ELECTROLYSIS
AND
ELECTROSYNTHESIS
OF
ORGANIC COMPOUNDS.

BY

DR. WALTHER LÖB,
h
Privatdocent in the University of Bonn.

AUTHORIZED TRANSLATION FROM THE AUTHOR'S
ENLARGED AND REVISED EDITION

BY

H. W. F. LORENZ, A.M., Ph.D.,
Graduate of the University of Berlin.

FIRST EDITION.

FIRST THOUSAND.

NEW YORK:
JOHN WILEY & SONS.
LONDON: CHAPMAN & HALL, LIMITED.
1898.

78666

ROBERT DRUMMOND, PRINTER. NEW YORK.

AUTHOR'S PREFACE TO THE AMERICAN EDITION.

In the two and a half years that have passed since the appearance of the first edition of the present work, the application of the electric current in organic chemistry has undergone such a marked development that the book in its original form could no longer claim to give an adequate idea of our present knowledge of organic electrolysis and electrosynthesis. During these last two years in particular a series of important researches which systematically invade this new field of chemistry have been brought out in rapid succession.

Since I am now engaged in the preparation of a new German edition, the desire of Dr. H. W. F. Lorenz to translate the book affords an excellent opportunity for presenting the revised and completed edition directly to his fellow countrymen. I hope that his excellent translation may also tend to draw the attention of his American colleagues to this broad and interesting field, and that electricity, possessing such a diversity of applications, may soon obtain a recognized position in organic chemistry. In the realization of this hope the author and translator see a rich reward for their efforts.

Dr. WALTHER LOB.

BONN, June, 1898.

TRANSLATOR'S PREFACE.

IN presenting this excellent little work, with the permission of the author, to the English-reading public, scarcely anything remains to be added to what Dr. Löb has already said in his prefaces to the German and American editions. He has read the manuscript and made the necessary changes and additions so as to have it correspond to the second German edition which is about to appear.

The translator has adhered as closely as possible to the original text. He has made some additions and added a table of contents and a complete index, which he thinks will enhance the value of the book.

To Dr. B. B. Boltwood of the Sheffield Scientific School of Yale University, who has had the kindness to revise the manuscript, grateful acknowledgments are due for his painstaking and valuable services.

SPRINGFIELD, OHIO,
November, 1898.

AUTHOR'S PREFACE TO THE FIRST GERMAN EDITION.

THE object of electrochemistry is, among others, that of performing, with the aid of the electric current, reactions which have up to the present been carried out by the employment of other forms of energy. Its very nature suggests the possibility of solving synthetical and analytical problems which have as yet remained unanswered. In this respect its province is both that of inorganic and organic chemistry. Experiments have recently been made for utilizing electricity in the latter. Few only of the many tasks presenting themselves have been undertaken. This book aims to give, as briefly as possible, a review of what has already been accomplished, and at the same time to create an interest in the performance of experiments on the electrolysis and electrosynthesis of organic compounds.

AACHEN,
Electrotechnical Laboratory
of the Polytechnic Institute.
November. 1895.

CONTENTS.

I.

ELECTROLYSIS AND ELECTROSYNTHESIS OF ALIPHATIC COMPOUNDS.

1. (*a*) Hydroxyl Compounds.

(*b*) Ketones.

(*c*) Acids.

EXPERIMENTS OF MILLER AND HOFER.

ELECTROSYNTHESES OF BROWN AND WALKER.

ELECTROSYNTHESES OF MULLIKEN AND WEEMS.

2. Cyanogen Compounds.

II.

ELECTROLYSIS AND ELECTROSYNTHESIS OF AROMATIC COMPOUNDS.

6. Electrolytic Oxidation of Nitro-Compounds.

7. Electrolysis of Alkaloids.

8. Camphor and Glucosides.

11. Electrolysis and Electrosynthesis with Alternating Currents.

INTRODUCTION.

WHILE the electrolysis of inorganic compounds has already obtained a recognized position in pure and applied science, the action of the electric current, as a productive means for carrying out the synthesis or decomposition of organic substances, has not given results which are entirely satisfactory. The reason for this lies in the great difficulty that is encountered in investigations aimed in this direction by the appearance of secondary, complicated processes in the cell, in contrast to the generally simple decompositions of inorganic compounds by the electric current. The very different conditions required for inorganic and organic electrolysis give a distinctive character to the history of these two branches. In inorganic electrolysis one investigation follows as a continuation of those preceding it. The later investigators stand upon the shoulders of their predecessors. A systematic and regular development is the result. The case is different in organic electrolysis. Difficulties which were seldom surmounted have caused each investigator wishing to arrive at profitable results to attack the problem from a new standpoint. Its history, therefore, is not that of a gradual development, but consists of many, in great part incoherent, facts.

This characteristic is plainly reflected in the literature. Scattered in all possible periodicals are found researches which, although having the same end in view, frequently diverge considerably in their results. While engaged in investigations on organic electrolysis and electrosynthesis, I undertook to compile the literature on the subject as completely as possible, at first only for my own guidance. On the supposition that it may be of service to some fellow investigator I publish this résumé. Considering the difficulty of becoming acquainted with the entire literature of this field, this publication does not claim to possess an exhaustive completeness. I hope, however, that nothing of importance has been overlooked. While in inorganic electrolysis chief attention is given to the primary processes in the cell, in organic electrolysis the secondary actions claim our special interest, since the factors which are chiefly active in effecting the synthesis or decomposition of organic compounds, i.e., hydrogen, oxygen, etc., are the result of a primary decomposition of the organic electrolyte. In a systematic description of the results obtained it would therefore be better for the sake of clearness not to consider the actual electrolytic processes, but to make a division, according to the final chemical products, into oxidation, reduction, substitution or addition, and condensation reactions. But here we are confronted by the difficulty that frequently several different processes occur at the same time, making the indicated classification difficult to accomplish. I regard it as the simplest method to treat the subject in accordance with the chemical character of the electrolytes.

ELECTROLYSIS AND ELECTROSYNTHESIS OF ALIPHATIC COMPOUNDS.

I. (*a*) Hydroxyl Compounds.

The investigations on the behavior of the monatomic alcohols have been confined almost entirely to methyl and ethyl alcohol, both of which show complete analogy in their reactions. In those cases where platinum electrodes were used and similar results were obtained both with and without porous separating cells, the decompositions are almost without exception oxidation processes. Being in the pure state poor conductors, the alcohols require strong currents for their electrolysis. The addition of potassium carbonate or dilute acid increases the conductivity of the solution, but of course influences the results.

The manner in which the primarily formed decomposition products, oxygen and hydrogen, act in the simplest case, i.e., in aqueous solution, depends solely upon the chemical constitution of the electrolytes. It is evident, therefore, that in the electrolysis of aliphatic hydroxyl compounds, only oxidation products will appear. In fact hydrogen is evolved at the negative pole, while the greater part of the oxygen is absorbed.

The first attempts to electrolyze alcohols were confined to the action of the electric spark from an induction apparatus on the vapor of an alcohol. By thus treating *ethyl alcohol* M. Quet[1] and Perrot[2] obtained, besides some carbon, a substance which exploded on being heated, the chemical nature of which they were unable to determine. Perrot found that no water was formed in the decomposition of the alcohol; he was also unable to prove the presence of carbonic acid gas. Maquenne[3] obtained a gas which possessed a strong aldehydic odor, and contained hydrogen, ethane, ethylene, acetylene, carbon monoxide, and carbon dioxide.

The results obtained by the use of direct currents were much more satisfactory than the above. We are indebted to Renard,[4] Almeida and Dehérain, Jaillard,[6] and Habermann[7] for the most thorough experiments on this subject.

Methyl Alcohol.—The results obtained with methyl alcohol can be summed up as follows: Hydrogen being evolved, the oxidation products formed are:

---

[1] Comp. rend., **46**, 903.

[2] Comp. rend., **46**, 180.

[3] Bull. soc. chim., **37**, 298.

[4] Comp. rend., **80**, 105, 236.

[5] Comp. rend., **51**, 214.

[6] Comp. rend., **58**, 203.

[7] Monatsch. Wien, **7**, 259.

1. In aqueous sulphuric acid solution: methyl formate, methylal, methyl acetate, acetic acid, and methyl-sulphuric acid, a little carbon dioxide and monoxide, but no formic aldehyde.

Renard considers the formation of acetic acid as due to reciprocal action between the alcohol and carbon monoxide,

$$CH_3OH + CO = CH_3.COOH.$$

Jahn[1] thinks the formation must be traceable to the presence of ethyl alcohol.

2. In aqueous solution, on the addition of potassium acetate (Habermann): besides carbon dioxide and carbon monoxide, methane and potassium methylcarbonate.

3. Without a solvent, by itself or with the addition of a little alkali: chiefly potassium carbonate; also hydrogen, oxygen, carbon monoxide, and carbon dioxide.

Ethyl Alcohol.—In the case of this alcohol the more important results have been obtained by the investigators above mentioned. Schönbein[2] and Becquerel[3] later also carried out some investigations on the same subject. The results of the researches are, in general, that the final products formed are the following:

---

[1] Jahn, Grundriss d. Elektrochemie, 1894, p. 291.

[2] Tommasi, Traité d'Electrochimie, 1889, p. 726.

[3] Comp. rend., **81**, 1002, and various other places in the same journal; Tommasi, Traité d'Electroch., 1889, p. 726.

1. In sulphuric acid solution: aldehyde, acetic ester, formic ester, ethylidene oxy-ethyl ether  $\left(CH_3—CH\begin{matrix}\diagup OH\\ \diagdown OC_2H_5\end{matrix}\right)$ (Renard) and ethyl-sulphuric acid.

2. Almeida and Dehérain state that in the electrolysis of a nitric acid solution they observed, in addition to these oxidation products, carbonaceous derivatives of ammonia at the negative pole.

3. In hydrochloric acid solution,[1] chlor-acetic acids occur in addition to the corresponding oxidation products (Riche[2]). Habermann, on electrolyzing the alcohol in alkaline solution, obtained, besides carbon dioxide, an aldehyde resin (Lüdersdorf[3] and Connel[4]) from which he isolated a body closely related to cinnamic aldehyde. In aqueous solution, on the addition of potassium acetate, the alcohol was split up into ethane, potassium ethyl-carbonate, carbon dioxide, and acetic ester. Also with *propyl and butyl alcohols*, to which potassium acetate had been added, analogous results were obtained by Habermann.

Exact statements regarding the strength of the current are in no case given. In consideration of the

---

[1] Pogg. Ann., 19, 77.
[2] Tommasi, Traité d'Electrochimie, 1889, 728.
[3] Pogg. Ann., 19, 77.
[4] Pogg. Ann., 36, 487; Phil. Mag., 18, 47.

importance of these data and the fact that the result of the electrolysis is dependent upon the density and potential of the electric current and the influence of the dissociative power of solutions, a strong incentive for repeating the experiments, with the help of modern scientific and technical advancement, is offered to the investigator.

Iodoform.[1]—The complete conversion of ethyl alcohol into iodoform by electrolysis in alkaline iodide solution is a process now made use of in industrial chemistry. The course of the reaction is illustrated by the equation (K. Elbs[2] and Herz[3])

$$CH_3CH_2OH + 10I + H_2O = CH_{\cancel{2}}I_3 + CO_2 + 7HI.$$

The electrolysis is best performed as follows: A solution of 10–15 g. calcined soda and 10 g. potassium iodide in 100 cc. water and 20 cc. alcohol is placed in a porous earthenware cylinder with platinum anode. The cathode, of nickel, is surrounded by a strong solution of sodium hydroxide. The electrolysis is carried out at a temperature of 70° C., with a current density at the anode of 1 amp. per 100 sq. cm., and is continued for 2–4 hours.

After standing for several hours iodoform crystallizes from the solution, the current yield being 60–

---

[1] German Patent, 29,771.

[2] Ztschr. f. Elektroch., 4, 113.

[3] Oettel, Elektroch. Uebungsaufg., 1897, p. 53.

70%. Sodium iodide remains in the mother-liquor as the principal secondary product.

Chloroform and *Bromoform* are formed if the chloride or bromide of the alkalies is used (comp. Elbs and Herz,[1] who deny this*). Analogous to these substitution reactions is the formation of *aristol*,[2] a di-thymol-di-iodide, as made by Messinger and Vortmann,[3] by the electrolysis of thymol with the addition of potassium iodide. Similar to this also is the preparation of *nosophene*, a tetra-iodo-phenol-phthaleïn (Classen and Löb[4]).

