H_{35}(SO_4H)O_2$; on boiling this product with water, sulphuric acid is split off and ι-hydroxystearic acid is formed conjointly with a small quantity of stearolactone (Geitel), (*see* SAPONIFICATION). A similar change takes place on heating oleic acid with zinc chloride to 185°. By the catalytic reduction of oleic acid with hydrogen, oleic acid is converted quantitatively into stearic acid (*see* Lewkowitsch, J. Soc. Chem. Ind. 1908, 489).

Sodium oleate, $NaC_{18}H_{33}O_2$. The pure salt is prepared by crystallisation from absolute alcohol (not from dilute alcohol). It dissolves in 10 parts of water at 12°, or in 20·6 parts of alcohol, sp.gr. 0·821 at 13°. It also dissolves in 100 parts of boiling ether. The anhydrous salt melts at 232°–235°.

Potassium oleate, $KC_{18}H_{33}O_2$, forms a transparent, jelly-like mass, which is far more readily soluble in water, alcohol, and ether than the sodium salt. One part of the salt requires for complete solution 4 parts of water, or 2·15 parts of alcohol, or 29·1 parts of boiling ether.

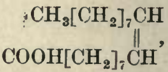
Ammonium oleate, $NH_4C_{18}H_{33}O_2$, forms 'liquid crystals.'

The metallic oleates are mostly soluble in alcohol, benzene, chloroform, carbon tetrachloride, carbon disulphide, nitrobenzene, pyridine, or light petroleum; some oleates are also soluble in ether.

Methyl ester, sp.gr. 0·879 at 18°; boils under a pressure of 15 mm. at 212°–213°.

Ethyl ester, sp.gr. 0·871 at 16°.

(*b*) **Elaïdic acid**



$$\begin{array}{l}\qquad\mathrm{CH_3[CH_2]_7CH}\\ \qquad\qquad\qquad\|\\ \mathrm{COOH[CH_2]_7CH}\end{array}$$

, discovered by Boudet (1832), is obtained by allowing nitrous acid fumes, or a nitrite and nitric acid, to act on oleic acid at the ordinary temperature; after a short time, the oleic acid is changed into its stereoisomeride, elaïdic acid. The separation of elaïdic acid from the unchanged oleic acid is readily effected by crystallisation from alcohol or ether, or by separating the lead salts by means of ether or benzene. It crystallises from alcohol in plates, melting at 44·5°; sp.gr. 0·8505 at 79·4°/4°. It can be converted, in its turn, into ordinary oleic acid by boiling iodostearic acid, prepared from elaïdic acid, with alcoholic potash; simultaneously some '*iso*öleic' acid is formed.

(*c*) ***iso*Oleic acid (Para-oleic), Solid Oleic acid**, was described as an individual acid by M., C., and A. Saytzeff and was prepared by distilling ι-hydroxystearic acid under diminished pressure, when a mixture of ordinary oleic and '*iso*öleic' acids, together with some unchanged hydrostearic acid, passed over.

The constitution $CH_3[CH_2]_{14}CH{=}CH{\cdot}COOH$ ascribed to this acid, has been shown to be erroneous. Arnaud and Pasternak (Compt. rend. 150, 1525) state that '*iso*öleic' acid is not an individual, but represents a mixture of several acids from which hitherto the ordinary 9 : 10-elaïdic acid, the ordinary 9 : 10-oleic acid, an 8, 9-elaïdic acid, and a hydroxystearic acid, $C_{18}H_{36}O_3$, could be isolated, but these acids do not yet exhaust the number of acids occurring in the mixture hitherto considered as '*iso*öleic' acid.

(*d*) **Rapic acid,** $C_{18}H_{34}O_2$, is the 'oleic acid' occurring in rape oil; it does not solidify on cooling nor does it yield a solid isomeride when acted upon with nitrous acid.

Erucic acid, $C_{22}H_{44}O_2$, discovered by Darby (1849), occurs in the oils belonging to the rape oil group. The acid crystallises from alcohol in long fine needles. Erucic acid simulates in its properties ordinary oleic acid; thus it is converted by nitrous acid into its stereoisomeride, *brassidic acid*; it is reduced by suitable treatment to the saturated behenic acid. On being melted with caustic potash, it splits up into acetic and arachidic acids.

'*isoErucic*' acid is obtained by boiling iodobehenic acid with alcoholic potash. No doubt this acid like *iso*öleic acid will be found to consist of a mixture of acids.

III. Acids of the Linolic Series, $C_nH_{2n-4}O_2$.

The acids belonging to this series are characterised by their property of absorbing four atoms of halogen, or two molecules of iodochloride. Hence these acids must be looked upon as containing two pairs of doubly-linked carbon atoms. They readily absorb oxygen on exposure to the air; this important property is made use of in the arts (*Drying oils*). They assimilate two molecules of ozone. On oxidation with potassium permanganate solution in the cold they yield tetrahydroxylated acids (*v. infra*). Nitrous acid does not convert them into solid isomerides. By suitable treatment with hydrogen they are converted into acids of the saturated series. It appears, therefore, that the acids belonging to this series are open chain acids.

Linolic acid, $C_{18}H_{32}O_2$, occurs in considerable proportions in drying and semi-drying oils. Pure linolic acid was obtained by saponifying its methyl ester. The acid is a colourless oily liquid, sp.gr. 0·9026 at 18°. On brominating linolic acid, a crystalline tetrabromide $C_{18}H_{32}O_2Br_4$, melting at 114°–115°, is obtained. On oxidising linolic acid with a dilute solution of potassium permanganate in the cold, tetrahydroxystearic (sativic) acid, $C_{18}H_{36}O_6$, melting at 173°, is formed. According to Erdmann and Bedford, there exist an α- and a β-linolic acid, the latter of which yields a liquid tetrabromide. The formation of the crystalline tetrabromide permits of the detection and also approximate quantitative determination of linolic acid.

Several other 'linolic acids' differing from the ordinary linolic acid by their yielding different tetrabromides and tetrahydroxystearic acids have been described. Thus *telfairic acid* yields a tetrabromide, melting at 57°–58°, and a tetrahydroxystearic acid, melting at 177°.

Elaeomargaric acid, $C_{18}H_{32}O_2$
$CH_3[CH_2]_3CH : CH[CH_2]_2CH : CH[CH_2]_7COOH$ (*Majima*), crystallises in rhombic plates, melting at 43°–44°. It absorbs oxygen readily from the air and is thereby converted into a resinous mass. In an alcoholic (or ethereal) solution the acid remains unchanged if protected from light. On exposure to light, however, crystals melting at 71° are deposited from the alcoholic solution. These crystals have the same composition as elaeomargaric acid. According to Maquenne, the higher melting acid, termed by Cloëz elaeostearic acid, is a stereoisomeride of elaeomargaric acid, and stands to it in the same relationship as does elaïdic acid to oleic acid. On bromination it yields a tetrabromide, which is identical with the solid tetrabromide obtained from linolic acid. On oxidising elaeomargaric acid with potassium permanganate, Kametaka obtained dihydroxystearic acid, and also azelaïc acid and an unknown crystalline substance melting at 123°–125°, soluble in water and alcohol, but insoluble in ether.

IV. Acids of the Cyclic (Chaulmoogric) Series: $C_nH_{2n-4}O_2$.

The acids belonging to this group are cyclic compounds and therefore contain only one pair of doubly-linked carbon atoms; hence they absorb only two atoms of halogen. The acids are also remarkable on account of their property of rotating the plane of polarised light.

Hydnocarpic acid, $C_{16}H_{28}O_2$, was isolated from the mixed fatty acids of hydnocarpus oil by crystallisation from alcohol. It is sparingly soluble in the usual organic solvents in the cold, with the exception of chloroform, in which the acid is easily soluble; $[\alpha]_D + 68{\cdot}1°$. On keeping, the acid becomes yellow, the melting-point, at the same time, being lowered; on distilling under diminished pressure, a brown resinous substance is left in the distilling flask.

Chaulmoogric acid, $C_{18}H_{32}O_2$, was prepared from the mixed fatty acids of chaulmoogra oil by crystallisation from light petroleum, subsequent distillation under diminished pressure and recrystallisation from alcohol. The crystals form colourless, glistening leaflets; $[\alpha]_D + 62{\cdot}1°$.

V. Acids of the Linolenic Series: $C_nH_{2n-6}O_2$.

The acids of this series assimilate six atoms of hydrogen, or three molecules of iodochloride. They are therefore assumed to contain three pairs of doubly-linked carbon atoms. They readily absorb oxygen from the air, a property of which extensive use is made in the arts (*Drying oils*). According to Molinari, they absorb three molecules of ozone. By treatment with hydrogen in the presence of a catalyst, linolenic acid is converted into stearic acid.

Linolenic acid, $C_{18}H_{30}O_2$,
$CH_3{\cdot}CH_2{\cdot}CH{:}CH{\cdot}CH_2{\cdot}CH{:}CH{\cdot}CH_2CH{:}CH[CH_2]_7CO_2H$ occurs in notable quantities in the drying oils, especially in linseed oil. According to Erdmann there exist two linolenic acids, α- and β-linolenic acid, of which the α-linolenic acid gives a crystalline hexabromide, melting at 179°. On reducing this crystalline hexabromide and again brominating the reduced linolenic acid, only 23 p.c. of the crystalline hexabromide is obtained, whence Erdmann and Bedford conclude that the reduced acid consists of a mixture of two, α- and β-linolenic, acids. The isolation and determination of the crystalline hexabromide is made use of in the analytical examination of drying oils (*v. infra*).