Glycol.—Of diatomic alcohols only glycol seems to have been the subject of investigation. Renard[5] observed in the electrolysis of a sulphuric acid solution of glycol, besides the formation of hydrogen, carbon monoxide, carbon dioxide, and oxygen, that trioxy-methylene, glycolic acid, formic acid, and a substance isomeric with glucose were present in the solution.

Ethylene Glycol under similar conditions gives the same products (Renard[6]).

Glycerine.—Renard[6] also investigated the behavior

---

[1] Zeitschr. Elektroch., **4**, 118.

[2] German patent, 64405.

[3] German patent, 64405; Lum. él., **52**, 226.

[4] Chem. Ber., **28**, 1603.

[5] Traité d'Electrochimie p. Tommasi, 1889, p. 730.

[6] Ann. chim. phys., [5] **17**, 303, 313; Comp. rend., **81**, 188; *ibid.*, **82**, 562.

---

* Translator.

of glycerine. In the electrolysis of a dilute sulphuric acid solution he obtained besides the gases, hydrogen, oxygen, carbon monoxide and dioxide,—trioxymethylene, formic acid, acetic acid, glyceric aldehyde, and a body to whose barium compound he gave the formula $(C_3H_3O_4)_2Ba$ (glyceric acid?).

Further electrolysis of *glyceric aldehyde* gave the ordinary oxidation products, and, as in the case of glycol, a substance closely related to ordinary glucose. Bartoli and Papasogli[1] repeated these experiments, varying the material of the electrodes, and obtained the following results:

Carbon anode and platinum cathode gave trioxymethylene, formic acid, glyceric acid, a substance similar to glucose, and a resin.

Graphite and platinum electrodes yielded the same products, but a larger per cent of formic acid was formed on using the latter. The alkaline solution of glycerine, electrolyzed by Stone and McCoy,[2] gave condensation products of glyceric aldehyde similar to those which have been obtained in the synthesis of glucose. Glyceric acid also was found present.

Tommasi[3] electrolyzed a sulphuric acid solution of *chloral hydrate* and was able to prove the presence of hydrochloric acid. On working with isolated elec-

---

[1] Gazz. chim., **13**, 287.
[2] Amer. Chem. Journ., **15**, 656.
[3] Tommasi, Traité d'Electrochimie, 1889, p. 741.

trodes, an abundance of chlorine was given off at the cathode and acetic aldehyde collected at the anode.

Hexatomic Alcohols.—The decomposition phenomena of hexatomic alcohols and sugars are similar to those of glycerine. A part is completely oxidized either to carbon monoxide and carbon dioxide or to formic acid, while the remainder, on timely interruption of the experiment, gives lower oxidation products which vary with the configuration of the alcohols and sugars.

Mannite.[1]—In the electrolyzed fluid from mannite Renard obtained formic acid, trioxy-methylene, oxalic acid, a sugar isomeric with glucose, and an acid, $C_6H_8O_8$, which he regarded as the aldehyde of saccharic acid. He could detect no mannonic acid.

Grape Sugar.—This sugar, investigated by Renard, on being subjected to the action of the current broke up into carbon monoxide, carbon dioxide, formic acid, trioxymethylene, and saccharic acid.

Cane Sugar.—Brester[2] found on electrolyzing cane sugar that the solution turns strongly acid and possesses reducing properties, very little carbon dioxide being given off. He was not able to determine the nature of the substance which he isolated by distillation and which was free from formic and acetic acid. On further electrolysis it gave the usual final oxida-

---

[1] Ann. chim. phys., [5] 17, 289.

[2] Bull. soc. chim., 8, 23.

tion products. The experiments made by the same author on the electrolysis of *dextrine*, *gum arabic*, *collodion*, and *starch* gave no noteworthy results.

The general impression gained from the investigations of the alcohols, aldehydes, and alcohol-aldehydes mentioned, is that the general reaction is one of successive oxidation. The electrolytic oxygen gradually oxidizes the substances, the final product being carbon dioxide. Intermediate products are formed, their quantity depending upon the duration of the electrolysis. In following these processes it is of especial importance whether the oxidation products are soluble or insoluble and whether they are electrolytes or not. The possibility of isolating the products which are formed depends on these properties. If the product of oxidation first formed is a good conductor of the electric current it will, of course, undergo further oxidation; if it is insoluble it escapes the further action of the current. In order, therefore, to obtain a comprehensive idea of the decomposition of organic substances it is necessary immediately to withdraw the electrolyzed fluid from the action of the current. Miller and Hofer[1] accomplished this by allowing the solution to flow slowly over the electrodes. But very few experiments of this nature have been made. Mannite serves as an illustration of such an oxidation process. As already mentioned, it

---

[1] Chem. Ber., **27**, 461.

breaks up into formic acid, oxalic acid, a sugar, and an acid, $C_6H_8O_8$. The reactions are probably the following:

$$C_6H_{14}O_6 \rightarrow C_6H_{12}O_6 \rightarrow C_3H_6O_3 \rightarrow C_6H_8O_8$$
$$\rightarrow CH_2O_2 \rightarrow C_2H_2O_4 \rightarrow CO \rightarrow CO_2.$$

Whether any intermediate products have escaped observation, and the nature of these, can naturally be determined only by new and careful experiments.

Since organic substances, apart from acids, bases, and salts, are poor conductors of electricity, the addition of a mineral acid to an organic electrolyte produces a complication of conditions, since oxidation reactions occur in combination with substitutions. After it is once made possible to establish and regulate the oxidizing and reducing effects of the current, the field of substitution reactions is the one which offers the most promising results.

(*b*) Ketones.

Acetone.—Acetone has been electrolyzed by Mulder,[1] Riche,[2] and Friedel.[3] The electrolysis of an acetone solution acidified with sulphuric acid gave carbon dioxide, acetic acid, and formic acid. In hydrocloric acid solution *mono-chlor-acetone* and *di-chlor-acetone* could be isolated; in hydrobromic acid

---

[1] Jahresber. f. Chemie, 1859, p. 339.

[2] Comp. rend., 49, 176.

[3] Ann. Chem. Phar., 112, 376.

solution *mono-brom-acetone*. Wilde[1] investigated the action of the electric spark on acetone vapor in Torricelli's vacuum. Acetylene was formed in the gas mixture and carbon was deposited on the sides of the vessel. According to Maquenne[2] acetone vapor is decomposed by the electric discharge into hydrogen, ethane, and carbon monoxide, a small quantity of acetylene and carbon dioxide being formed. On the other hand, Hemptinne[3] syntheticized both acetone and aldehyde by passing a silent electric discharge through a mixture of carbon monoxide and ethane, the gases being kept cool by the use of a freezing mixture.

Isonitroso-acetone.—Ahrens and Meissner[4] tried to reduce this compound electrolytically to amido-acetone. They, however, obtained dimethyl-pyrazine, ketine, $C_6H_8N_2$, in small quantity.

Acetyl-acetone.[5] — Acetyl-acetone in an alcoholic solution on electrolysis gave tetracetyl-ethane.

(*c*) Acids.

The investigation of acids has been much more extensive than that of those classes of bodies which have been thus far discussed. The conditions here

---

[1] Bull. soc. chim., [2] 5, 267.

[2] Bull. soc. chim., 39, 306; *ibid.*, 40, 60.

[3] Bull. Acad. roy. Belge, [3] 34, 269.

[4] Chem. Ber., 30, 532.

[5] Ahrens, Handb. d. Chemie, p. 482 (1896).

are much simpler, since the acids are mostly good conductors of electricity, both in solution and in the free condition, as well as in the form of salts. Kolbe's[1] classical investigations on the electrolysis of organic compounds, in which he demonstrated the formation of the hydrocarbons from the acids, are the foundation of later investigations. A continuation along the same line are the researches of Kékulé,[2] Brown and Walker,[3] Mulliken,[4] and Weems.[5] They employed the electric current as a valuable means for effecting the synthesis of a complete series of compounds.

For the sake of clearness the researches here given will be arranged chiefly in accordance with their chemical characteristics.

Formic Acid.—Although up to this point, in the investigations mentioned, it has been necessary to consider chiefly oxidizing reactions, we now enter upon a field comprising those reactions which involve the process of reduction, and in which compounds of a relatively high stage of oxidation are the starting-points. The electrolytic formation of formic acid from oxalic acid, as observed by Royer,[6] is a reduction reaction of this nature.

---

[1] Lieb. Ann., 69, 257.

[2] Lieb. Ann., 131, 79.

[3] Lieb. Ann., 261, 107.

[4] Amer. Chem. Journ., 15, 523.

[5] Amer. Chem. Journ., 16, 569.

[6] Comp. rend., 70, 731; Bull. soc. chim., [2] 14, 226.

Wilde[1] found that the action of the electric spark on gaseous mixtures of oxygen and alcohol, hydrogen and carbon dioxide, methane and carbon dioxide produced formic acid. Losanitsch and Jovitschitsch[2] obtained formic acid by treating carbon monoxide or dioxide and water in Berthelot's ozone apparatus. The behavior of the acid itself as well as its salts has been made the subject of thorough investigation carried out chiefly by Brester,[3] Renard[4] and Bourgoin,[5] Bartoli and Papasogli.[6]

The progress of the decomposition is accompanied by the evolution of carbon dioxide and oxygen at the positive pole and hydrogen at the negative pole. The quantitative relations of the decomposition products vary with the concentration of the solution and the density of the current. The reactions occur according to the following equations:

$$\begin{aligned}&HCOOH = HCOO + H,\\&HCOO + HCOO = H_2 + 2CO_2,\\&2HCOO + H_2O = 2HCOOH + O.\end{aligned}$$

It is therefore theoretically impossible to effect the complete decomposition of the formic acid present. In the electrolysis of sodium formate, carbon dioxide

---

[1] Bull. soc. chim., [2] 5, 267.

[2] Chem. Ber., **30**, 135.

[3] Zeitschr. f. Chemie, 1866, p. 60.

[4] Ann. chim. phys., [5] **17**, 289.

[5] Ann. chim. phys., [4] 14, 157.

[6] Gazz. chim., **13**, 22 and 88.

and formic acid are in fact always formed at the positive pole and hydrogen and sodium hydroxide at the negative pole. The discussion of the other salts is unnecessary since their behavior is quite analogous.

Formyl Chloride (?) has been obtained by Losanitsch and Jovitschitsch from a mixture of carbon monoxide and hydrochloric acid by the action of the electric discharge, and by a like method *formamide* has been prepared from carbon monoxide and ammonia.

Acetic Acid.—Acetic acid is formed in the electrolysis of methyl and ethyl alcohol when the electric spark is passed through a mixture of alcohol vapor and oxygen, or methane and carbon dioxide. On the other hand acetic acid can be converted into alcohol by electrolytic reduction, if the acid is substituted in place of nitric acid in the porous cup of a Bunsen element.[1]

Glacial acetic acid is a poor conductor of electricity. According to Lapschin and Tichanowitsch[2] its decomposition when effected with the use of 900 Bunsen elements yields at the anode, carbon monoxide and carbon dioxide; at the cathode, carbon and a small quantity of a gas the nature of which could not be established. Bourgoin,[3] on electrolyzing the dilute

---

[1] Tommasi, Traité d'Electrochimie, 724; Comp. rend., **69**, 1374; *ibid.*, **70**, 731; Chem. Ber., **29**, 1390.

[2] Neue Peters. Acad. Bull., **4**, 81.

[3] Ann. chim. phys., [4], **14**, 157.

acid, observed hydrogen at the negative pole and oxygen, carbon dioxide, and traces of carbon monoxide at the positive pole.

The reactions involved in the decomposition of the *alkali salts* are more interesting. Kolbe,[1] on decomposing a concentrated solution of potassium acetate, obtained a hydrocarbon in addition to other decomposition products. According to the idea then prevailing acetic acid underwent oxidation in the sense that it was thereby changed into carbon dioxide and methyl, both of which appeared at the positive pole, while at the negative pole only hydrogen was evolved, and a part of the methyl was oxidized to methyl oxide. The hydrocarbon evolved was in fact ethane, which always accompanies the decomposition of potassium acetate solutions, while the other decomposition products formed vary with the density of the electric current and the temperature of the solutions. Thus Kolbe identified methyl ether and methyl acetate in the solution, while Bourgoin observed no decomposition products other than carbon monoxide and dioxide. Jahn,[2] who employed currents of very low electrode density, obtained by the electrolysis of an almost saturated solution of sodium acetate only carbon dioxide, ethane, and hydrogen. The formation

---

[1] Lieb. Ann., **69**, 279.

[2] Grundriss d. Elektrochemie, 1895, p. 292.

of ethane can be explained by assuming either the direct oxidation of the acetic acid,

$$\left.\begin{matrix}\mathrm{CH_3COOH}\\ \mathrm{CH_3COOH}\end{matrix}\right\} + \mathrm{O} = \mathrm{C_2H_6} + 2\mathrm{CO_2} + \mathrm{H_2O},$$

or the decomposition of the anion,

$$\left.\begin{matrix}\mathrm{CH_3COO}\\ \mathrm{CH_3COO}\end{matrix}\right\rangle = \mathrm{C_2H_6} + 2\mathrm{CO_2}.$$

Kékulé[1] advanced a theory based on the phenomena of decomposition, and from this deduced certain formulæ which make it possible to predict the nature of the products resulting from the electrolysis of monobasic and dibasic acids of the fatty acid series.

Since, however, the reaction is influenced by the slightest variation of conditions, his formulæ hold good only in the case of the decomposition of perfectly pure substances, a condition seldom met in practice.

Löb[2] is in favor of accepting the theory advanced by Kékulé, who in the case of phthalic and acetic acids sought by experiment to prove the intermediate formation of the anhydride, while Schall[3] assumes the formation of an acid superoxide:

$$\mathrm{R.COO—} + \mathrm{R.COO—} = \left.\begin{matrix}\mathrm{R.COO}\\ \mathrm{R.COO}\end{matrix}\right\rangle$$

$$\left.\begin{matrix}\mathrm{R.COO}\\ \mathrm{R.COO}\end{matrix}\right\rangle = \mathrm{R.R} + 2\mathrm{CO_2}.$$

---

[1] Lieb. Ann., **131**, 79.

[2] Ztschr. f. Elektrochemie, 3, 42.

[3] Ztschr. f. Elektrochemie, 3, 83.

This conclusion is drawn from the observed fact that the dithionic acids upon the electrolysis of their alkali salts give acid supersulphides which correspond with the superoxides:

$$\mathrm{R.CSS}\text{—} + \mathrm{R.CSS}\text{—} = \left.\begin{array}{l}\mathrm{R.CSS}\\ \mathrm{R.CSS}\end{array}\right>.$$

In contrast to the acid superoxides, the acid supersulphides are stable compounds.

The reactions and the corresponding electrolytic products which occur in the electrolysis of the alkali salts of the fatty acids were thoroughly investigated by Rohland,[1] who electrolyzed the alkali salts of capronic, caprylic, and heptylic acids.

Potassium Capronate gave normal decane, $C_{10}H_{22}$;

Potassium Caprylate analogously gave normal tetradecane, $C_{14}H_{30}$; while

Potassium Heptylate gave besides dodecane, $C_{12}H_{26}$, a small quantity of an unsaturated hydrocarbon, probably octylene, C_8H_{16}.

The fatty acids with ethylene bond behave differently. In their case no smooth reaction occurs. The electrolysis of *undecylenic acid*, for example, yielded a mixture of several unsaturated hydrocarbons, a result similar to that obtained in the investigation of *potassium oleate*, the only outcome of which was a mixture of various compounds which could not be separated.

---

[1] Ztschr. f. Elektrochemie, 4, 120.

Kolbe and Kemp[1] obtained by the electrolysis of a concentrated potassium acetate solution, at the anode, hydrogen, methyl-acetic ester, methyl-formic ester, ethane, ethylene, and carbon dioxide; at the cathode, hydrogen and potassium hydroxide. In an alkaline solution of the same salt Bourgoin[2] obtained a mixture of sodium formate, but so far as hydrocarbons were concerned could only prove the presence of ethane and ethylene.

Besides the alkali salts, the copper, lead, manganese, and uranium salts were subjected to electrolysis by Dupré,[3] Wiedemann,[4] Despretz,[5] and Smith.[6] The metals were precipitated at the anode, a portion of the manganese and lead in the form of superoxides.

According to Bauer,[7] in the electrolysis of the acetic acid salts of metals possessing a constant valence (K, Na, NH_4, Mg, Ca, Zn, and Al), when cold, moderately dilute solutions and relatively high current densities are employed, gases consisting chiefly of ethane and carbon dioxide are given off at the anode. No inconsiderable quantities of ethylene are formed in the case of calcium, magnesium, and potas-

---

[1] Journ. prakt. Chemie, [2] 4, 46.

[2] Ann. chim. phys., [4] 14, 157.

[3] Archiv. ph. nat., 35, 998.

[4] Pogg. Ann., 104, 162.

[5] Comp. rend., 45, 449.

[6] Chem. Ber., 13, 151.

[7] Dissert. Giessen, 1897; Wied. Beibl., 21, 601.

sium acetate solutions. Very small amounts on the contrary result from the electrolysis of the sodium, ammonium, and zinc salts. At the boiling temperature the gases consist mostly of oxygen and contain in addition a little carbon dioxide and a very small quantity of ethane. Metals with several valences change to the higher valence.

Monochlor-acetic Acid, according to Kolbe,[1] breaks up on electrolysis into hydrochloric and acetic acids, as a result of the action of the electrolytic hydrogen:

$$CH_2Cl.COOH + 2H = CH_3COOH + HCl.$$

Trichlor-acetic Acid gives the same products and in addition also, according to Elbs, tri-chlor-methyl ester, $CCl_3.CO_2.CCl_3$.

Cyan-acetic Acid.—Moore[3] obtained at the positive pole carbon dioxide besides traces of nitrogen, and ethylene cyanide; at the negative pole hydrogen and potassium hydroxide, bodies analogous to the decomposition products of sodium acetate.

Thio-acetic Acid.[4]—This compound gives acetyl disulphide.[5] The acid is formed at the positive pole if a solution of pure acetic acid which has been saturated with hydrogen sulphide is subjected to elec-

---

[1] Tommasi, Traité d'Electrochimie, 1889, p. 750.

[2] Journ. prakt. Chemie, [2] 47, 1104; *ibid.*, [2] 55, 502.

[3] Chem. Ber., 4, 519.

[4] Zeitschr. f. Elektroch., 3, 42.

[5] Chem. Ber., 3, 297.

trolysis and a slow current of the gas is conducted through the solution during the operation.

Propionic Acid.—The electrolysis of a concentrated solution of sodium propionate was carried out by Jahn[1] and yielded, when the density of the currents employed was not too great, hydrogen, ethylene, and carbon dioxide, but no butane.

Butyric Acid.—The two butyric acids were electrolyzed by Bunge.[2] With isobutyric acid it was not possible to obtain hexane, but the normal acid yielded some butane besides larger quantities of propylene.

The great influence of concentration, current density, and especially of temperature is again emphasized in the researches of Bunge. The various conditions which were followed by the individual investigators explain sufficiently the frequent differences occurring in the results. The repetition of an electrolytic experiment is only possible when an exact statement of all the factors is given. This requirement is, however, entirely omitted in the published experiments above mentioned.

Careful and reliable investigations on the electrolysis of the potassium salts of *butyric and isobutyric acids* have been published by M. F. Hamonet.[3] His

---

[1] Grund. d. Elektroch., 1895, 293.

[2] Journ. d. russ. phys. Gesellsch., 1, 525.

[3] Comp. rend., 123, 252.

apparatus consisted of a copper beaker 23 cm. high and 8 cm. in diameter, which served as the cathode. A porous earthenware cell, which contained the anode and was closed with a three-hole stopper, stood in the beaker. Through the perforations of the stopper passed a thermometer, a gas-conducting tube, and the electric conductor leading to the anode. The anode used in some experiments was a platinum wire 1 mm. in diameter and 2 m. in length, in others a platinum cylinder 14 cm. high and 2.5 cm. in diameter. This variation of current density was, however, of secondary importance. Solutions of the potassium salts having a specific gravity of 1.08–1.12 were used as the electrolyte. Current strengths of 4–5 amperes were reached with a difference of potential at the poles of 6–8 volts. The electrolysis was continued 2–3 hours, the solution being kept cool. The following results were obtained:

Potassium Butyrate,

$$CH_3.CH_2.CH_2.COOK.$$

225 g. propylene bromide ($CH_3.CHBr.CH_2Br$), corresponding to 47 g. propylene ($CH_3 - CH = CH_2$); 18 g. isopropyl alcohol ($CH_3.CHOH.CH_3$); 4.5 g. butyric isopropyl ester ($CH_3.CH_2.CH_2.COOCH(CH_3)_2$); 4.5 g. complicated products, which became resinous when the ester was saponified by boiling with alkali hydroxide.

Hexane ($CH_3.CH_2.CH_2.CH_2.CH_2.CH_3$) and propyl alcohol ($CH_3.CH_2.CH_2OH$) could not be detected. They could, therefore, only have been formed in extremely small quantities. The very remarkable formation of isopropyl alcohol can only be explained by assuming the hydration of propylene or the molecular rearrangement of the group $CH_3.CH_2.CH_2$—.

Potassium Isobutyrate,

$$(CH_3)_2 : CH.COOK.$$

This salt gave 300 g. propylene bromide ($CH_3.CHBr.CH_2Br$), equivalent to 62 g. propylene ($CH_3.CH : CH_2$); 20 g. isopropyl alcohol ($(CH_3)_2:CHOH$); over 12 g. isobutyric isopropyl ester,

$$((CH_3)_2 : CH.COOCH(CH_3)_2);$$

6 g. of an oil having a pepper-like odor and boiling at 130–160°.

In this case also the paraffine isohexane $(CH_3)_2:CH.CH:(CH_3)_2$ was not formed.

Hamonet draws the following conclusions from these results:

1. The equation

$$2C_nH_{2n+1}.COO— = C_nH_{4n+2} + 2CO_2,$$

representing the reaction in the electrolysis of the alkali salts of the fatty acids, which since the experiments of Kolbe has been almost universally accepted, can no longer claim to represent the true fact in the case, since no or almost no paraffines result from this operation.

2. The olefine C_nH_{2n} sometimes predominates among the products formed by the electrolysis of the alkali salts of the fatty acids,

$$C_nH_{2n+1}COOK.$$

The general nature of the reactions is represented by the following equation:

$$2C_nH_{2n+1}.COO— = C_nH_{2n+1}.COOH + C_nH_{2n} + CO_2.$$

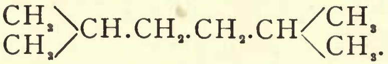
3. An alcohol with n carbon atoms is always formed if the acid contains $(n + 1)$ carbon atoms. The structure of the alcohol is not always that which is expected. Frequently more than a third of the energy of the current is expended in the formation of the alcohol. Whether the alcohol is generated by the saponification of the ester present, according to the equation

$$2C_nH_{2n+1}.COO— = C_nH_{2n+1}.COOC_nH_{2n+1} + CO_2,$$

or whether it is formed by the hydration of the olefines, $C_nH_{2n} + H_2O = C_nH_{2n+1}OH$, is still uncertain.

To decide this question a more thorough investigation of the substances resulting from the electrolysis of compounds possessing higher molecular weights is required.

Valeric Acid.—Kolbe[1] electrolyzed the potassium salt and obtained as the chief product octane (diisobutane),



$$\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>CH.CH_2.CH_2.CH<\!\!\begin{matrix}CH_3\\CH_3.\end{matrix}$$

Besides this there appeared as decomposition products water, carbonic acid gas, butylene, and the butyl ester of valeric acid.

Brester,[2] who performed his experiments under different conditions, obtained at the anode a gaseous mixture of carbon dioxide, butylene, and oxygen.

Capronic Acid.—A concentrated solution of the potassium salt gave decane and traces of the amyl ester of capronic acid, both of which are normal decomposition products. The electrolyses were made by Brazier and Gossleth,[3] by Würz,[4] and by Rohland.

Œnanthylic Acid.—The normal acid was electrolyzed by Brazier and Gossleth[5], under conditions similar to those for capronic acid, and gave two hydrocarbons, $C_{12}H_{26}$ and $C_{12}H_{24}$, in addition to hydrogen, potassium carbonate and acid potassium carbonate.

---

[1] Lieb. Ann., **69**, 257.

[2] Jahresber. f. Chem., 1859, p. 86; *ibid.*, 1866, p. 87.

[3] Tommasi, Traité d'Electroch., 1889, p. 757.

[4] *Ibid.*

[5] *Ibid.*

Oxalic Acid.—The deportment of the saturated solution of the free acid on electrolysis was determined by Brester,[1] Bourgoin,[2] Balbiano and Alessi,[3] Bunge,[4] and Renard.[5] The general result was that oxygen and carbon dioxide were obtained at the anode and hydrogen at the cathode. It is possible to completely oxidize oxalic acid to carbon dioxide. On this property depends the great importance of oxalic acid in quantitative electrolytic analysis, into which it has been introduced by Classen.[6]

The ability of ammonium oxalate to form soluble double salts with many difficultly soluble or insoluble metallic salts is in accord with the favorable conduct of the acid on electrolysis, by which operation it may be entirely removed from the solution in the form of gas. The reducing effects of the current on oxalic acid were also observed. Thus on electrolyzing both the free acid and its sodium salt Balbiano and Alessi were able to prove the presence of glycolic acid.