Pure α-linolenic acid is a colourless liquid of sp.gr. 0·9046; on exposure to the atmosphere it absorbs oxygen rapidly and increases thereby in sp.gr. The iodine value of the pure acid corresponds to that demanded by theory. On oxidising linolenic acid, a hexahydroxystearic acid (linusic acid), m.p. 203°–205°, is obtained.

***iso*Linolenic acid**, $C_{18}H_{30}O_2$. The existence of this acid was inferred by Hazura from the fact that he obtained on oxidising the mixed linseed oil acids with potassium permanganate an isomeride of linusic acid, termed *iso*linusic acid. This second hexahydroxy acid melts at 173°–175°. The existence of *iso*linolenic acid is doubtful.

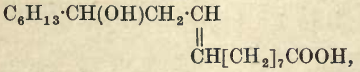
VI. ACIDS OF THE CLUPANODONIC SERIES: $C_nH_{2n-8}O_2$.

Clupanodonic acid, $C_{18}H_{28}O_2$, has been prepared from its octobromide by reduction with zinc and alcoholic hydrochloric acid. It is a pale yellow liquid having a fishy smell. The acid is characteristic of all fish, liver, and blubber oils. The most important derivative of this acid is the octobromide which permits the isolation of clupanodonic acid from a mixture of fatty acids and thus the recognition of fish, liver, and blubber oils (*v. infra*). The octobromide is insoluble in the usual organic solvents; it is only slightly soluble in hot benzene. It does not melt below 200°, but begins to blacken above this temperature.

VII. ACIDS OF THE RICINOLEIC SERIES: $C_nH_{2n-2}O_3$.

The acids belonging to this series are best characterised as 'oleic' acids in which one atom of hydrogen is replaced by a hydroxyl group. The most important representative of this series is :—

Ricinoleic acid, $C_{18}H_{36}O_3$



$$\begin{array}{l} C_6H_{13}{\cdot}CH(OH)CH_2{\cdot}CH \\ \qquad\qquad\qquad\qquad \| \\ \qquad\qquad\qquad\quad CH[CH_2]_7COOH, \end{array}$$

discovered by Bussy and Lecanu in castor oil.

Pure ricinoleic acid is miscible with alcohol and ether in every proportion. The acid contains an asymmetric carbon atom; hence it is optically active: $[\alpha]_D + 6{\cdot}25°$ to $+7{\cdot}5°$ (in acetone solution). On standing, the acid becomes spontaneously polymerised to form polyricinoleic acids, which are easily re-converted into ricinoleic acid by boiling with alcoholic potash and acidification of the soap. Ricinoleic acid assimilates two atoms of bromine or one molecule of iodochloride. The bromide is liquid. By hydrogen, in the presence of a catalyst, it is converted into hydroxystearic acid. The acid does not absorb oxygen on exposure to air. On treatment with ozone, it absorbs four atoms of oxygen, forming a perozonide.

By oxidation with an alkaline solution of potassium permanganate in the cold, two hydroxyl groups are assimilated with formation of trihydroxystearic acid. The statement by Hazura and Gruessner that two isomeric trihydroxystearic acids are formed and that consequently castor oil contains two isomeric acids, viz. ricinoleic and *iso*ricinoleic acids, is open to grave doubts (*see* Lewkowitsch, Chem. Techn. [i.] 165).

For the complicated reaction taking place on treating ricinoleic acid with concentrated sulphuric acid, *cp.* Lewkowitsch, *l.c.* On subjecting ricinoleic acid to dry distillation, optically active hydrocarbons are obtained.

Ricinelaïdic acid is formed by treating ricinoleic acid with nitrous acid. It also is optically active; $[\alpha]_D + 6{\cdot}670°$ (in absolute alcohol). The acid crystallises in needles, melting at 52°–53°.

VIII. DIHYDROXYLATED ACIDS: $C_nH_{2n}O_4$.

Dihydroxystearic acid $C_{18}H_{36}O_4$. Only one dihydroxystearic acid has been found hitherto in a natural oil; it occurs to the extent of about 1 p.c. in castor oil. The acid is insoluble in ether, petroleum ether, and benzene, slightly soluble in cold toluene, more so in the hot solvent; it dissolves in boiling alcohol and boiling acetic acid. Reducing agents readily convert it into stearic acid.

IX. DIBASIC ACIDS, ACIDS OF THE SERIES $C_nH_{2n-2}O_4$.

Three dibasic acids belonging to this series have been isolated from Japan wax by fractionating its insoluble mixed fatty acids *in vacuó*. The best known of the three acids is :—

Japanic acid, $C_{21}H_{40}O_4$, which appears to form, together with palmitic acid, a mixed glyceride. The acid crystallises from alcohol and chloroform in white laminæ; it is heavier than water; it dissolves very sparingly in water.

In addition to the above naturally occurring fatty acids, there are found in various products of the fat industries several hydroxylated acids or their inner anhydrides. These hydroxylated acids belong to the same series as the dihydroxylated, trihydroxylated, tetrahydroxylated, and hexahydroxylated acids obtained respectively from oleic, ricinoleic, linolic, and linolenic acids by oxidation with potassium permanganate in the cold. These acids are of great importance for the identification of the unsaturated fatty acids from which they have been derived.

A full description of these acids exceeds the limits of this article, all the more so as quantitative methods for their determination still require to be worked out. It must suffice, therefore, to refer to Chapters III. and VIII. of Lewkowitsch's Chem. Techn., and to the tables, p. 777, detailing briefly the properties of the more important hydroxylated acids and of their acetylated products. The second table shows that the hydroxylated acids are best characterised by their notable acetyl values.

The methods applicable to the examination of fatty acids divide themselves naturally into (*a*) physical methods; (*b*) chemical methods.

(*a*) PHYSICAL METHODS.

The physical methods, embracing the determination of the specific gravity, refractive index, rotatory power, and solubility, are applied in the same manner as described above for the glycerides.

Acid	Formula	Melting-point °C.	Solubility of the acid in					Obtained from
			Water		Alcohol		Ether	
			Cold	Hot	Cold	Hot		
α-Hydroxystearic	$C_{18}H_{35}O_2(OH)$	81–81·5	insoluble	insoluble	sparingly soluble	soluble	sparingly soluble	oleic; elaïdic acid
α-Hydroxystearic	$C_{18}H_{35}O_2(OH)$	77–79	insoluble	insoluble	sparingly soluble	less soluble than 1:10 acid	more soluble than 1:10 acid	'*iso*oleic' acid
Dihydroxy-stearic	$C_{18}H_{34}O_2(OH)_2$	137	insoluble	insoluble	sparingly soluble	soluble	sparingly soluble	ordinary oleic acid
Sativic . .	$C_{18}H_{32}O_2(OH)_4$	173	insoluble	sparingly soluble	sparingly soluble	soluble	insoluble	linolic acid
Linusic . .	$C_{18}H_{30}O_2(OH)_6$	203–205	sparingly soluble	soluble	sparingly soluble	sparingly soluble	insoluble	linolenic acid
*iso*Linusic .	$C_{18}H_{30}O_2(OH)_6$	173–175	sparingly soluble	readily soluble	soluble	soluble	insoluble	*iso*linolenic acid

Acid	Formula	Acetylated acid				Increase in weight on acetylating
		Formula	Molecular weight	Acetyl value	Saponification value	Per cent.
Hydroxystearic . . .	$C_{18}H_{35}O_2(OH)$	$C_{18}H_{35}O_2(O{\cdot}C_2H_3O)$	342	164·0	328·0	14·00
Dihydroxystearic . .	$C_{18}H_{34}O_2(OH)_2$	$C_{18}H_{34}O_2(O{\cdot}C_2H_3O)_2$	400	280·5	420·75	26·58
Trihydroxystearic . .	$C_{18}H_{33}O_2(OH)_3$	$C_{18}H_{33}O_2(O.C_2H_3O)_3$	458	367·4	489·9	37·95
Tetrahydroxystearic (sativic)	$C_{18}H_{32}O_2(OH)_4$	$C_{18}H_{32}O_2(O{\cdot}C_2H_3O)_4$	516	434·8	543·6	48·27
Pentahydroxystearic . .	$C_{18}H_{31}O_2(OH)_5$	$C_{18}H_{31}O_2(O{\cdot}C_2H_3O)_5$	574	488·7	586·4	57·69
Hexahydroxystearic (linusic)	$C_{18}H_{30}O_2(OH)_6$	$C_{18}H_{30}O_2(O{\cdot}C_2H_3O)_6$	632	532·5	621·3	66·31

More important than the determination of the solidifying and melting points of the glycerides is the determination of the solidifying point of the fatty acids, as valuable information of a discriminative nature can be obtained therefrom.

The *solidifying point of the fatty acids* forms the basis of the commercial valuation of such fats as tallow, bonefat, palm oil, and other vegetable fats. This number is known in commerce as 'titre test' and denotes the solidifying point taken under exactly determined conditions (*v. infra*).

The solidifying point is not a physical constant, inasmuch as it depends on the rate of cooling of a definite quantity examined under certain conditions; hence it is obvious that by varying these conditions, different results will be obtained. For commercial purposes, it is therefore most essential that a certain *modus operandi* be adhered to as strictly as possible. The mode of procedure proposed by Dalican has been adopted in this country, in the United States, and in France. This method has proved itself reliable in the author's own experience, extending over a great number of years. Fifty grams of the fat under examination are saponified, the separated fatty acids are freed from water and finally filtered through a dry plaited filter into a porcelain dish. The fatty acids are allowed to solidify and to stand overnight under a desiccator. (At the seventh International Congress, it was agreed that in those cases where rapidity in obtaining a result was of greater importance than strictest accuracy, the fatty acids may be allowed to stand for a few hours only.) The fatty substance is carefully melted in an air-bath or over a free flame, and as much of it is poured into a test-tube, 16 cm. long and 3·5 cm. wide, as will fill the tube more than half full. The tube is then fastened by means of a cork into a wide-mouthed bottle, 10 cms. wide and 13 cms. high, and an accurate thermometer (graduated in tenths of degrees from about −5° to +60°, having a mercury bulb about 3 cms. long and 6 mm. in diameter, and carefully standardised with the aid of a 'normal thermometer'), is inserted in the fatty acids, so that the bulb is in the middle of the mass. When a few crystals appear at the bottom of the tube, the mass is stirred by giving the thermometer a rotary movement, first three times from right to left, and then three times from left to right. Next stir continually, with a quick circular movement of the thermometer, without allowing it to touch the sides of the vessel, and taking care that all solidified portions, as they form, are well stirred into the mass until the latter has become cloudy throughout. The thermometer should now be observed carefully. A good plan is to write down the temperature at short intervals. At first the mercury will continue to fall, or at least remain stationary, then it will rise suddenly some tenths of a degree and reach a maximum, remaining stationary thereat for some little time before it falls again. This point is called the 'titre' or solidifying point of the mixed fatty acids. In the case of dark coloured fats, it may be impossible to observe the separation of crystalline matter. In such cases, it is best to make a preliminary experiment which affords the necessary guidance.

In Germany, Austria, and in the United States, slightly different methods of operating have been proposed (*see* Lewkowitsch, [i.] 406–408), but as Dalican's method has been made the basis of commercial transactions in this country, the United States, and France, new proposals for determining the 'titre,' however acceptable they may appear, have little chance of superseding the established method. The following table gives a list of titre tests collated from a very large number of observations made by the author.

TITRE TESTS OF MIXED FATTY ACIDS (Lewkowitsch).

Class of oil	Kind of oil	Titre test °C.	Remarks
Drying oils	Linseed oil	20·6	
	Tung oil	37·2	
	Hemp seed oil	16·6	
	Safflower oil	16·0	
	Poppy seed oil	16·2	
	Soya bean oil	21·2	
Semi-drying oils	Cotton seed oil	32·0	Lowest
	,, ,,	35·2	Highest
	Maize oil	19·0	
	Sesamé oil	23·8	
	Croton oil	19·0	
	Curcas oil	28·6	
	Rape oil	13·6	
Non-drying oils	Peach kernel oil	13·5	
	Almond oil	11·8	
	Arachis oil	29·2	
	Koëme oil	38·8	
	Olive oil	17·2	Lowest
	,, ,,	26·4	Highest
	Ben oil	37·8	
Marine animal oils	Japanese sardine oil	28·2	
	Cod liver oil	13·9	Lowest
	,, ,,	24·3	Highest
	Seal oil	15·9	
	Whale oil	23·9	
Terrestrial animal oils	Sheep's foot oil	21·1	
	Horses' foot oil	28·6	
	Neat's foot oil	26·5	

Class of fat	Kind of fat	Titre test °C.	Remarks
Vegetable fats	Chaulmoogra oil	39·6	
	Pongam oil	44·4	
	Laurel oil	15·1	
	Carapa oil	34·9	
	Margosa oil	42·0	
	Niam fat	42·5	
	Mowrah seed oil	40·3	
	Shea butter	53·8	
	Palm oil, Bonny	35·9	
	,, ,, Bassam	38·47	
	,, ,, Lagos	43·925	
	,, ,, Old Calabar	44·60	
	,, ,, Salt Pond	44·475	
	,, ,, New Calabar	45·55	
	,, ,, Congo	45·05	
	Macassar oil	51·6	Lowest
	,, ,,	53·2	Highest
	Sawarri fat	47·0	
	Nutmeg butter	35·95	
	Cacao butter	48·3–49·6	
	Chinese vegetable tallow	45·2	Lowest
	,, ,, ,,	53·4	Highest
	Palm nut oil	20·5	Lowest
	,, ,,	25·5	Highest
	Cocoa nut oil, commercial	22·55	Lowest
	,, ,, ,,	25·2	Highest
	,, ,, Cochin	25·2	
	Japan wax	59·4	
Animal fats	Horse fat	33·7	
	Horse marrow fat	38·55	
	Lard	42·0	
	Beef tallow, English	38·7	Lowest
	,, ,, ,,	45·1	Highest
	,, ,, N. American	41·1	Lowest
	,, ,, ,,	44·15	Highest
	,, ,, S. American	42·95	Lowest
	,, ,, ,,	46·25	Highest
	,, ,, Australian	38·3	Lowest
	,, ,, ,,	43·3	Highest
	Mutton tallow, English	41·5	Lowest
	,, ,, ,,	48·3	Highest
	,, ,, Australian	42·35	Lowest
	,, ,, ,,	48·05	Highest
	,, ,, New Zealand	45·9	Lowest
	,, ,, ,,	48·0	Highest
	Beef marrow fat	38·0	

(*b*) *Chemical Methods.*

The chemical methods are arranged here in a logical order, so that the order of the description may serve at the same time as a guide in the technical examination. (For other methods, which involve strictly scientific examination, *see* Lewkowitsch, vol. I. Chap. XII.)

(1) Neutralisation Value—Mean Molecular Weight.

The neutralisation value indicates the number of milligrams of potassium hydroxide required to saturate one gram of the mixed fatty acids.

The determination of the neutralisation number is carried out in exactly the same manner as is described under the heading 'Acid Value.' As a rule, about 5 grams of the substance should be taken; smaller quantities should not be employed (if avoidable), as otherwise the errors of the method have too great an influence on the result. From the neutralisation number thus found, the mean molecular weight of the fatty acids can be calculated as follows: Let M be the molecular weight expressed in grams. Theory requires that M grams be neutralised by 56·1 grams of potassium hydroxide, KOH. Let n be the number of grams of potassium hydroxide found by experiment to neutralise 1 gram of fatty acids; then we have the proportion

$$M : 56{\cdot}1 :: 1 : n\text{; hence, } M = 56{\cdot}1/n.$$

n is found by multiplying the number found for 1 gram of fatty acid by 0·0561. If that number be a, we have

$$n = a \times 0{\cdot}0561.$$

By substitution we obtain

$$M = \frac{56{\cdot}1}{a \times 0{\cdot}0561} = \frac{1000}{a}.$$

The following table contains the theoretical molecular weights and calculated[1] neutralisation values of pure fatty acids; they will serve as a guide to the proper interpretation of results obtained in the practical examination of mixed fatty acids.

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[1] For H = 1; O = 16; C = 12.

NEUTRALISATION VALUES OF FATTY ACIDS.

Acids	Formula	Molecular weight	Neutralisation value. Mgrms. KOH
Acetic	$C_2H_4O_2$	60	935·0
Butyric	$C_4H_8O_2$	88	637·5
Caproic	$C_6H_{12}O_2$	116	483·6
Caprylic	$C_8H_{16}O_2$	144	389·6
Capric	$C_{10}H_{20}O_2$	172	326·2
Lauric	$C_{12}H_{24}O_2$	200	280·5
Myristic	$C_{14}H_{28}O_2$	228	246·1
Palmitic	$C_{16}H_{32}O_2$	256	219·1
Stearic	$C_{18}H_{36}O_2$	284	197·5
Oleic	$C_{18}H_{34}O_2$	282	198·9
Linolic	$C_{18}H_{32}O_2$	280	200·4
Hydnocarpic	$C_{16}H_{28}O_2$	252	222·6
Chaulmoogric	$C_{18}H_{32}O_2$	280	200·4
Linolenic	$C_{18}H_{30}O_2$	278	201·8
Clupanodonic	$C_{18}H_{28}O_2$	276	203·2
Ricinoleic	$C_{18}H_{34}O_2$	298	188·3
Arachidic	$C_{20}H_{40}O_2$	312	179·8
Gadoleic	$C_{20}H_{38}O_2$	310	181·0
Erucic	$C_{22}H_{42}O_2$	338	166·0
Cerotic	$C_{26}H_{52}O_2$	396	141·7
Melissic	$C_{30}H_{60}O_2$	452	124·1
Hydroxystearic	$C_{18}H_{36}O_3$	300	178·0
Dihydroxystearic	$C_{18}H_{36}O_4$	316	177·6
Trihydroxystearic	$C_{18}H_{36}O_5$	332	169·0
Sativic	$C_{18}H_{36}O_6$	348	161·2
Linusic	$C_{18}H_{36}O_8$	380	147·6

(2) Lactones—Anhydrides.

If the fatty acids, instead of being titrated with aqueous alkali in the cold, were boiled with an excess of alcoholic potash (*see Saponification value*), the number of milligrams of potassium hydroxide thus required to saturate 1 gram of fatty acids should be the same as that found for the neutralisation value, provided the amount of unsaponifiable matter be negligible. In other words, the neutralisation and saponification values of fatty acids should be identical. In case, however, the fatty acids contain lactones, or anhydrides of the fatty acids, which do not combine with aqueous alkali in the *cold*, and are only hydrolysed on boiling with alcoholic potash, then the saponification value of the fatty acids will be higher than the neutralisation number.