The oxidation is not complete if the electrolysis is conducted in the cold solution, carbon monoxide as well as carbon dioxide being then formed at the positive pole.

---

[1] Jahresber. f. Chemie, 1866, p. 87.

[2] Comp. rend., **67**, 97.

[3] Gazz. chim., 1882, p. 190; Chem. Ber., **15**, 2236.

[4] Chem. Ber., **9**, 78.

[5] Ann. chim. phys., [5] **17**, 289.

[6] Classen, Quan. Analysis by Electrolysis (Wiley & Sons, N. Y.).

The decomposition reactions of oxalic acid salts are entirely analogous to those of the free acid. In alkaline solution the oxidation proceeds more rapidly than in neutral solution because of the better conductivity of the alkalies.

Malonic Acid.—This acid was investigated by Bourgoin.[1] In a concentrated solution of sirupy consistency it, like oxalic acid, is only slowly oxidized to carbon dioxide, with the evolution of hydrogen. A strongly concentrated solution of the unaltered acid is found surrounding the positive electrode, even after an electrolysis of long duration. On the electrolysis of the sodium salt carbon monoxide is also present in the escaping gas mixture. The ratio of the different gases, carbon dioxide, carbon monoxide, and oxygen, remains fairly constant during the period of electrolysis (85.8%, 9.7%, 4.5%).

In alkaline solution the decomposition products are the same as in neutral solution, the ratio only of the separate gases being different, and varying with the duration of the electrolysis.

Succinic Acid.—Bourgoin[2] and Kékulé[3] found that the free acid underwent oxidation with difficulty, only a small quantity of carbon monoxide in addition to some oxygen and carbon dioxide being formed.

---

[1] Ann. chim. phys., [1] **14**, 157; Comp. rend., **90**, 608.

[2] Bull. soc. chim., [2] **9**, 301; *ibid.*, **21**, 1695.

[3] Lieb. Ann., **131**, 84.

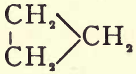
The neutral sodium salt gave the same products, as did also the alkaline solution of this salt, except that in the latter experiment the formation of carbon monoxide predominated. If, however, four molecular equivalents of sodium succinate were treated with one equivalent of sodium hydroxide, ethylene and a little acetylene could also be detected. Kolbe[1] states that methyl oxide is also formed; Bourgoin, however, was unable to confirm this statement.

Glutaric Acid. — The results which Reboul and Bourgoin[2] obtained with this acid are the following:

The greater part of the acid remains unchanged, while a small part only is decomposed according to the equation

$$C_5H_8O_4 + 7O = 2CO_2 + 3CO + 4H_2O.$$

A hydrocarbon of the composition



was not formed.

Similar observations were made in the electrolysis of potassium glutarate, likewise in alkaline solution.

Pyrotartaric Acid.—The investigators just mentioned, on electrolyzing a solution of the neutral potassium salt, observed the immediate precipitation

---

[1] Lieb. Ann., **113**, 244.

[2] Comp. rend., **84**, 1231.

of the acid salt. (Different behavior from glutaric acid, in the case of which the formation of the acid salt does not take place.) After a time the crystals disapppear, the free acid being regenerated. In alkaline solution also, the formation of the acid salt occurs, after a longer period of electrolysis. Nevertheless the continuous, though limited, evolution of carbon dioxide and carbon monoxide is a proof of partial oxidation.

Itaconic Acid.—The concentrated solution of the alkali salt electrolyzed by Aarland[1] gave a hydrocarbon isomeric with allylene, C_3H_4, which is said to have the formula $CH_2 = C = CH_2$. Along with this compound, some propylene was formed, while a portion of the acid was always regenerated.

Citraconic Acid.[2]—The concentrated solution of the sodium salt, likewise electrolyzed by Aarland, yielded, besides a hydrocarbon, C_3H_4, small traces of acrylic and mesaconic acid.

Mesaconic Acid, under the same conditions, gives the same hydrocarbon and traces of acrylic and itaconic acid.

Malic Acid.—The electrolysis of malic acid was performed by Bourgoin[3] and Brester.[4] The free acid,

---

[1] Journ. prakt. Chem., [2] 6, 256.

[2] Journ. prakt. Chem., 7, 142.

[3] Bull. soc. chim., [2] 9, 427.

[4] Jahresb. f. Chem., 1866, p. 87.

which is only slowly decomposed, and the neutral alkali salt both gave the same products, carbon dioxide and a little carbon monoxide and oxygen. After the completion of the experiment the solution contained some aldehyde and acetic acid.

Tartaric Acid (Dextrorotary).—For our knowledge of the deportment of this acid on electrolysis we are also indebted to Bourgoin.[1] The free acid is partially oxidized to carbon dioxide and carbon monoxide, while the solution contains acetic acid. Neutral potassium tartrate gives principally carbon dioxide besides a little carbon monoxide and oxygen, acid potassium tartrate being at the same time deposited. In alkaline solutions the gases carry with them traces of ethane, the formation of which is due to potassium acetate which is found present in the solution at the end of the operation.

Before proceeding to a discussion of the acids still to be considered, the deductions which Bourgoin[2] draws from his numerous experiments will be mentioned briefly. He regards the intermediate formation of the anhydride as the most important process in the electrolysis of organic acids, since by the splitting off of oxygen this produces secondary oxidation products. He considers, moreover, the transformation of the acid anhydride into the hydrate, by the addition of

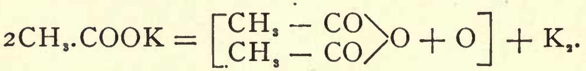
---

[1] Comp. rend., 65, 1144.

[2] Annal. chim. phys., [4], 14, 157.

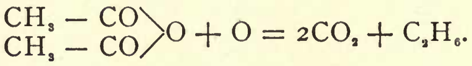
water, and the oxidation of the acids by oxygen formed from the acid itself as belonging to the secondary processes. This explanation coincides with the fact that water is not an electrolyte, or at least only a poor one, and acts chiefly as a dissociation medium. The typical reactions in the electrolysis of acetic acid are, for instance, the following:

Electrolytic decomposition,



$$2CH_3.COOK = \left[\begin{matrix}CH_3 - CO\\ CH_3 - CO\end{matrix}\Big> O + O\right] + K_2.$$

Characteristic oxidation,



$$\begin{matrix}CH_3 - CO\\ CH_3 - CO\end{matrix}\Big> O + O = 2CO_2 + C_2H_6.$$

A too strict adherence to the chemical arrangement is not conducive to clearness. After mentioning the investigations of Kékulé,[1] the later experiments of Miller and Hofer, Brown and Walker, etc., will be discussed in this connection.

Kékulé[1] investigated the electrolysis of *maleic acid* and *brom-maleic acid.* The former gave acetylene, besides a small quantity of succinic and fumaric acid; the latter, on the contrary, gave only hydrobromic acid and carbon monoxide. Like malic acid, *fumaric acid*, at the beginning of the experiment, gave only pure acetylene, but after the operation had continued

---

[1] Lieb. Ann., 131, 79.

for some time the acetylene was found to be mixed with oxygen.

EXPERIMENTS OF MILLER AND HOFER.[1]

1. The investigations carried out by Miller and Hofer are improvements over those previously made, since they give a much clearer insight into the process of the decomposition. In the method which was employed, namely, that of allowing the solutions to slowly flow over the electrodes, the compounds first formed were removed from the region of electrolytic action.

In this way it was possible to isolate certain substances which would otherwise have undergone secondary decomposition. In the researches cited below, however, accurate data concerning current relations are lacking. Classen[2] has accurately explained what data are necessary for repeating an electrolytic experiment.

Glycolic Acid.—The concentrated solution of the sodium salt yielded at the positive pole formaldehyde in large quantities and some formic acid, the latter breaking up from the action of the current into carbon monoxide and dioxide.

---

[1] Chem. Ber., 27, 461.

[2] Classen, "Quan. Analysis by Electrolysis," page 23.

Ordinary Lactic Acid.—As Kolbe[1] had already discovered, the concentrated solution of the potassium salt gave carbon dioxide and acetic aldehyde. The investigators above mentioned also remarked the presence of some formic acid. When the solution about the positive pole was kept slightly alkaline, aldol and crotonic aldehyde were formed instead of acetic aldehyde.

Sarco-lactic Acid.—When the solution surrounding the positive pole was kept neutral a concentrated solution of the sodium salt yielded acetic aldehyde and carbon dioxide.

α-Oxy-butyric Acid.—This substance was converted into carbon dioxide, propionic aldehyde, and formic acid.

α-Oxy-isobutyric Acid.—This compound gave carbon dioxide, carbon monoxide, and acetone.

Tartaric Acid.—From the electrolysis of a concentrated solution of potassium tartrate, carbon dioxide, carbon monoxide, oxygen, a little formic aldehyde, and some formic acid were obtained, but no acetic acid and ethylene, as stated by Bourgoin.

Hydracrylic Acid.—Resin and a little formic acid were found present in the electrolyte about the positive pole.

β-Oxy-butyric Acid.—From this acid were obtained carbon monoxide, carbon dioxide, crotonic aldehyde,

---

[1] Lieb. Ann., 113, 214.

a little formic acid, a resin, and a number of unsaturated hydrocarbons which were not further investigated.

Phenyl-β-lactic Acid.—The solution after electrolysis contained benzaldehyde, besides resinous bodies.

Methyl-glycolic Acid.—The solution of this acid after electrolysis contained formic aldehyde, formic acid, and possibly methyl alcohol. Oxygen, carbon monoxide, and carbon dioxide were evolved.

Mandelic Acid.—The electrolysis of this acid resulted in the formation of benzaldehyde and the gases mentioned above.

Glyceric Acid.—Like mandelic acid, glyceric acid was decomposed into carbon monoxide, carbon dioxide, and oxygen, formic aldehyde and formic acid being found in the solution.

Phenyl-glyceric Acid.—The products resulting from the electrolysis of this acid were the same as those obtained from mandelic acid.

Malic Acid.—This compound yielded carbon dioxide, oxygen, carbon monoxide, acetic aldehyde, and crotonic aldehyde.

Racemic Acid.—On the electrolysis of this acid the gases given above were obtained and also an aldehyde which was not further investigated.

Ethyl-tartaric Acid.—This gave the same gases, but any other gases which may have been formed were not identified.

2. *Electrosyntheses.*—The same investigators recently[1] added to our knowledge on this subject by submitting to electrolysis solutions containing the potassium salts of mono-basic acids and the ethyl esters of the mono-potassium salts of dibasic acids dissolved in equi-molecular proportion. This was in accordance with the experiments made by Brown and Walker.

In this way they prepared *butyric ethyl ester* from potassium acetate and *potassium-ethyl succinate.* The synthesis of the *ethyl ester of valeric, capronic, and isobutyl-acetic acid* was also effected.

The reactions all take place according to the following equation:

$$\mathrm{XCOOK + COOKY.COOC_2H_5} \\ = \mathrm{K_2 + 2CO_2 + XY.COOC_2H_5}.$$

In accordance with a similar principle they obtained *ethyl alcohol* from potassium acetate and *potassium glycolate.* If *potassium-ethyl malonate* was taken as one of the salts and a solution of this with potassium acetate, propionate, or butyrate was electrolyzed there was formed the *ethyl ester of propionic, butyric, or valeric acid*, respectively.

v. Miller[2] applied this method to a number of other mixtures. Thus upon the electrolysis of a mixture of acetic ester with *tricarballylic ester*, one third

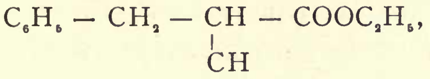
---

[1] Chem. Ber., **28**, 2427; Zeitschr. f. Elektroch., 4, 55.

[2] Ztschr. f. Elektroch., 4, 55.

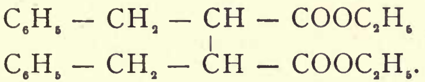
of which was saponified, there was formed principally *ethyl-succinic ester*. If aromatic ester acids were electrolyzed with potassium acetate a similar synthesis occurred.