The difference between saponification and neutralisation values furnishes a measure of the lactones or anhydrides present. The determination of lactones is of importance in the commercial examination of candle materials (*v.* Lewkowitsch, [i.] 422–423).

(3) Insoluble Fatty Acids.

Three to four grams of fat are saponified as described under *Saponification Value*, using, of course, double the amount of alcoholic potash stated there. The soap is dissolved in 100–150 c.c. of water (the alcohol is driven off completely until the soap has become pasty), acidified with dilute sulphuric acid and warmed until the liberated fatty acids float on the top as a clear oily layer. This is brought on to a filter-paper of about 4–5 inches diameter, previously dried at 100° and accurately weighed in a weighing bottle or a small beaker (covered with a watch-glass). The filter-paper should be of stout material, as ordinary filtering paper readily allows the liquid to run through turbid. A good plan to prevent this is to have the filter half full of hot water, before the fatty matter is transferred to it, and to keep it full until all the liquid is added. Finally, the fatty acids are washed on the filter with boiling water until a few c.c. of the wash-water do not redden sensitive tincture of litmus. In the case of fats belonging to the cocoa-nut oil or dika fat group, as also in the case of butter fat, 2000–3000 c.c. of wash-water are required. The washing being completed, the funnel with the filter is immersed in a vessel of cold water, so that the water outside and the acid inside are at the same level. The water is then allowed to drain off, the filter is transferred to the beaker in which it had previously been weighed, is dried at 100° for 2 hours, and weighed. The fatty matter is dried for another hour or an hour and a half, and weighed again. The difference between the two weights will, as a rule, be below 1 milligram.

Strictly concordant results are not obtainable by this method, as it entails a number of inherent errors, detailed consideration of which is required in each special case (see Lewkowitsch, Chem. Techn. [i.] 424).

Most oils and fats yield about 95 p.c. of insoluble fatty acids ; only those fats which are characterised by high Reichert values yield less than 95 p.c. It should be noted that the 'fatty acids' include the unsaponifiable matter, unless the latter has been removed from the soap solution. In the majority of cases, and especially in analyses of unadulterated fats for commercial purposes, the amount of unsaponifiable matter may be neglected.

(4) Volatile Fatty Acids.

A notable amount of volatile fatty acids is indicated by a definite Reichert-Meissl value of the glycerides, as also by a notable titration number of the insoluble volatile fatty acids. The approximate separation of the soluble volatile fatty acids has been described above. (For further details and the application of the method for the determination of the volatile fatty acids in the examination of butter fat and mixtures thereof with cocoa-nut oil and palm-kernel oil, *see* Lewkowitsch, [i.] 430).

(5) Separation of Insoluble Saturated from Unsaturated Fatty Acids.

The presence of unsaturated fatty acids in the mixed insoluble fatty acids is detected in the readiest manner by determining the iodine value of the mixed fatty acids ; this method offers an additional advantage in that it furnishes a measure of the unsaturated fatty acids, much as the iodine value of the oils and fats affords a measure of the unsaturated glycerides. The mixed fatty acids as obtained from the natural oils and fats will always have a definite iodine value.

The best—although still imperfect—method of separation is based on the solubility of the lead salts of the insoluble fatty acids in ether;

in this menstruum the lead salts of the solid fatty acids, if free from liquid acids, are almost insoluble. This method is best carried out in the following manner as worked out in the author's laboratory; it consists of a combination of the several modifications of the original Gusserow-Varrentrapp method, proposed by Muter and de Koningh, and by Lane:—

3 to 4 grams of fatty acids are neutralised in a 300 c.c. flask with 50 c.c. of approximately half-normal aqueous potash. In case the original oil or fat be employed, 3–4 grams are saponified in the usual manner with 50 c.c. of approximately half-normal alcoholic potash in a 300 c.c. flask. Phenolphthalein is added, the solution is slightly acidified with acetic acid, and finally titrated with alcoholic potash until neutral. The solution is then diluted with water to about 100 c.c., 30 c.c. of a 10 p.c. solution of lead acetate are diluted with 150 c.c. of water, heated to the boiling-point and gradually run into the soap solution with constant shaking. The flask, containing the lead soap, is filled completely with hot water, and then allowed to cool. When the liquid has become clear it is poured off through a filter. As a rule, the solution is so clear that no solid particles will be found on the filter; should there be any, they must be brought back into the flask. The precipitate in the flask is washed thoroughly with boiling water, using the precaution of cooling the hot solutions before filtering, thus causing the lead salts to adhere to the sides of the flask. The last drops of water may be removed by means of a thin roll of filter-paper. It is not advisable to dry the lead salts, as in the case of drying oils they absorb oxygen from the air somewhat rapidly. Next, 150 c.c. of ether are added to the lead salts, and the flask is corked and shaken repeatedly, so that the salts may disintegrate. The flask is then attached to a reflux condenser and heated on a water-bath for some little time with frequent shaking. The lead salts of the liquid fatty acids dissolve readily in the hot ether, conjointly with some fractions of the salts of the saturated acids; undissolved salts, if any, settle out at the bottom of the flask as a fine powder. If all operations are conducted somewhat rapidly and unnecessary exposure to the air is avoided, working in an atmosphere of an inert gas can be dispensed with. The ethereal solution is then allowed to cool down to the ordinary temperature and the solution filtered through a plaited filter (kept covered with a watch-glass) into a separating funnel. The insoluble salts are brought on to the filter by washing the flask three or four times with ether, using 30 c.c. each time. The ethereal solution is then shaken with a mixture of one part of hydrochloric acid and four parts of water, in order to decompose the lead salts. The ether dissolves the free fatty acids as they are liberated, whilst the undissolved lead chloride settles out at the bottom of the separating funnel. After separation into two layers has taken place, the acid liquid is drawn off and the ethereal layer is washed with small quantities of water until the wash-water is free from acid. Finally, the ethereal solution is filtered through a small plaited filter into an ordinary flask. In case the liquid fatty acids consist chiefly of oleic acid, the results will be sufficiently accurate, if the ether be evaporated off on the water-bath and the residue dried in a water-oven. If, however, the presence of less saturated fatty acids (from linseed, soya bean, maize, marine animal oils) than oleic is suspected, the ethereal solution should be distilled off in a current of dry hydrogen or dry carbon dioxide. The flask is then immersed up to the neck in warm water, which is finally brought to the boiling-point. Thus the last traces of moisture are removed.

On the filter there remain the lead soaps of the saturated fatty acids which are decomposed by treatment with hydrochloric acid, so that the saturated fatty acids can be recovered and further examined. The determination of the iodine value of the liquid fatty acids will furnish an approximate indication of the composition of the liquid fatty acids.

(6) Separation and Determination of Individual Saturated Fatty Acids.

In the present stage of our knowledge only the following solid acids can be determined with approximate accuracy.

Arachidic acid.—The solid fatty acids obtained from 10 grams of oil by the lead-salt-ether method are dissolved in 50 c.c. of 90 p.c. alcohol. In the presence of arachidic acid, a crystalline mass separates out from the cooled solution. This consists, in the case of arachis oil, of a mixture of arachidic and lignoceric acids. The crystals are filtered off and washed on the filter, first with a measured quantity of 90 p.c. alcohol, then of 70 p.c. (by volume) alcohol which dissolves but small quantities of the crude arachidic acid. The crystals are finally dissolved by pouring boiling absolute alcohol on the filter. The filtrate is received in a porcelain dish or in a flask, evaporated to dryness, and the residue is weighed. To the weight of crude arachidic acid thus found, the quantity dissolved by the 90 p.c. alcohol used for washing (taking as basis for calculation that 100 c.c. dissolve 0·0022 gram at 15°, or 0·045 gram at 20°) is added. Finally, the melting-point of the crude arachidic acid is determined. This should be from 71° to 72° (*cf.* Lewkowitsch, Chem. Techn. [ii.] 253).

Stearic acid.—The determination of stearic acid is based on the principle stated by David, that on treating mixed fatty acids with an alcoholic solution of pure stearic acid saturated at 0°, all the lower saturated fatty acids as also the unsaturated fatty acids are dissolved, whereas stearic acid remains undissolved.

It should be noted that if any arachidic acid be present as well as stearic acid, the separated acid consists of a mixture of the two. In such cases, it is advisable first to separate off the arachidic acid by the method described above.

David's principle has been worked out by Hehner and Mitchell to a method which yields in many cases, but not in every case, reliable results (*cf.* Lewkowitsch, [i.] 452).

The stearic acid solution is prepared by dissolving about 3 grams of pure stearic acid in 1000 c.c. of warm (methylated) alcohol of sp.gr. 0·8183 (containing 94·4 p.c. of alcohol by volume) in a stoppered bottle. The bottle is immersed up to the neck in ice-water (kept in an ice-chest well protected against radiation of heat), and allowed to stand in the ice-water overnight. After 12 hours, the mother liquor is siphoned off without removing the flask from the ice-water, by means of a small thistle funnel immersed in the alcoholic solution and covered with a piece of fine calico (so as to retain the separated stearic acid crystals in the flask). The funnel is twice bent at right angles, and is best fitted into a suction bottle, so that the clear liquor can be drawn off by means of a filter-pump. The method is carried out as follows: 0·5 gram to 1 gram of the mixed fatty acids, if solid, or 5 grams if liquid, are weighed accurately in a flask and dissolved in 100 c.c. of the above alcoholic stearic acid solution. The flask is placed in ice-water overnight, the mixture is agitated the following morning while the flask is still kept in the ice-water, and then allowed to stand for at least half an hour in the ice-water in order to promote crystallisation. The alcoholic solution is then filtered off as described above, care being taken to draw off the solution as completely as possible. The residue in the flask is washed three times in succession with 10 c.c. of the alcoholic stearic acid solution, previously cooled down to 0°. The crystals adhering to the calico of the thistle funnel are then washed with hot alcohol into the flask, the alcohol is evaporated off, the residue dried at 100° and weighed. In case the melting-point be much below 68·5°, the author considers it necessary to treat the residue once more as described above. A correction of 0·005 gram should be made for the stearic acid retained on the walls of the flask and in the adhering stearic acid solution.