By this method *α-methyl-hydrocinnamic ester*,



$$C_6H_5 - CH_2 - \underset{\displaystyle CH}{\underset{|}{CH}} - COOC_2H_5,$$

was prepared from *potassium-ethyl benzyl-malonate* and potassium acetate. *Dibenzyl-succinic ester* is formed at the same time, according to the reaction of C. Brown:



$$\begin{array}{l} C_6H_5 - CH_2 - CH - COOC_2H_5 \\ \qquad\qquad\qquad\quad | \\ C_6H_5 - CH_2 - CH - COOC_2H_5. \end{array}$$

This reaction does not take place if potassium acetate is not present.

If the deportment of the alkali salts of the *monobasic oxyacids* upon electrolysis is analogous to that of sodium acetate the chief products to be expected are symmetrical glycols:

$$2C_nH_{2n}(OH)COO - = C_{2n}H_{4n}(OH)_2 + 2CO_2.$$

According to Walker's[1] experiments this is not generally the case. From the potassium salt of *mandelic acid* the expected product, i.e., a mixture of *hydrobenzoïn* and *isohydrobenzoïn*, is formed only in small quantities; benzaldehyde, however, is formed in larger quantities.

---

[1] Journ. Chem. Soc., 45, 1278.

The alkali salts of oxyacids give, in addition to the above, many other substances, principally *aldehydes*, and the results are the same even if the attempt is made to weaken the action of the electrolytic oxygen by converting the alcohols into esters.

Thus from the sodium salt of *glycolic acid* ($CH_2OH.COOH$), *ethyl-glycolic acid* ($CH_2OC_2H_5.COOH$), and *α-lactic acid* ($CH_3.CH(OH)COOH$) the chief product obtained is acetic aldehyde, and it is quite possible that the production of hydrobenzoïn and isohydrobenzoïn from mandelic acid is due to the electrolytic reduction of the benzaldehyde originally formed.

This view is supported by the investigations of Kauffmann,[1] who actually obtained hydrobenzoïn and isohydrobenzoïn by the direct electrolytic reduction of benzaldehyde.

Elbs[2] emphasizes the fact that it is not necessary to suppose that aldehydes are a result of secondary oxidation produced by the oxygen available in the region of the anode, but that their formation can also be regarded as analogous to that of ethylene from propionic acid:

$$2CH_3.CH_2.COO- = CH_3.CH_2.COOH + CO_2 + CH_2 = CH_2,$$

$$2CH_3.CH(OH)COO- = CH_3.CH(OH).COOH + CO_2 + CH_3.CHO.$$

---

[1] Ztschr. f. Elektroch., 2, 367.

[2] Jahrbuch. d. Elektroch., 3, 295.

A still further advance in this field is the successful substitution of iodine and of nitro-groups by electrolysis. On electrolyzing propionic acid and potassium iodide in aqueous solution *β-iodo-propionic acid* was formed, due to the intermediate formation of succinic acid:

$$\begin{aligned} &\mathrm{COOH.CH_2.CH_2.COOK + KI} \\ &\qquad = \mathrm{ICH_2.CH_2.COOH + 2K + CO_2}. \end{aligned}$$

Nitro-ethane was probably obtained in small quantities from sodium propionate and sodium nitrite.

ELECTROSYNTHESES OF BROWN AND WALKER.[1]

A systematic synthesis with the aid of the electric current was first attained in the researches of Brown and Walker. Their investigations are based partly on the fact observed by Kolbe that monobasic fatty acids yield hydrocarbons, and partly on the results of the experiments of Guthries,[2] who found that the ester group is electrolytically inactive. These facts justified the hypothesis that the mono-esters of dibasic acids would behave, under the action of the current, like monobasic acids, i.e., carbon dioxide

---

[1] Lieb. Ann., **261**, 107; *ibid.*, **274**, 41.

[2] Lieb. Ann., **99**, 65.

would be split off and esters of higher dibasic acids would be formed according to the equations

$$2C_2H_5.OOC - CH_2 - COOK$$
$$= C_2H_5.OOC - CH_2 - CH_2 - COOC_2H_5 + 2K_2 + CO_2,$$
$$2C_2H_5 - OOC.CH_2.CH_2.COOK$$
$$= C_2H_5.OOC.CH_2.CH_2.CH_2.CH_2.COOC_2H_5$$
$$+ 2CO_2 + K_2.$$

Their experiments, conducted in fairly concentrated solutions with currents of high density, completely confirmed this supposition. Under these conditions the following syntheses were made:

1. *Succinic acid* from *ethyl-potassium malonate.*

2. *Adipic acid* from *ethyl-potassium succinate.*

3. *Suberic acid* from *ethyl-potassium glutarate.*

4. *Sebacic acid* from the *ethyl-potassium salt* of *adipic acid.*

5. *n-Dodecane-dicarboxylic acid* from the ethyl-potassium salt of *suberic acid.*

6. *n-Deca-hexane-dicarboxylic acid* from the ethyl-potassium salt of *sebacic acid.*

If the ethyl-potassium salts of substituted acids are taken as a starting-point it is possible to obtain disubstituted acids according to the above reaction.

1. *Ethyl-potassium methyl-malonate* gave the two *symmetrical dimethyl-succinic acids*, having the melting-points 193° and 121°.

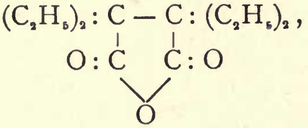
2. *Ethyl-potassium ethyl-malonate* gave the corre-

sponding *symmetrical diethyl-succinic acids*, with the melting-points 192° and 130°.

3. *Ethyl-potassium dimethyl-malonate* gave *tetramethyl-succinic acid.*

4. From *ethyl-potassium diethyl-malonate* a substance of the composition $C_{14}H_{26}O_4$, which differs from the expected tetraethyl-succinic acid by C_2H_4, was obtained. The nature of this body has not yet been determined.

Hydrobromic acid splits off alcohol the compound $C_{12}H_{20}O_3$, which has perhaps the furfurane formula



being formed.

All these reactions did not take place smoothly, but were accompanied by secondary reactions, principally oxidations, which were limited as much as possible by working with strong concentrated solutions and low temperatures. Moreover, the formation of esters also is always possible according to the equation

$$2CH_3.COO - = CH_3COOCH_3 + CO_2;$$

and, finally, the formation of unsaturated esters may take place as illustrated in the simplest case:

$$2C_2H_5COO - = C_2H_4 + CO_2 + C_2H_5COOH,$$
$$2C_2H_5OOC.CH_2CH_2.COO - = 2C_2H_5OOC.CH_2$$
$$-CH_2.CH : CH_2 + C_2H_5OOC.CH_2.CH_2.COOH + CO_2.$$

In this way it was possible to isolate *methyl-acrylic acid* by the electrolysis of *ethyl-potassium dimethyl-malonate*, and *ethyl-crotonic acid* by electrolyzing a solution of the ethyl-potassium salt of *diethyl-malonic acid*. On the electrolysis of *sebacic acid* the ethyl ester of an unsaturated acid, $CH_2 : CH(CH_2)_6.COOH$, was formed.

Brown and Walker[1] also electrolyzed the sodium-ethyl salt of *camphoric acid* and obtained two esters which they were able to separate by means of fractional distillation. One of these (boiling-point 212–213°) on being saponified yielded an unsaturated monobasic acid, $C_9H_{14}O_2$, *campholytic acid;* the other, having a higher boiling-point (240–242°), was the neutral ester of a dibasic acid, $C_{18}H_{30}O_4$, to which Walker gave the name of *camphothetic acid.* The experiments are of great importance, because they prove the dibasic nature of camphoric acid, a fact which is doubted by Friedel.

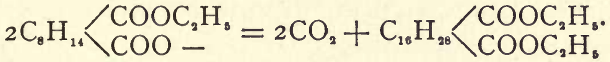
Walker and Henderson[2] found, moreover, that upon the electrolysis of concentrated aqueous solutions of the potassium salt of *allocamphoric ester* there

---

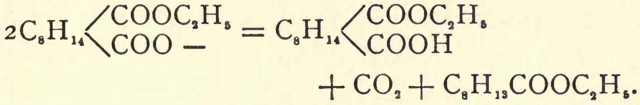
[1] Lieb. Ann., 274, 71.

[2] Journ. Chem. Soc., 67, 337.

are formed as chief products the ethyl esters of a dibasic acid, $C_{16}H_{28}(COOH)_2$, and of a monobasic acid, $C_8H_{13}COOH$:

1. 

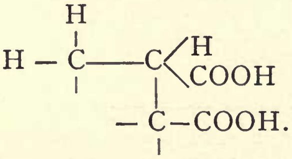
$$2C_8H_{14}\left\langle\begin{array}{l}COOC_2H_5\\COO-\end{array}\right. = 2CO_2 + C_{16}H_{28}\left\langle\begin{array}{l}COOC_2H_5.\\COOC_2H_5\end{array}\right.$$

2. 

$$2C_8H_{14}\left\langle\begin{array}{l}COOC_2H_5\\COO-\end{array}\right. = C_8H_{14}\left\langle\begin{array}{l}COOC_2H_5\\COOH\end{array}\right. + CO_2 + C_8H_{13}COOC_2H_5.$$

It has been found on further investigation[1] that besides the strongly dextrorotary unsaturated acid designated as *allocampholytic acid*, $C_8H_{13}COOH$, an isomeric acid is formed which, although slightly dextrorotary as obtained, is perhaps even lævorotary in an entirely pure condition. The latter on being heated to 200° splits off carbon dioxide and yields a hydrocarbon, C_8H_{14}, which boils at 120–122° and appears to be identical with *laurolene*, made from camphoric acid.

A ketonic acid, $C_8H_8O.COOH$, melting-point 228°, is also found as an additional product of the electrolysis of potassium allocamphoric ethyl ester. The authors conclude from their observations that camphoric acid contains the group



---

[1] Journ. Chem. Soc., 69, 748.

It is expected that these results will give the structural formula for camphoric acid.

Following the experiments of Brown and Walker, Schields[1] investigated the deportment of *ethyl-potassium maleate* and *fumarate* on electrolysis. His results confirm the experiments of Kékulé. During the electrolysis carbon dioxide, oxygen, and unsaturated hydrocarbons were evolved, and the unchanged maleic or fumaric acid and the corresponding ethyl esters, respectively, remained in the solution.

From these experiments it would appear that *unsaturated acids* form no synthetic products on electrolysis, and the *aromatic acids—phthalic acid* and *benzyl-malonic acid*—conduct themselves in a similar manner. Finally may be mentioned the electrolysis of ethyl-potassium oxalate, which yielded ethylene in addition to carbon dioxide.

ELECTROSYNTHESES OF MULLIKEN[2] AND WEEMS.[3]

Mulliken electrolyzed the sodium compounds of the diethyl esters of dibasic acids in alcoholic solution and obtained the same compounds which were formed when sodium was removed by iodine. He thus made:

---

[1] Lieb. Ann., **274**, 64; Journ. Chem. Soc., **69**, 737.

[2] Amer. Chem. Journ., **15**, 323.

[3] *Ibid.*, **16**, 569.

1. *Ethane-tetracarboxylic ester* from *sodium-diethylmalonic ester.*

2. *Ethane-hexacarboxylic ester* from *sodium-methane-tricarboxylic ester.*

3. *Tetracetyl-ethane* from *acetyl-acetone.*

4. A thick oil which contained a small quantity of *diacetyl-succinic ester* from *aceto-acetic ester.*

The conclusion reached by Mulliken, that in the electrolysis of certain weak organic acids a portion of the anions unite in pairs without undergoing decomposition, was closely examined by Weems as to its general applicability and as to the exact nature of the chemical changes which take place. All direct attempts to oxidize malonic ester with hydrogen peroxide, potassium permanganate, and chromic acid, and to produce an effect similar to that caused by the current, were without success.

Weems, on electrolyzing the sodium salt of methylmalonic ester in alcoholic solution, obtained *dimethyl-ethane-tetracarboxylic ester; ethyl-malonic ester* yielded *diethyl-ethane-tetracarboxylic ester;* and *aceto-acetic ester* was changed to *diacetyl-succinic ester.*

In the electrolysis of *cyan-acetic ester* the formation of dicyan-succinic ester could not be observed; likewise a union of the anions of benzyl-malonic ester, acetyl-malonic ester, and acetyl-dicarboxylic ester did not take place. Electrolysis of *acid amides* in the form of their sodium or mercury compounds yielded unchanged amides.

The review which has been given of the investigations on the electrolysis of the aliphatic carboxylic acids is believed to include all present information on this subject. Of the investigations mentioned, an advance is shown only in those of Kolbe-Bourgoin, Brown-Walker, and Mulliken-Weems. The action of the electric current has been used, in these cases at least, for effecting a limited number of organic syntheses. A number of papers on the action of the electric current on compounds containing cyanogen and sulphur will next be mentioned.