(7) Detection, Separation, and Approximate Determination of Individual Liquid Fatty Acids —Oleic, Linolic, Linolenic, Clupanodonic.

The liquid fatty acids are separated from the total mixed fatty acids by the lead-salt-ether method; thus preliminary information is obtained as to which fatty acids may be present. In the present state of our knowledge, attention can only be directed to the detection and determination of oleic, linolic, linolenic, and clupanodonic acids. If the iodine value be found to lie in the neighbourhood of 90, the liquid fatty acids may be considered as consisting of practically pure oleic acid. If the iodine value be much higher than in the case of the majority of pure vegetable oils, the presence of linolic and linolenic acids must be suspected; in the case of oils, belonging to the marine animal oils, the presence of clupanodonic acid must be expected: in the case of mixtures, of course, the presence of all these acids has to be assumed.

The presence of linolenic and (or) clupanodonic acids, is ascertained by the bromide test, which permits at the same time of a quantitative determination of the insoluble bromides. The bromination test can be applied to the original mixed fatty acids without it being required to separate the solid from the liquid acids. The mixed fatty acids are brominated in the same manner as already described in the bromide test: 0·3 grams of the fatty acids are dissolved in glacial acetic acid, and the solution is cooled in a corked flask to 5°. The further treatment is identical with that described above (*Bromide test*). The ether-insoluble bromo derivatives consist either of octobromide or of hexabromide, or of a mixture of both. If the melting-point of the insoluble bromides lies between 175°–180°, linolenic hexabromide derived from a drying oil has been obtained. If the bromide has not melted at 180° or not completely melted, and blackens on heating to 200° or above, then an octobromide, characteristic of a marine animal oil, is present. If a mixture of hexabromides and octobromides be suspected, the bromides are separated by boiling with benzene in which the octobromides are insoluble (*cp.* Lewkowitsch, [i.] 462). Recent researches (unpublished), made by the author, prove that it is not permissible to calculate the amount of hexabromides to drying oil, as not only a certain amount of hexabromides remains dissolved, but also because liquid isomerides of hexabromides appear to be formed.

The filtrate from the octobromides and (or) hexabromides contains in addition to some dissolved hexabromides, tetrabromides and dibromides; the former can be isolated by evaporating off the ether and treating the residue with boiling light petroleum. On cooling crystals separate out which represent, in most cases, a mixture of hexabromides and tetrabromides and exhibit melting-points lying between 170° and 136°. Thus the author found in linseed oil fatty acids after separating off, 39·37 p.c. of hexabromides of m.p. 181°, 3·09 p.c. of bromides, m.p. 151°; 7·83 p.c. of bromides, m.p. 142°, and 2·38 p.c. of bromides, m.p. 135°–136°. By repeating the treatment with ether and by renewed re-crystallisation from boiling petroleum ether, tetrabromides of the approximately correct melting-point of pure crystalline linolic tetrabromide, viz. 114°, can be obtained.

The following table contains the amounts of insoluble bromides found in the mixed fatty acids from vegetable and oils marine animal oils.

——	Kind of oil	Yield of ether-insoluble bromide from fatty acids per cent.
Hexa-bromides	Linseed (iodine value 181)	29·06; 29·34
	,, (,, ,, 184)	31·31; 30·44; 30·80
	,, ,, ,, 190·4)	38·1; 42·0
	,, liquid acids (iodine value 208)	34·9
	Candle nut	11·53; 11·23; 12·63
	Stillingia	25·78
	Safflower	1·65; 0·65
	Soya bean	5·1
	Rape	2·4; 3·4
Octo-bromides	Japan fish (old sample)	23·04; 23·32
	,, (fresh samples)	44·2; 47·1
	Deodorised fish	38·42; 39·27
	Cod liver, Norwegian	29·86; 30·36
	Newfoundland cod	39·1; 37·76
	Shark liver	12·68; 15·08
	Seal	19·83; 19·93
	Whale (old sample)	12·38; 12·44
	,, (fresh samples)	22·59; 27·77
	Herring	12·7; 21·7

In the case of semi-drying oils, which are practically free from linolenic acid and contain considerable amounts of linolic acid, the bromination can be carried out in light petroleum when linolic tetrabromide of the melting-point, 112°–113°, can be obtained readily. In this case also, isomeric, soluble bromides, especially if an excess of bromine had been used, are formed, so that the weight of the tetrabromides is much (by 50 p.c.) below the actual amount of linolic acid present. The following tables contain a number of determinations carried out in the author's laboratory.

Oil	Linolic acid calculated from separated tetrabromide
Soya Bean oil . .	21 p.c.
Maize oil . . .	28 ,,
Cotton seed oil . .	21–24 ,,
Sesamé oil . . .	15·6–16·4 ,,

(8) Determination of Oxidised Fatty Acids.

Under the term 'oxidised' acids, the author comprises a class of fatty acids occurring in those oils and fats which have been treated with oxidising agents, as in the process of blowing with air or oxygen. The change which some of the unsaturated acids undergo is not yet fully understood, but this much is certain, that through 'blowing' or 'oxidising,' a certain proportion of acids are obtained which are characterised by their insolubility in light petroleum.

The quantitative determination of oxidised acids is carried out by Fahrion's method as follows: 4 to 5 grams of the sample are saponified in the usual manner with alcoholic potash; the alcohol is evaporated off, the soap is dissolved in hot water, transferred to a separating funnel, and decomposed with hydrochloric acid. After cooling, the liquid is shaken with light petroleum (boiling below 80°) and allowed to stand until it has separated completely into two clear layers. The insoluble oxidised fatty acids will be found to adhere to the sides of the funnel or form a sediment in the petroleum layer. The aqueous layer is drawn off, the petroleum layer poured off, if necessary through a filter, and the oxidised acids are washed with light petroleum to remove adhering ordinary fatty acids. In case the amount of oxidised fatty acids be large, it is advisable to dissolve them in alkali, decompose the soap with hydrochloric acid, and shake out again with petroleum, so as to remove completely any occluded soluble fatty acids. The oxidised acids are then dissolved in warm alcohol or ether, the alcoholic or ethereal solution is transferred to a tared basin, the alcohol or ether is evaporated off, and the residue dried until the weight remains constant. Thus the proportion of oxidised acids is found. (For further information, *cp.* Lewkowitsch, [i.] 469; [iii.] 134.)

III. Examination of the Unsaponifiable Matter.

The unsaponifiable matter is isolated in substances as described above and can be immediately examined further. In case a sample under examination has not been adulterated with mineral oil, rosin oil or tar oil, the amount of unsaponifiable matter will, as a rule, be very small. As stated already, the unsaponifiable matter consists chiefly of sterols; in the case of vegetable oils of *phytosterol* (mostly *sitosterol*); and in the case of animal oils and fats of *cholesterol*.

In addition to sitosterol, there has also been found in a number of vegetable oils, *stigmasterol*; and in rape oil, *brassicasterol*. The last two phytosterols cannot be considered here (*cp.*, however, Lewkowitsch, [i.] 208, 542).

The examination of the unsaponifiable matter furnishes, therefore, a means of distinguishing between vegetable and animal oils and fats. In case a mixture of both vegetable and animal products be present, a mixture of phytosterol and cholesterol is, of course, obtained.

For the examination of the unsaponifiable matter, the isolated substance is dissolved in the smallest possible amount of absolute alcohol and allowed to crystallise. If notable amounts of colouring matters and resinous substances are absent, as a rule well-defined crystals are obtained. Otherwise, the unsaponifiable matter must be dissolved in 95 p.c. alcohol and the solution decolorised by animal charcoal. The crystals should then be examined under the microscope. Cholesterol crystallises in the forms shown in Fig. 5, sitosterol in crystals shown in Fig. 6.

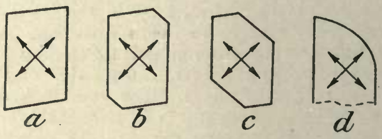

Fig. 5.

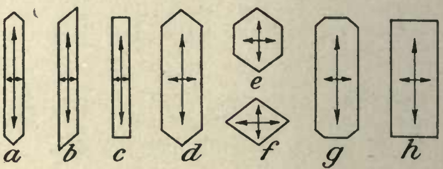

Fig. 6.

In the presence of both cholesterol and sitosterol, the microscopic examination furnishes very uncertain results (*cp.* Lewkowitsch, [i.] 472).

The uncertainty inherent in the microscopic test is removed by carrying out Boemer's phytosteryl acetate test.

Phytosteryl acetate test.—The alcoholic solution containing the crystals is brought to dryness on a water-bath, and the residue heated for 2 or 3 minutes in a small porcelain dish with acetic anhydride (2 to 3 c.c. per 100 grams of original oil or fat) over a small flame until the solution boils, the dish being covered with a watch-glass. The watch-glass is then removed, and the excess of acetic anhydride evaporated off on the water-bath. The contents of the dish are next heated with the smallest possible quantity of absolute alcohol; in order to prevent immediate solidification or crystallisation, a few c.c. of alcohol are added, when the mass is allowed to crystallise. By spontaneous evaporation, about one-half or one-third of the alcohol volatilises and the acetates crystallise out. The crystals are filtered off through a small filter, and washed with a little 95 p.c. alcohol. The acetates are brought back from the filter into the dish, dissolved in 5 to 10 c.c. of absolute alcohol, and again allowed to crystallise. The crystals are filtered off, and their melting-point is determined. Since cholesteryl acetate melts at 114·3°–114·8° (corr.), whereas crystals of sitosteryl acetate obtained from different oils and fats melt above 125°, the melting-point of the second crop of crystals will furnish *preliminary* information as to whether cholesterol only, or sitosterol only is present. Ultimate reliance should not, however, be placed on the melting-point of the second crop of crystals; for in most cases it is necessary to recrystallise the crystals at least three more times. If the melting-point of the fifth (or seventh) crop of crystals be found to lie below 115° or 116°, the absence of sitosterol can be pronounced with certainty. A gradual and distinct rise of the melting-points, above 114°, in the successive crops of crystals, is the best indication as to the procedure to be adopted.

This test is absolutely reliable, and superior to all other tests aiming at the detection of vegetable oils and fats in animal oils, such as the detection of cocoa-nut oil in butter fat or of vegetable fats and oils in lard. The sensitiveness of this test is so great that even 1 p.c. of an added vegetable oil or fat can be detected. This great sensitiveness has led to endeavours to circumvent and render illusory the indications of the phytosteryl acetate test by adding to fats adulterated with vegetable oils or fats, minute quantities of paraffin wax. For the determination of such added paraffin wax and the removal thereof, *see* Lewkowitsch, [i.] 477; [ii.] 592.

If large quantities of unsaponifiable substances have been admixed with an oil or fat—which is readily ascertained in the saponification test by obtaining an abnormally low saponification value—then fraudulent admixture with solid or liquid hydrocarbons may be considered as established. Solid hydrocarbons are recognised by their consistence and identified by their melting-points. Liquid unsaponifiable substances consist of hydrocarbons, belonging to one of the following three groups:—

(*a*) mineral oils, (*b*) rosin oils, (*c*) tar oils.

For the identification and approximate determination of these, *see* Lewkowitsch, Chem. Techn., [i.] 485.

The foregoing methods should enable the analyst to identify individual oils and fats and recognise them when mixed, and to determine approximately their relative proportion. In order to facilitate the problem, the following tables, arranged in the order of a practically natural system, should be consulted. For a number of examples which may be of assistance in the examination of complicated mixtures, cp. Lewkowitsch, [i.] chap. XI.

VEGETABLE

		Oils	Characteristics							
			Specific gravity		Solidifying point	Melting point	Saponification value	Iodine value	Reichert (R.) or Reichert-Meissl (R.-M.) value	Insoluble fatty acids +unsaponifiable
			°C.		°C.	°C.	KOH mg	Per cent.	$\frac{1}{10}$N.-KOH cc.	Per cent.
Drying oils		Perilla	20·0	0·9306	—	—	189·6	206	—	—
		Linseed	15·0	0·9315–0·9345	–27	–20	192–195	171–201	—	95·5
		Tung (*a*) Chinese (*b*) Japanese	15·0	0·9360–0·9432	below –17	—	193·0	150–165	—	92·2
		Candlenut	15·5	0·9256	—	liquid at –18	192·6	163·7	—	95·5
		Hempseed	15·0	0·9255–0·9280	–27	—	192·5	148·0	—	—
		Walnut; Nut	15·0	0·9250–0·9260	–27·5	—	195·0	145·0	—	95·4
		Safflower	15·5	0·9251–0·9280	—	—	186·6–193·3	129·8–149·9	1·54(R.-M.)	95·37
		Poppy seed	15·0	0·9240–0·9270	–18·0	—	195·0	133–143	0	95·2
		Sunflower	15·0	0·9240–0·9258	–18·5	—	193·5	119–135	—	95·0
		Soya bean	15·0	0·9242–0·9270	–8·0	—	192·7	137–141	—	95·5
Semi-drying oils		Cameline (German Sesame)	15·0	0·9200–0·9260	–18·0	—	188·0	135–142	—	—
	Cotton seed oil group	Pumpkin seed	15·0	0·9237	–15·5	—	188·4	123–130	—	96·2
		Maize; corn	15·5	0·9213–0·9255	–10 to –20	—	188–193	113–125	4–5(R.-M.)	93–96
		Madia	15·0	0·9285	–12·0	—	192·8	117–119	—	—
		Beech nut	15·0	0·9200–0·9225	–17·0	—	191–196	104–111	—	95·2
		Kapok	18·0	0·9199	—	—	181·0	116·0	—	94·9
		Cotton seed	15·0	0·9220–0·9250	—	3 to 4	193–195	108–110	—	95–96
		Sesamé	15·0	0·9230–0·9237	–5·0	—	189–193	103–108	1·2 (R.-M.)	95·7
		Curcas, purging nut	15·5	0·9204	–8·0	—	193·2	98–110	0·5 (R.-M.)	95·3
		Brazil nut	15·0	0·9180	0·4	—	193·4	90–106	—	—
		Croton	15·0	0·9500	–16·0	—	210–215	102–104	12–13·6 (R.-M.)	89·0
	Rape oil group	Ravison	15·5	0·9183–0·9217	–8·0	—	174–179	101–122	—	—
		Hedge mustard	15·0	0·9175	–8·0	—	174	105	—	—
		Rape (Colza)	15·5	0·9132–0·9168	–2 to –10	—	170–179	94–102	0·3	95·1
		Black mustard	15·0	0·916–0·920	–17	—	174	96–110	—	95·1
		White mustard	15·5	0·914–0·916	–8 to –16	—	170–174	92–97	—	96·2
		Radish seed	15·0	0·9175	–10 to –17·5	—	173–178	93–96	0·33(R.-M.)	95·9
		Jamba	15·0	0·9154	–10 to –12	—	172·3	95·4	—	—
Non-drying oils	Almond oil group	Cherry kernel	15·0	0·9234	–19 to –20	—	193–195	110–114	—	—
		Apricot kernel	15·5	0·9195	–14	—	192·5	96–108	0	95·4
		Plum kernel	15·0	0·9160–0·9195	–5 to –6	—	191·5	93·3–100·3	—	—
		Peach kernel	15·0	0·918–0·9215	below –20	—	192·5	93–109	—	—
		Almond	15·0	0·9175–0·9195	–10 to –20	—	191	93–97	—	96·2
	Olive oil group	Arachis (ground nut	15·0	0·9170–0·9209	–3 to 0	—	190–196	83–100	—	95·8
		Hazel nut	15·0	0·9146–0·9170	–17	—	192	83–90	0·99(R.-M.)	95·6
		Olive	15·0	0·916–0·918	–6 to 2	—	185–196	79–88	0·3	95·0
		Olive kernel	15·0	0·9184–0·9191	—	—	183	87·4	—	—
		Ben	15·0	0·9120–0·9198	0	—	—	82·0	—	—
	Castor oil group	Grape seed	15·0	0·935	–10 to –13	—	178·5	96·0	0·46(R.-M.)	92·13
		Castor	15·5	0·9600–0·9679	–10 to –18	—	183–186	83–86	1·4	—

ILS.