2. Cyanogen Compounds.

Cyanogen.—Berthelot[1] observed that cyanogen was decomposed into its elements by the action of the electric spark. The slightest trace of water in the gas caused the formation of hydrocyanic acid and acetylene. By submitting moist cyanogen gas to the action of the voltaic arc Buff and Hofmann[2] noted the formation of carbon dioxide, carbon monoxide, and ammonia.

Cyanogen can be obtained by the electrolysis of a solution of potassium ferrocyanide.[3]

---

[1] Comp. rend., **82**, 1360.

[2] Lieb. Ann., **113**, 135.

[3] See potassium ferrocyanide, p. 45.

Hydrocyanic Acid. — *Electrosynthesis:* Berthelot[1] obtained hydrocyanic acid by passing the electric spark through a mixture of acetylene and nitrogen. The reaction is, however, reversible. On allowing the electric spark to act on hydrocyanic-acid gas it was decomposed into acetylene and nitrogen. Hydrocyanic acid is also obtained by passing the electric spark through mixtures of ethylene or aniline vapor with nitrogen, acetylene with nitric oxide (Huntington[2]), nitrogen with benzol (Perkin[3]), etc.

Electrolysis: In sulphuric-acid solution hydrocyanic acid breaks up smoothly, according to Gay-Lussac,[4] into hydrogen and cyanogen. Concentrated hydrocyanic acid to which a drop of sulphuric acid has been added gives carbon monoxide and ammonia (Schlagdenhauffen[5]).

Potassium Cyanide.—In the investigation of this salt, conducted by the author last mentioned, it was found that no oxygen escaped at the anode, but the potassium cyanide was oxidized to potassium cyanate.

Potassium Ferrocyanide.—This compound gives at the anode hydrocyanic acid and Prussian blue and at the cathode hydrogen and potassium hydroxide

---

[1] Bull. soc. chim., 13, 107.

[2] English patent, 14855; German patent, 93852.

[3] Jahresb. f. Chem., 1870, p. 399.

[4] Gilbert's Ann., 1811–1815; Ann. chim. phys., **78**, 245.

[5] Jahresb. f. Chem., 1863, p. 305.

(Perrot[1]); also cyanogen, according to Schlagdenhauffen.[2]

Potassium Ferricyanide likewise gives on electrolysis Prussian blue at the anode.

Sodio-nitro-prusside.—On electrolyzing a dilute solution of this salt for a prolonged period Weith[3] noted the formation of ammonia and the precipitation of metallic iron; at the positive electrode Prussian blue appeared, and nitrogen, oxygen, and, if the operation was long continued, nitric oxide also were given off. In a concentrated solution much ammonia was formed at the cathode and nitric oxide appeared at the anode.

Prussian blue can also be obtained according to Luckow's method[4] for the general preparation of insoluble compounds.

Nitriles.—Ahrens,[5] by means of the electrolytic addition of hydrogen, succeeded in converting nitriles into primary amines, while simultaneously with the reduction a partial saponification of the nitriles occurred, as represented by the following equation:

$$R.CN + 2H_2O = R.COOH + NH_3.$$

Aceto-nitrile.—This substance yields only a small quantity of ethylamine, although a considerable

---

[1] Tommasi, Traité d'Electrochimie, 720.

[2] Jahresb. f. Chem., 1863, p. 305; J. prakt. Chem., **30**, 145.

[3] Jahresb. f. Chem., 1863, p. 306; *ibid.*, 1868, p. 311; Bull. soc. chim., [2] **10**, 121.

[4] German patent, 91707.

[5] Ztschr. f. Elektroch., **3**, 99.

quantity of *n*-propylamine is formed from *n-propionitrile.*

The reduction of *aromatic nitriles* takes place without the occurrence of secondary reactions. This is illustrated in the formation of benzylamine from *benzo-nitrile* and of phenyl-ethylamine from *benzyl-cyanide.*

3. Compounds Containing Sulphur.

Mercaptans.—Bunge[1] electrolyzed the alkali salts of mercaptans and observed the formation of disulphides at the positive pole. In the case of the sulpho-compounds, however, the free acids were regenerated.

Sodium-isethionate.—The same author also investigated sodium isethionate, but could note the formation of only the free acid at the positive pole.

Methyl-sulphuric Acid.—This acid, investigated by Renard,[2] yielded hydrogen at the negative pole, while formic acid, carbon dioxide, carbon monoxide, and trioxy-methylene, besides free sulphuric acid, were found present at the positive pole.

Potassium-trichlor-methyl Sulphate. — This compound, electrolyzed by Bunge,[3] gave hydrogen and alkali at the negative pole, at the positive pole

---

[1] Chem. Ber., **3**, 911.

[2] Ann. chim. phys., [5] **17**, 289; Comp. rend., **90**, 175, 531; *ibid.*, **92**, 965.

[3] Chem. Ber., **3**, 911.

oxygen, carbonic-acid gas, chlorine, sulphuric acid, and perchloric acid.

Potassium-trichlor-methyl Sulphonate.—This salt was electrolyzed by Kolbe[1] in neutral concentrated aqueous solution and gave the following results:

The solution became strongly acid and contained free hydrochloric and sulphuric acid. Hydrogen was gradually evolved at the negative pole. After the decomposition was complete the solution contained potassium perchlorate, which was also observed in the case of potassium-trichlor-methyl sulphate.

Ethyl-sulphuric Acid.—Ethyl-sulphuric acid gave, according to Renard,[2] on being subjected to electrolysis, at the negative pole hydrogen, and at the positive pole acetic acid, some formic acid, aldehyde, and sulphuric acid. In concentrated solution a greater proportion of acetic acid was formed. The potassium salt on electrolysis breaks up, according to Hittorf,[3] into $K -$ and $- OSO_2.OC_2H_5$.

Potassium-isoamyl Sulphate, according to Guthries, is decomposed into oxygen, valeric acid, and sulphuric acid.

Potassium Xanthate.—C. Schall[4] obtained, by the electrolysis of potassium xanthate in aqueous solution, xanthogen supersulphide, as might be expected:

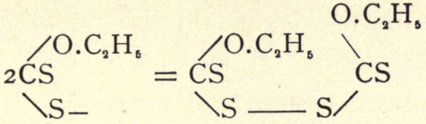
---

[1] Journ. prakt. Chem., **62**, 311.

[2] Ann. chim. phys., [5] **17**, 289.

[3] Pogg. Ann., **106**, 530.

[4] Ztschr. f. Elektroch., **2**, 475.



Dimethyl-dithiocarbamic Acid.—According to Schall[1] the electrolysis of the potassium salt of dimethyl-dithiocarbamic acid resulted in the formation of tetra-ethyl-thiuram disulphide,

$$[CS.N(C_2H_5)_2]_2S_2.$$

Thiophene.—This compound under the influence of the electric discharge absorbs as much as 8.6% of its own weight of nitrogen, $(C_4H_4S)_2N$ being formed (Berthelot[2]).

---

[1] Ztschr. f. Elektroch., 3, 83.

[2] Ann. chim. phys., 11, 35.

ELECTROLYSIS AND ELECTROSYNTHESIS OF AROMATIC COMPOUNDS.

THE data on the results of investigation in this branch of the subject are considerably more limited than in the case of the aliphatic series. One of the reasons for this is the difficulty with which the benzene nucleus undergoes oxidation, a condition which permits of comparatively few reactions. Nearly all the reactions involve substituted groups only. In almost all cases the benzene nucleus remains unaltered.

In accordance with the method of presentation previously adopted, the investigations on the electrolysis of the hydroxyl compounds will be first discussed in the following synopsis.

I. Phenols.

Phenol.—Bunge,[1] Bartoli and Papasogli[2] submitted phenol to the action of the electric current. Bunge

---

[1] Chem. Ber., 3, 296.

[2] Gazz. Chim., 14, 19.

observed that the decomposition of potassium phenolate was analogous to that of an acid or a salt; the potassium phenolate was split up into K— (cathion) and C_6H_5O—(anion), the latter combining with water to form phenol, with the liberation of oxygen. Bartoli and Papasogli, on electrolyzing solutions of phenol in potassium and sodium hydroxide, and using electrodes of coke, graphite, and platinum, obtained an acid having the composition $C_7H_6O_4$, which melted at 93°, reduced ammoniacal silver solution and Fehling's solution on being heated, and when in aqueous solution was not precipitated by acids. When, however, coke was used as the positive electrode, an extensive decomposition of the phenol occurred and a resin was formed.

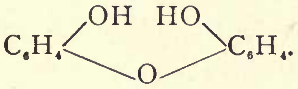
On subjecting a neutral potassium phenolate solution to the action of the electric current they were able to isolate a compound, $C_{66}H_{48}O_{22}$, soluble in alkali and precipitated from such solutions by mineral acids. This latter compound on being oxidized with nitric acid formed picric acid. When allowed to remain in solution in the presence of dilute acids for a prolonged period, it underwent decomposition according to the following equation:

$$C_{66}H_{48}O_{22} + H_2O = C_{44}H_{30}O_{15} + C_{21}H_{20}O_8.$$

The electrolysis of neutral sodium phenolate solution gave an acid with the formula $C_{29}H_{20}O_8$ which likewise is decomposed on boiling with dilute acids:

$$C_{29}H_{20}O_8 = C_{17}H_{10}O_6 + C_{12}H_{10}O_3.$$

The compound $C_{12}H_{10}O_3$ is soluble in alcohol, melts at 75°, and is isomeric with the hydroquinone ether, obtained by Étard from chlorchromic acid and phenol. It has the composition



$$C_6H_4\begin{array}{c}\diagup OH \quad HO\diagdown \\ \diagdown \quad O \quad \diagup\end{array}C_6H_4.$$

Christomanos[1] observed that while sodium acts only very slowly on dissolved monobrom-benzene, diphenyl can speedily be obtained by placing sodium in the solution and connecting this metal with the positive pole of a battery of two Bunsen elements, whose electrodes are immersed in the solution; diphenyl is likewise obtained by using zinc instead of sodium.

Phenyl-mercaptan.—Bunge[2] investigated phenyl-mercaptan in the same manner as the corresponding alkyl compound. Phenyl-disulphide, $(C_6H_5)_2S_2$, was formed at the positive pole.

---

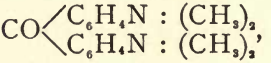
[1] Gazz. Chim., 1875, p. 402.

[2] Chem. Ber., 3, 911.

2. Aldehydes and Ketones.

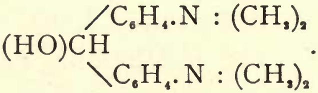
Benzaldehyde.—Kauffmann,[1] by the electrolysis of benzaldehyde in a 12–15% solution of potassium bisulphide, obtained at the cathode a mixture of hydro-benzoïn and iso-hydrobenzoïn. According to his statements,[2] an alcoholic solution of sodium hydroxide is more suitable for the reaction than the aqueous solution of bisulphide. Other aldehydes and ketones show a behavior similar to benzaldehyde.

Tetramethyl-diamido-benzophenone.—Michler's ketone,



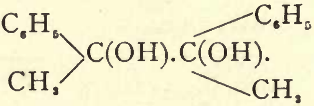
$$\mathrm{CO}\left\langle\begin{array}{l}\mathrm{C_6H_4N:(CH_3)_2}\\ \mathrm{C_6H_4N:(CH_3)_2}\end{array}\right.,$$

gives the corresponding benzhydrol,



$$\mathrm{(HO)CH}\left\langle\begin{array}{l}\mathrm{C_6H_4.N:(CH_3)_2}\\ \mathrm{C_6H_4.N:(CH_3)_2}\end{array}\right..$$

Aceto-phenone, $C_6H_5.CO.CH_3$.—Aceto-phenone yields aceto-phenone pinacone,



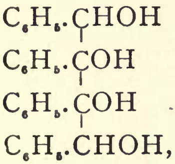
$$\left.\begin{array}{r}\mathrm{C_6H_5}\\ \mathrm{CH_3}\end{array}\right\rangle\mathrm{C(OH).C(OH)}\left\langle\begin{array}{l}\mathrm{C_6H_5}\\ \mathrm{CH_3}\end{array}\right..$$

---

[1] Ztschr. f. Elektroch., 2, 365.

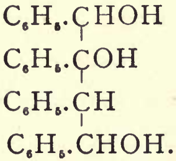
[2] *Ibid.*, 4, 461.