Refraction		Acetyl value	Variables		Characteristics of Fatty Acids									
Butyro-refractometer			Acetyl value	Acid value	Specific gravity		Solidifying point		Melting point	Neutralisation value	Iodine value		Refraction	
C.	Scale division			KOH mg.	°C.		°C.	Titre °C.	°C.	KOH mg.	Total fatty acids	Liquid fatty acids	°C.	
—	—	—	—	—	—	—	—	—	−5	197	210·0	—	—	—
0	84–90	—	3·98	0·8–8·4	15·5	0·9233	13–17	19·4–20·6	17–21	197	179–182	190–201	60	1·4546
0	72·5	—												
—	—	—	—	7·6–12	—	—	31–34	37·2	31 ; 43·8	188·8	144–159	—	—	—
5	76·0	—	9·86	8·1	—	—	15·0	—	20–21	—	—	—	—	—
—	—	—	—	—	—	—	15·0	16·6	18–19	—	141·0	—	—	—
0	64·8	—	—	—	—	—	16·0	—	16–18	—	150·0	167	—	—
0	65·2	—	16·1	0·33–20	—	—	—	—	—	—	—	—	—	—
0	63·4	—	—	0·7–11	100	0·8886	16·5	16·2	20·5	199	139·0	150	60	1·4506
25	72·2	—	—	11·2	—	—	18·0	—	22–24	201·6	124–134	154·3	60	1·4531
—	—	—	—	4·5	—	—	24·0	—	28·0	—	119·0	—	—	—
—	—	—	—	—	—	—	14–13	—	18–20	—	136·8	165·4	—	—
5	70·2–72·5	—	—	—	—	—	24·5	—	28–29	197	—	—	—	—
—	—	—	7·5–8·75	1·7–20·6	—	—	16–14	—	18–20	198·4	119·5	140–144	—	—
—	—	—	—	—	—	—	20–22	—	23–26	—	120·7	—	—	—
—	—	—	—	—	—	—	17·0	—	23–24	—	114·0	—	—	—
—	—	—	—	—	—	0·9162	24–23	—	29·0	191	108·0	—	—	—
5	67·6–69·4	—	7·6–18	0	15·5	0·9206–0·9219	32–35	32–35	35–38	202–208	111–115	147–151	60	1·4460
5	68·0	—	—	0·23–66 (!)	—	—	23·5	22·9–23·8	26–32	200·4	110·45	129–136	69	1·4461
5	65·0	—	7·5	0·7–8·5	—	—	26·5–25·7	28	27·5–30·5	—	105·1	—	—	—
0	56·5										—			
—	—	—	—	—	—	—	31·1	—	28–30	—	108·0	—	—	—
7	77·5	—	19–32	—	—	—	16·7	19	—	201	111·5	—	—	
	73–74	—	—	4·8–12	100	0·8802	—	—	—	—	—	124·2	—	—
	70·5–71·5	—	—	—	—	—	—	—	—	—	—	—	—	—
5	68·0	—	14·7	1·4–13·2	100	0·8758	16·0	12–13	16–19	185	99–103	121–125	60	1·4991
0	59·5	—	—	1·36–7·35	—	—	15·5	—	16·0	—	109·6	—	—	—
0	58·5	—	—	5·4	—	—	—	—	15–16	—	95·3	—	—	—
0	57·5	—	—	14·5	—	—	15–13	—	20·0	—	97·1	—	—	—
—	—	—	—	—	—	—	16–11	—	19–21	173·9	96·1	—	—	—
—	—	—	—	—	—	—	15–13	—	19–21	189	109·0	124·7	—	—
5	66·6	—	—	0·64	—	—	0	—	3·4	194	103·0	111·5	—	—
—	—	—	—	0·55	—	—	15–13	—	20–22 3·5	200·5	103(!)	98·6	—	—
5	66·1–67·2	—	—	—	—	—	—	13–13·5	10–18	200·9	94–101	101·9	—	—
5	64·4	—	—	—	—	—	5·0	10·1–11·8	13–14	204	93–96·5	101·7	60	1·4461
5	66–67·5	—	—	1·5	100	0·8790	26·0	29·2	27·7–32	201·6	96–103	105–128	60	1·4461
—	—	—	3·2	—	—	—	19–20	—	22–24	200·6	90·3	91·3–97·6	—	—
5	62·4	—	10·64	1·9–50	100	0·8749	22–17	17·2–26·4	24–27	193	86–90	93·5–103·5	60	1·4410
—	—	—	—	2–3·5	—	—	—	—	—	—	—	—	—	—
—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
—	—	—	—	16·2	—	—	20–18	—	24·0	187·4	99·0	—	—	—
	78	146·7–150	—	0·14–14·61	15·5	0·9509	3·0	—	13·0	192·1	87–93	106·9	60	1·4546

VEGETABLE

Fat	Characteristics							
	Specific gravity		Solidifying point	Melting point	Saponification value	Iodine value	Reichert (R.) or Reichert-Meissl (R.-M.) value	Insoluble fatty acids + unsaponifiable matter
	°C.		°C.	°C	KOH mg	Per cent.	$\frac{1}{10}$N.-KOH c.c.	Per cent.
Laurel oil group [1]								
Laurel	15·0	0·9332	25·0	32–34	197·9	68–80	1·6	—
Palm oil group								
Mowrahseed oil Mahua butters	15·0	0·9175	36·0	42·0	188–192	50–62	—	94·76
Mowrah butter Illipé butter	100·0 (100=1)	0·8981	19–22	28–31	190–194	53–67	0·5–0·9 (R.-M.)	94·82
Macassar oil Kusum oil	15·0	0·9240	10·0	22·0	221·5	48–55	—	91·5
Palm oil	15·0	0·921–0·9245	—	27–42·5	196–202	51·5	0·5	94·97
Phulwara butter	100·0	0·8970	—	39·0	190·8	42·1	0·44	94·86
Myristica group								
Mace butter (Nutmeg butter)	15·0	0·945–0·996	41–42	38–51	154–191	40–52 (50–81)	1–4·2 (R.-M.)	—
Cacao butter group								
Shea butter (Galam butter)	15·0	0·9175	17–18	25·3	179–192	56·6	—	94·76
Mkanyi fat	15·0	0·9298	38·0	40–41	190·5	41·9	1·21 (R.-M.)	95·65
Malabar tallow	15·0	0·9150	30·5	36·5	188·7–192	38·2	—	0·2–0·44 (R.-M.)
Cacao butter	15·0	0·9500–0·976	23–21·5	28–33	193·55	32–41	0·2–0·8 (R.-M.)	94·59
Chinese vegetable tallow	15·0	0·9180	27–31	36–46	200·3	28–37	—	—
Kokum butter (Goa butter)	40·0 (15=1)	0·8952	37·6–37·9	41–42	187–191	33·6	0·1–1·5 (R.-M.)	95·1
Borneo tallow	—	—	—	35–42	—	(31 ?)	—	—
Cocoanut oil group								
Mocaya oil	—	—	22·0	24–29	240·6	24·63	7·0 (R.-M.)	—
Maripa fat	100·0 (15·5=1)	0·8686	24–25	26·5–27·0	270·5	17·35	4·45 (R.-M.)	88·88
Palm kernel oil Palm nut oil	15·0 (15·5=1)	0·9520	20·5	23–28	242–250	13–14	5–6 (R.-M.)	87·6–91·1
Cocoa-nut oil	40·0 (15·5=1)	0·9115	22–14	21–24	246–260	8–9·5	7–8·4 (R.-M.)	88·6–90
Dika fat group								
Dika Oil (oba oil, wild mango oil)	—	0·8200	34·8	41·6	—	31·1	—	—
Japan wax	15·0	0·9700–0·980	48·5–53	50–54	217–237·5	4·9–8·5	—	90·6
Myrtle wax	15·0	0·995	39–43	40–44	208·7	10·7	—	—

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[1] *Cp.* Lewkowitsch, Bulletin Société Chimique de

FATS.

		Variables		Characteristics of fatty acids									
Refraction		Acetyl value	Acid value	Specific gravity		Solidifying point		Melting-point	Neutralisation value	Iodine value		Refraction	
Butyro-refractometer													
°C.	Scale divisions		KOH mg.	°C.		°C.	Titre °C.	°C.	KOH mg	Total fatty acids	Liquid fatty acids	°C.	
—	—	—	26·3	—	—	—	15·1	—	—	81·8	—	—	—
—	—	—	34·56	—	—	38–40	40·3	45·0	—	56·6	—	—	—
40	52·1	—	—	—	—	—	—	—	—	—	—	—	—
—	—	—	6·2–35·4	—	—	—	51·6–53·2	52–55	191·6	50–58	103·2	—	—
—	—	18·0	24–200	100·0	0·8701	—	35·9–45·5	47–50	205·6	53·3	94·6	—	—
40	48·2	—	—	—	—	—	—	—	—	—	—	—	—
40	48–85	—	17–44·8	—	—	40·0	35·9	42·5	—	—	—	—	—
—	—	—	29·4	—	—	38·0	53·8	58·0	—	56–57·2	—	—	—
—	—	—	23·3	—	—	57·5	61·5	59–61·5	—	42.1	—	—	—
—	—	—	38·0	—	—	54·8	—	56·6	—	—	—	—	—
40	46–47·8	2·8	1·1–1·88	—	—	47–45	48·3	48–50	190·0	33–39	—	60	1·422
	—	—	2·2–7·5	—	—	—	45·2–53·5	53–57	182–208	30–39	—	—	—
25	1·4628	—	21·0	—	—	59·4	—	60–61	198·9	—	—	—	—
—	—	—	20·0	—	—	53·5–54	—	—	—	—	—	—	—
—	—	—	—	—	—	22–20	—	23–25	254·0	—	—	—	—
—	—	—	—	100·0 (15·5=1)	0·8230	25·0	—	27·5–28·5	—	12·15	—	—	—
40	36·5	1·9–8·4	8·36	—	—	—	20·5–25·5	25–28·5	258–264	12·0	—	60	1·4310
40	+ 34	0·9–12·3	5–50	98–99 (15·5=1)	0·8354	20–16	22·5–25·2	25–27	258–266	8·4–9·3	18·6	60	1·4295
—	—	—	19·6	—	—	—	—	—	—	—	—	—	—
—	—	27–31·2	7·33	98–99 (15·5=1)	0·8480	53·0–56·5	59·4	56–62	213·7	—	—	—	—
—	—	—	3–4·4	—	—	46·0	—	47·5	230·9	—	—	—	

France, 1909 (Conférence: Les Corps Gras), XLII.

ANIMAL

	Oils	Specific gravity		Solidifying point	Melting point	Saponification value	Iodine value	Reichert (R.) or Reichert-Meissl (R.-M.) value	Insoluble fatty acids + unsaponifiable matter
		°C.		°C.	°C.	KOH mg.	Per cent.	$\frac{1}{10}$N.-KOH c.c.	Per cent.
Fish oils	Menhaden	15·5	0·927–0·933	– 4	—	190·6	139–173	1·2	—
	Sardine	15	0·9330	—	—	—	161–193	—	94·5
	Japanese Sardine	15	0·9160	—	20–22	189·8–192·1	100–164	—	96–97
	Salmon	15·5	0·9258	—	—	182·8	161·4	0·55	95·02
	Herring	15·5	0·9202–0·939	—	—	171–194	123·5–142	—	95·64
	Stickleback	—	—	—	—	—	162·0	—	95·78
	Sturgeon	15	0·9236	—	—	186·3	125·3	—	—
	Sprat	15·5	0·9284	—	—	—	—	—	—
Liver oils	Cod liver	15	0·9210–0·9270	0 to –10	—	171·0–189	167	—	95·3
	Skate liver	15	0·9307	—	—	185·4	157·3	—	94·7
	Tunny liver	—	—	—	—	—	155·9	—	95·79
	Shark (arctic)	15	0·9163	—	—	161·0	114·6	—	86·9
	Coal fish	15	0·925	—	—	177–181	137–162	—	—
	Hake liver	15·5	0·9270	—	—	—	—	—	—
	Ray liver	15·5	0·9280	—	—	—	—	—	—
	Ling liver	15	0·9200	—	—	184·1	132·6	—	—
Blubber oils	Seal	15	0·9155–0·9263	–2 to –3	—	189–196	127–141	0·07–0·22	95·45
	Whale	15·5	0·9250	under –2	—	188·0	121–136	0·7–2·04	93·5
	Dolphin black fish								
	Body oil	15	0·9180	under –3	—	197·3	99·5	5·6	93·07
	Jaw oil	—	—	—	—	290	32·8	65·92	66·28
	Porpoise, Body oil	15	0·9258	–16	—	195	—	23·5	—
	,, Jaw oil	15	0·9258	—	—	254–272	22–50	47·77–65·8	70·23
Non-drying oils	Sheep's foot	15	0·9175	0–15	—	194·7	74·2	—	—
	Horses' foot	15	0·913–0·927	—	—	195·9	73·8–90	—	—
	Neat's foot	15	0·914–0·916	0–15	—	194·3	69·3–70·4	—	—
	Egg	15	0·9144	8–10	22–25	184·4–190·2	68·5–81·6	0·40–0·7 (R.-M.)	95·16

ANIMAL

	Fat	Specific gravity		Solidifying point	Melting point	Saponification value	Iodine value.	Reichert (R.) or Reichert-Meissl (R.M.) value	Insoluble fatty acids + unsaponifiable matter	Refraction Butyro-refractometer	
		°C.		°C.	°C.	KOH mg.	Per cent.	$\frac{1}{10}$N—KOH c.c.	Per cent.	°C.	Scale division
Drying fats	Ice bear	15	0·9256	—	—	187·9	147·0	—	—	—	—
	Rattlesnake	15	0·9217	—	—	210·9	105·6	—	—	—	—
Semi-drying fats	Blackcock	15	0·9296	—	—	201·6	121·1	2·1	—	—	—
	Hare	15	0·9349	17–23	35–40	200·9	102·2	1·59	95·4	40	49·0
	Rabbit, wild	15	0·9393	17–22	35–38	199·3	99·8	0·7	—	—	—
	Rabbit, tame	15	0·9342	22–24	40–42	202·6	67·6	2·8	95·5	40	49·0
	Wild duck	—	—	15–20	—	198·5	84·6	1·3	—	—	—
	Domestic duck	—	—	22–24	36–39	—	58·5	—	—	—	—
Non-drying fats	Horses' fat	15	0·9189	43–30	34–54	195–197	71–86	0·2–0·4	95–96	40	53·7
	Horse marrow fat	15	0·9204–0·9221	24–20	35–39	199·8	79·1	1·0	—	—	—
	Domestic goose	15	0·9274	18–20	32–34	193·1	67–71	0·98	95·0	40	50–50·5
	Wild goose	15	0·9158	18–20	—	196·0	99·6	0·2–0·3 (R.-M.)	—	—	—
	Lard: Hog, domestic	15	0·934–0·938	27·1–29·9	36–40·5	195·4	50–70	—	93–96	40	48·6–51·2
	Lard: Hog, wild	15	0·9424	22–23	40–44	195·1	76·6	0·68	—	—	—
	Beef marrow	15	0·9311–0·9380	31–29	37–45	199·0	55·4	1·1	—	—	—
	Bone	15	0·914–0·916	15–17	21–22	190·9	46–55·8	—	—	—	—
	Tallow, beef	15	0·943–0·952	35–27	45–40	193·2–200	38–46	0·25	95·6	40	49·0
	Tallow, mutton	15	0·937–0·953	36–41	44–45	192–195·2	35–46	—	95·5	—	—
Milk fat	Butter	15	0·926–0·940	20–23	28–33	227	26–38	12·5–15·2	86·5–89·8	40	41–42
	Stag	15	0·9670	39–48	49–52	199·9	20·5–25·7	1·66	—	40	44·5

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[1] European lards.

OILS.

Refraction		Variables		Characteristics of fatty acids									
Butyro-refractometer		Acetyl value	Acid value	Specific gravity		Solidifying point		Melting point	Neutralisation	Iodine value		Refraction	
°C.	Scale divisions		KOH mg.	°C.		°C.	Titre °C.	°C.	KOH mg.	Total fatty acids	Liquid fatty acids	°C.	
—	—	—	11·6	—	—	—	—	—	—	—	—	—	—
—	—	—	4–21	—	—	—	—	—	—	—	—	—	—
—	—	13·0	10–35	—	—	—	28·2	—	—	—	—	—	—
25	78	—	—	—	—	—	—	—	—	—	197·4	—	—
—	—	—	1·8–44	—	—	—	—	—	178·5	—	—	—	—
—	—	—	21	—	—	—	—	—	181·5	—	—	—	—
—	—	—	—	—	—	—	—	—	—	—	—	—	—
—	—	—	—	—	—	—	—	—	—	—	—	—	—
25	75	4–8	1–25	—	—	—	18·4–24·3	21–25	204–207	130·5–170	—	60	1·4521
—	—	10·6	—	—	—	—	—	—	—	—	—	—	—
—	—	—	0·2–34	—	—	—	—	—	177·0	—	—	—	—
—	—	11·9	—	—	—	—	—	—	—	—	—	—	—
—	—	—	1·26–1·68	—	—	—	—	—	—	—	—	—	—
—	—	—	—	—	—	—	—	—	—	—	—	—	—
—	—	—	—	—	—	—	—	—	—	—	—	—	—
—	—	—	11·0	—	—	—	—	—	—	—	—	—	—
—	—	16·5	1·9–40	—	—	—	15·5–15·9	22–23	193·2	—	—	—	—
25	70	—	0·5–37	100	0·8922	—	23·9	27·0	—	131·2	144·7	—	—
—	—	—	—	—	—	—	—	—	—	—	—	—	—
—	—	—	—	—	—	—	—	—	—	—	—	—	—
—	—	—	—	—	—	—	—	—	—	—	—	—	—
—	—	—	5·0	—	—	—	—	—	—	—	—	—	—
—	—	—	—	—	—	—	21·1	—	—	—	—	—	—
—	—	13·0	—	—	—	—	28·6	—	—	—	—	—	—
—	—	22·0	—	—	—	—	26·1–26·5	29·8–30·8	—	61·98–63·26	—	—	—
25	68·5	—	1·2	—	—	—	—	34–39	194·9	72·9	—	—	—

FATS.

Variables		Characteristics of fatty acids									
Acetyl value	Acid value	Specific gravity		Solidifying point		Melting-point	Neutralisation	Iodine value		Refraction	
	KOH mg	°C.		°C.	Titre °C.	°C.	KOH mg	Total fatty acids	Liquid fatty acids	°C.	
—	—	—	—	—	—	—	—	—	—	—	—
—	—	—	—	—	—	—	—	—	—	—	—
—	5·9	15·0	0·9374	25–28	—	30–33	199·3	120·0	—	—	—
—	2·73	15·0	0·9361	36–40	—	44–47	209·0	93·3	—	40	Butyro-ref. 36
—	7·2	15·0	0·9246	35–36	—	39–41	209·5	101·1	—	—	—
—	6·2	15·0	0·9264	37–39	—	40–42	218·1	64·4	—	40	Butyro-ref. 36
—	1·5	—	—	30–31	—	36–40	—	—	—	—	—
—	—	—	—	—	—	—	—	—	—	—	—
—	0–2·44	—	—	37·7	33·7	37·5–39·5	202·6	84–87	—	—	—
—	1·0	15·0	0·9182–0·9289	36–34	—	42–44	210·8–217·6	71·8–72·2	— —	— —	— —
—	0·59	15·0	0·9257	31–32	—	38–40	202·4	65·3	—	—	—
—	0·86	15·0	0·9251	33–34	—	34–40	196·4	65·1	—	—	—
2·6	0·54–1·28	99·0	0·8445	39·0	41–42	43–44	201·8	64·0	92·1[1]) — 90–106[2])	60 — 22	1·4395 Oleorefr. – 30
—	2·6	15·0	0·9333	32·5–33·5	—	39–40	203·6	81·2	—	—	—
4·2	1·6	15·0	0·9300–0·9399	37·9–38	—	44–46	204·5	55·5	—	—	—
11·3	29·6–53	—	—	28·0	—	30·0	200·0	55·7–57·4	—	—	—
2·7–8·6	3·5–50	100·0 (100=1)	0·8698	—	37·9–46·2	43–44	197·2	41·3	92·4	60	1·4375
—	1·7–14	—	—	41·0	40, 15–48·2	49–50	210·0	34·8	92·7	60	1·4374
1·9–8·6	0·45–35·38	37·75 (15·5=1)	0·9075	33–38	—	38–40	210–220	28–31	—	60	1·437
—	3·5	15·0	0·9685	46–48	—	50–52	201·3	23·6	—	—	—

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[2] American lards.

J. L.

END OF THE THIRD VOLUME.

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