Benzile.—The aromatic di-ketone benzile, $C_6H_5CO.CO.C_6H_5$, gives peculiar results. On reduction in an alkaline alcoholic solution a whole series of bodies is formed, i.e., benzoic acid, benzilic acid, tetraphenylerythrite, $C_{28}H_{26}O_4$ =



$$\begin{array}{l} C_6H_5.CHOH \\ \qquad\quad | \\ C_6H_5.COH \\ \qquad\quad | \\ C_6H_5.COH \\ \qquad\quad | \\ C_6H_5.CHOH, \end{array}$$

and a substance, $C_{28}H_{26}O_3$, containing one less atom of oxygen, which has probably the constitution



$$\begin{array}{l} C_6H_5.CHOH \\ \qquad\quad | \\ C_6H_5.COH \\ \qquad\quad | \\ C_6H_5.CH \\ \qquad\quad | \\ C_6H_5.CHOH. \end{array}$$

Tetraphenyl-erythrite is also formed by the direct reduction of benzoïn.

Anthraquinone,

According to Weizmann,[1] this compound when in sulphuric acid solution is converted by electrolytic oxidation into monoxy-, dioxy-, and trioxy-anthra-

---

[1] French Pat. 265292.

quinone. The cathode fluids employed were solutions of alkalies, alkali carbonates, chromates, permanganates, acidulated water, and dilute acids. Both direct and alternating currents were used. On the electrolysis of anthraquinone and potassium hydroxide alizarine is formed.

Nitro-aldehydes and **nitro-ketones** will be discussed in the chapter on nitro-compounds.

3. Acids.

Benzoic Acid.—Benzoic acid and its salts were examined by several investigators, first by Matteuci,[1] then by Brester,[2] and most thoroughly by Bourgoin.[3]

The result of all these investigations is to show that here no secondary reactions take place, as was observed in the case of the fatty acids, but that the only effect of the current is to produce a separation into hydrogen (or metal) and the acid radical, the latter regenerating the acid at the positive pole. In an alkaline solution it is possible to so increase the oxidation that the benzoic acid is destroyed. The decomposition products which then appear at the anode are carbon dioxide, carbon monoxide, and sometimes acetylene. The odor of bitter almonds is also frequently observed. A thorough investigation

---

[1] Bull. soc. chim., **10**, 209.

[2] Jahresb. f. Chem., 1866, p. 87.

[3] Bull. soc. chim., **10**, 431.

on the electrolytic decomposition of sodium benzoate was made by Löb.[1] He employed a current having a potential of 6–7 volts and a current density of 15–20 amp., and obtained a small quantity of a substance containing sodium, the empirical formula for which was

$$C_6H_5O_6Na,$$

but the chemical nature of which has not yet been determined. There is formed besides this compound a small amount of benzaldehyde, as well as acetylene and carbon monoxide. Under no circumstances do diphenyl or other hydrocarbons occur, nor do fatty acids appear, which is otherwise generally the case in an oxidation of this character.

Thio-benzoic Acid.—On electrolyzing this acid Bunge[2] obtained the bisulphide of benzoyl.

Sulpho-benzoic Acid.—This acid is not changed by the current according to the statements of the same investigator.

Phthalic Acid.—Bourgoin[3] states that the electrolysis of this acid and of its neutral or alkaline salts resulted in the formation of the unchanged acid at the positive pole. The appearance of small quantities of carbon dioxide and carbon monoxide, however, was an evi-

---

[1] Zeitschr. f. Elektroch., 2, 663, *ibid.*, 3, 3.

[2] Chem. Ber., 3, 296.

[3] Jahresb. f. Chem., 1871, p. 631.

dence that a small portion of the acid had undergone oxidation.

The potassium salt of the mono-ethyl ester of phthalic acid, when electrolyzed by Brown and Walker,[1] became dark-colored and a resinous substance was formed, but the isolation of any new electrolytic product was not possible.

Phenyl-acetic Acid.—This acid electrolyzed in the form of its potassium salt by Slawik[2] yielded free phenyl-acetic acid.

Cinnamic Acid.—Cinnamic acid, investigated by Brester,[3] showed a similar behavior in the electrolysis of both the free acid and the neutral solutions of its salts.

Benzyl-malonic Acid.—When this acid in the form of its ethyl-potassium salt was submitted to electrolysis by Brown and Walker[4] it showed a behavior materially different from that of malonic acid. The solution became dark-colored and contained no new compound. If oxidation occurred it was a complete oxidation into carbon dioxide and carbon monoxide, such as has been observed in the case of the unsaturated acids.

---

[1] Lieb. Ann., **274**, 67.

[2] Chem. Ber., 7, 1051.

[3] Jahresb. f. Chem., 1866, p. 87.

[4] Lieb. Ann., **274**, 67.

4. Amido-Compounds.

Aniline.—Destrem[1] investigated the action of the electric spark from an induction apparatus on aniline vapor and observed a decomposition into acetylene, hydrogen, hydrocyanic acid, and nitrogen. E. Rotundi[2] electrolyzed aniline. Since pure aniline is an extremely poor conductor he made the solution suitable for electrolysis by the addition of ammonia. After a period of three days, during which hydrogen was continually evolved at the negative pole and a tarry substance was deposited at the positive pole, Rotundi interrupted the electrolysis and was able, with more or less certainty, to establish the following processes:

1. The formation of diazo-compounds:

$$C_6H_5NH_2(HNO_3) + HNO_2 = C_6H_5N_2NO_3 + 2H_2O.$$

2. The formation of diazo-amido-compounds:

$$2C_6H_5NH_2 + HNO_2 = C_6H_5N_2NHC_6H_5 + 2H_2O.$$
$$C_6H_5N_2NO_3 + C_6H_5NH_2 = C_6H_5N_2NH.C_6H_5 + HNO_3.$$

3. The formation of azo-compounds by direct oxidation of aniline:

$$2C_6H_5NH_2 + 2O = 2H_2O + C_6H_5N_2C_6H_5.$$

---

[1] Jahresb. f. Chem., 1884, p. 272.

[2] Atti. d. R. Acad. d. Scienze d. Torino, 39, 4; Jahresb. f. Chem., 1884, p. 270.

4. The formation of amido-azo-compounds by molecular rearrangement of diazo-amido-compounds. The nitrous and nitric acids were oxidation products of the ammonia which was added.

INVESTIGATIONS OF GOPPELSROEDER.[1]

These relate to aniline and its derivatives, and aim at preparing the most important dyes of the aniline series. Although the reactions which take place in the cell have not as yet been explained, the researches form valuable material for consideration. Goppelsroeder has gathered the technical results in a small pamphlet: "Farbelektrochemische Mitteilungen" (Mühlhausen, 1889).

If a galvanic current is conducted through acid or neutral aqueous solutions of aniline there is formed at the positive pole, besides other coloring matters, aniline black, $C_{24}H_{21}N_4Cl$. Under similar conditions dyes are obtained at the positive pole from the salts of *toluidene*, *methyl-aniline*, *diphenylamine*, *ditolylamine* and *phenyl-tolylamine*.

Naphthylamine salts give naphthylamine violet. On electrolysis of *anthraquinone* and potassium hydroxide, Goppelsroeder succeeded in obtaining alizarine.[2]

---

[1] Dingler, Polytech. Journal, **221**, 75; *ibid.*, **223**, 317 and 634; *ibid.*, **224**, 92 and 209.

[2] See also p. 56.

All these reactions are to be attributed to the action of electrolytic oxygen. In the brief survey which will here be given it is not possible to go into the details of the researches. The following literary data will serve as a guide:

Research 1.[1] Preparation of aniline black.

Research 2.[2] Electrolysis of aniline with excess of aniline. Electrolysis of toluidene. Electrolysis of mixtures of aniline with toluic acids.

Research 3.[3] Electrolysis of aniline and toluidene salts in the presence of nitrate, nitrite, or chlorate of potassium in aqueous solution.

Research 4.[4] Electrolysis of the salts of methylaniline. Electrolysis of the salts of diphenylamine. Electrolysis of the salts of methyl-diphenylamine. Electrolysis of phenol. Electrolysis of the salts of naphthylamine.

Research 5.[5] Conversion of anthraquinone into alizarine by the electrolysis of a mixture of anthraquinone and potassium hydroxide.

Liebmann's[6] attempts to make *quinone* by the electrolytic oxidation of aniline or electrolytically prepared aniline black were unsuccessful.

---

[1] Dingler, Polytechn. Journ., **221**, 75.

[2] *Ibid.*, **223**, 317.

[3] *Ibid.*, **223**, 634.

[4] *Ibid.*, **224**, 92.

[5] *Ibid.*, **224**, 209.

[6] Ztschr. f. Elektroch., **2**, 497.

Hydroquinone in an aqueous solution acidified with sulphuric acid could be quantitatively converted into quinone at the anode:

$$2C_6H_4(OH)_2 + O = H_2O + C_6H_4(OH)_2.C_6H_4O_2.$$

The same compound was also formed when alternating currents were used.

Voigt,[1] by the electrolytic oxidation of suitable mixtures of bases, prepared rosaniline, chrysaniline, safranine, and p-leucaniline. His object in these researches was the same as that of Goppelsroeder; namely, the preparation of the important dyes of the aniline series.

If electrolytic oxygen is permitted to act upon aniline, dissolved in concentrated acetic acid solution, acetanilide is formed; by using a dilute solution, however, amido-hydroquinone is obtained.

So far as can be learned from the literature these investigations have not been concluded, which is also the case with those of Fölsing,[2] who by the oxidation of *p-phenylene-diamine* obtained a beautiful blue dye similar to indigo.

Fölsing obtained p-phenylene-diamine by the electrolytic reduction of amido-azo-benzene.

From the electrolysis of *benzene-p-phenylene-diamine*

---

[1] Ztschr. f. angew. Chem., 1894, p. 107.

[2] Ztschr. f. Elektrochemie, 2, 30.

there likewise resulted at the anode a blue dye, which showed a behavior analogous to that of the dye obtained from p-phenylene-diamine.

5. Electrolytic Reduction of Nitro-Compounds.

In general, azo-, hydrazo-, and amido-compounds result from the electrolytic reduction of nitro-compounds. In this way Kendall[1] obtained aniline from *nitro-benzene*, and Elbs[2] and Häussermann[3] prepared the normal reduction products of *nitro-phenol*. The formation of azoxy-, azo-, amido-, or hydrazo-compounds was dependent upon whether acid or alkaline solutions were employed. If nitro-benzene is reduced in a concentrated acetic or formic acid solution, to which a few drops of concentrated sulphuric acid (to increase the conductivity) have been added, the corresponding salts of benzidene result; a fact further confirmed by Löb.[4]

According to the investigations of the same author, in the electrolysis of an ammoniacal solution azobenzene is formed as the chief product and hydrazobenzene as a secondary product.

Gattermann and Koppert[5] obtained p-amido-phenol-

---

[1] German Pat., 21131.

[2] Journ. prakt. Chem., **49**, 39.

[3] Chem. Zeitung, **17**, 129, 209.

[4] Ztschr. f. Elektrochem., **3**, 471.

[5] Chem. Zeitung, **17**, 210.

sulphate by the reduction of *nitro-benzene-sulphonic acid.*

Noyes and Clement,[1] on the reduction of nitrobenzene in a concentrated sulphuric acid solution, obtained p-amido-phenol-sulphonic acid. Gattermann,[2] starting with a similar solution, by varying the conditions of the experiment obtained directly p-amido-phenol. He explains the reaction by assuming the intermediate formation of phenyl-hydroxylamine, which on further reduction changes by molecular rearrangement into the final product. By similar treatment were formed:

an amido-cresol-monosulphonic acid[3] from *o-nitro-toluene;*
the o-p-diamido-phenol from *m-dinitro-benzene;*
diamido-cresol from *o-p-dinitro-toluene;*
o-p-diamido-phenol from *m-nitraniline;*
a diamido-cresol from *o-nitro-p-toluidene;*
the same diamido-cresol from *p-nitro-o-toluidene;*
an amido-salicylic acid from *m-nitro-benzoic acid;*
an amido-cresotinic acid from *m-nitro-p-toluic acid;*
a corresponding amido-oxy acid from *nitro-terephthalic acid;*
a corresponding amido-oxy-acid from *nitro-isophthalic acid;*

---

[1] Chem. Ber., **26**, 990.

[2] *Ibid.*, **26**, 1840.

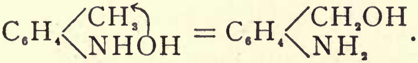
[3] *Ibid.*, **27**, 1929.

an amido-naphthalene-sulphonic acid from $\alpha_1\alpha_3$-*nitro-naphthalene-sulphonic acid.*

The following is true in all these cases where the reduction is carried out in a concentrated sulphuric acid solution:

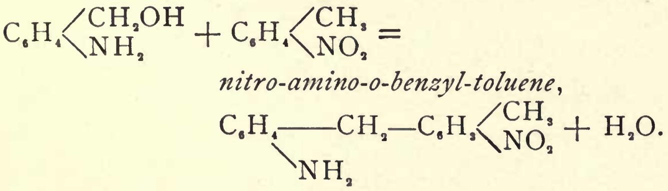
The nitro-groups are completely reduced to amido-groups and a hydroxyl-group is taken up, always in a para-position to one of the amido-groups. As in the case of o-nitro-toluene sometimes also a sulpho-group is taken up. *p-nitro-toluene* on electrolysis behaves differently. Here the final product has the composition $C_{14}H_{14}N_2O_2$, and its formation is as follows:

p-Amido-benzyl alcohol is formed from p-tolyl-hydroxylamine (an intermediate product in the reduction of p-nitro-toluene) by molecular rearrangement,



$$C_6H_4\left\langle\begin{matrix}CH_3\\NHOH\end{matrix}\right. = C_6H_4\left\langle\begin{matrix}CH_2OH\\NH_2\end{matrix}\right. .$$

The amido-benzyl alcohol thus formed condenses with one molecule of nitro-toluene (under the influence of the sulphuric acid), water being split off[1]:



$$C_6H_4\left\langle\begin{matrix}CH_2OH\\NH_2\end{matrix}\right. + C_6H_4\left\langle\begin{matrix}CH_3\\NO_2\end{matrix}\right. =$$

nitro-amino-o-benzyl-toluene,

$$\begin{matrix}C_6H_4\text{——}CH_2\text{—}C_6H_3\left\langle\begin{matrix}CH_3\\NO_2\end{matrix}\right. + H_2O.\\ \diagdown NH_2\end{matrix}$$

---

[1] Chem. Ber., **26**, 2810.

In a third paper[1] Gattermann applies this reduction to a large number of compounds which for lack of space cannot here be enumerated. The nature of the reaction is the same in all cases. The esters of the carboxylic acids show the same behavior as the acids themselves.

These reduction products have all become the subjects of patents.[2]

Löb and Gattermann have produced direct and indirect evidence that the amido-phenols are actually formed by the molecular rearrangement of phenylhydroxylamine, which occurs as an intermediate product.

Löb[3] has found that p- and o-chlor-aniline are obtained by the electrolytic reduction of nitro-benzene suspended in fuming hydrochloric acid, nitro-benzene dissolved in alcoholic hydrochloric acid, and nitrobenzene dissolved in mixtures of hydrochloric and acetic acid. With hydrobromic acid the corresponding brom-anilines are formed.

The reaction takes place as shown in the following equations:

1. $C_6H_5NO_2 + 4H = C_6H_5NHOH + H_2O.$
2. $C_6H_5NHOH + HCl = C_6H_5NHCl + H_2O.$

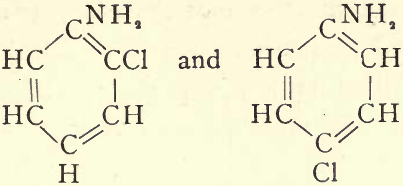
---

[1] Chem. Ber., 27, 1927.

[2] German Patent, 75260 and additions to the same.

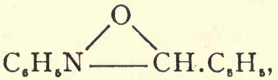
[3] Ztschr. f. Elektrochem., 3, 46.

3. C_6H_6NHCl =



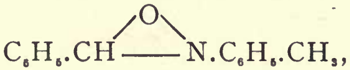
The phenyl-chloramine formed by the action of hydrochloric acid on phenyl-hydroxylamine changes, by molecular rearrangement, into o- and p-chloraniline.

Gattermann[1] has obtained direct proof of the intermediate formation of phenyl-hydroxylamine by adding benzaldehyde to the solution at the beginning of the electrolysis. He was thus able to isolate a condensation product of phenyl-hydroxylamine with benzaldehyde. In this way he obtained benzylidene-phenyl-hydroxylamine,



$$C_6H_5N \overset{O}{\text{——}} CH.C_6H_5,$$

from *nitro-benzene*, benzylidene-o-tolyl-hydroxylamine,



$$C_6H_5.CH \overset{O}{\text{——}} N.C_6H_4.CH_3,$$

from *o-nitro-toluene*, and the corresponding benzylidene compounds from *m-nitro-toluene*, *p-nitro-toluene*, *nitro-p-xylene*, and *m-nitro-benzoic acid*.

The presence of formaldehyde in the electrolytic

---

[1] Chem. Ber., 29, 3040.

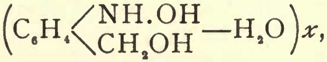
reduction of nitro-compounds produces an effect entirely different from that caused by the addition of benzaldehyde. The phenomena occurring in this case have been thoroughly investigated by Löb.[1]

The fundamental object of his researches differs from that of Gattermann, in that Löb undertakes to establish the separate phases of the reduction of the nitro-group.

This he accomplishes by the addition of formaldehyde to the electrolyte under varying conditions, and as a result the intermediate products, at the moment of their formation, combine with formaldehyde, producing condensation compounds which do not undergo further decomposition. By regulating the potential and density of the current the reaction can at will be checked at a perfectly definite phase of the reduction.

In the electrolysis of nitro-benzene by this method there were formed:

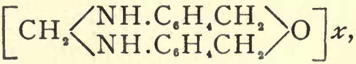
1. p-Anhydro-hydroxylamine-benzyl alcohol,



$$\left(C_6H_4\begin{matrix}\diagup NH.OH \\ \diagdown CH_2OH\end{matrix}-H_2O\right)x,$$

which may also be directly prepared by the action of formaldehyde on phenyl-hydroxylamine.

2. Methylene-di-p-anhydro-amido-benzyl alcohol,



$$\left[CH_2\begin{matrix}\diagup NH.C_6H_4CH_2\diagdown \\ \diagdown NH.C_6H_4CH_2\diagup\end{matrix}O\right]x,$$

---

[1] Ztschr. f. Elektroch., 4, 428.

a condensation product of formaldehyde and aniline.

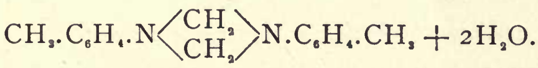
The behavior of *p-nitro-toluene* is different, since in this case, the p-position being occupied by the nitro-group, an analogous reaction with formaldehyde is impossible.

While p-nitro-toluene is converted in an alkaline solution smoothly into azo-toluene and in an acid solution into p-toluidene, nearly equal quantities of two different products are obtained in the presence of formaldehyde, viz.:

1. p-Dimethyl-toluidene.
2. Dimethylene-ditoluidene.

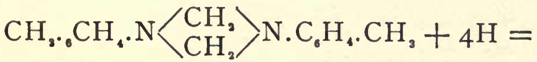
The nature of the reaction is such that the reduction proceeds until p-toluidene is formed, and not till then does a condensation with formaldehyde occur:

$2C_6H_4.CH_3.NH_2 + 2CH_2O =$



$$CH_3.C_6H_4.N\left\langle\begin{matrix}CH_2\\CH_2\end{matrix}\right\rangle N.C_6H_4.CH_3 + 2H_2O.$$

The dimethylene-ditoluidene thus formed on further reduction breaks up into dimethyl-toluidene and toluidene, the latter becoming again subject to the action of the formaldehyde:



$$CH_3.._6CH_4.N\left\langle\begin{matrix}CH_2\\CH_2\end{matrix}\right\rangle N.C_6H_4.CH_3 + 4H =$$

$$CH_3.C_6H_4.N(CH_3)_2 + H_2N.C_6H_4CH_3.$$

A state of equilibrium exists between the dimethyl-toluidene and the dimethylene-ditoluidene at the end of the operation.

A further application[1] of Gattermann's reaction has been found in the case of *aromatic nitramines*,[2] which if reduced in a concentrated solution of sulphuric acid give amido-phenol derivatives. The process can also be applied to the esters of nitro-carboxylic acids[3] and results in the formation of amido-phenol-carboxylic esters.

Nitro-sulphonic acids[4] show a similar behavior, while the p-nitro- or p-nitroso-alkyl-anilines[5] and toluidenes, as the case may be, are reduced to p-amido-derivatives of alkylated m-oxy-anilines or their homologues.

The nitro-derivatives of the *quinoline*[6] *series* show a deportment similar to that of the derivatives of benzene.

Nitro-aldehydes, which Gattermann[7] has also chosen for the subject of thorough investigation, conduct themselves differently from the nitro-compounds thus far described.

If the nitro-aldehydes are reduced there are formed either the free aldehyde-phenyl-hydroxylamines, or

---

[1] German Pat., 77806.

[2] *Ibid.*, 78829.

[3] *Ibid.*, 79865.

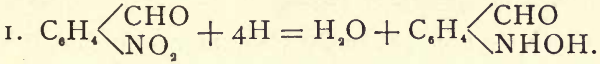
[4] *Ibid.*, 81621.

[5] *Ibid.*, 81625.

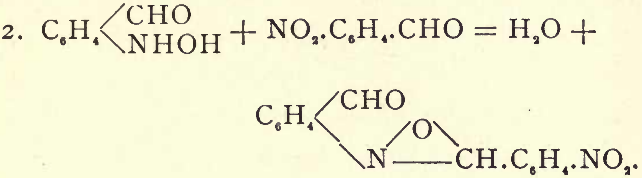
[6] *Ibid.*, 80978.

[7] Chem. Ber., **29**, 3037; German Pat. 85198.

condensation products of the same with the nitro-aldehyde present. The nitro-benzylidene-aldehydo-phenyl-hydroxylamines are thus formed:



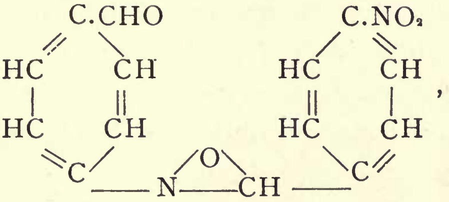
$$1.\quad C_6H_4\left\langle\begin{matrix}CHO\\NO_2\end{matrix}\right. + 4H = H_2O + C_6H_4\left\langle\begin{matrix}CHO\\NHOH.\end{matrix}\right.$$



$$2.\quad C_6H_4\left\langle\begin{matrix}CHO\\NHOH\end{matrix}\right. + NO_2.C_6H_4.CHO = H_2O +$$

$$C_6H_4\left\langle\begin{matrix}CHO\\ N\overset{O}{\frown}CH.C_6H_4.NO_2.\end{matrix}\right.$$

p-Nitro-benzylidene-p-aldehydo-phenyl-hydroxylamine,

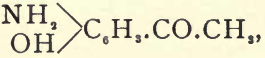


may thus be prepared from *p-nitro-benzaldehyde*.

From *m-nitro-benzaldehyde* an analogous compound is formed.

Gattermann,[1] on reducing several *aromatic nitro-ketones*, obtained the corresponding derivatives of amido-phenols.

By a similar treatment amido-oxy-acetophenone,

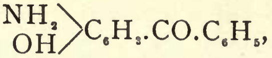


$$\left.\begin{matrix}NH_2\\OH\end{matrix}\right\rangle C_6H_3.CO.CH_3,$$

---

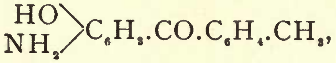
[1] Chem. Ber., 29, 3034.

is formed from *m-nitro-acetophenone;* amido-oxy-benzophenone,



$$\left.\begin{matrix}NH_2\\OH\end{matrix}\right\rangle C_6H_3.CO.C_6H_5,$$

from *m-nitro-benzophenone;* and amido-oxy-phenyl-p-tolylketone,



$$\left.\begin{matrix}HO\\NH_2\end{matrix}\right\rangle C_6H_3.CO.C_6H_4.CH_3,$$

from *m-nitro-phenyl-p-tolylketone.*

The process which Straub[1] employs to prepare hydrazo-compounds from nitro-hydrocarbons is yet to be mentioned. The chief feature of his experiments is that the original material and all intermediate products are retained in solution during the electrolysis by the selection of a suitable solvent, and the hydrazo-compounds are withdrawn from the action of the current by precipitation.

Straub attains this end by subjecting the nitro-hydrocarbons to electrolytic reduction in a solvent made a conductor by the addition of potassium hydroxide. The quantity of the liquid used must be sufficient to keep in solution the azo- and azoxy-compounds corresponding to the nitro-hydrocarbon.

Noyes and Dorrance[2] have applied Gattermann's reaction to *p-nitraniline* and some other substances. In this way they obtained p-diamido-benzene sulphate

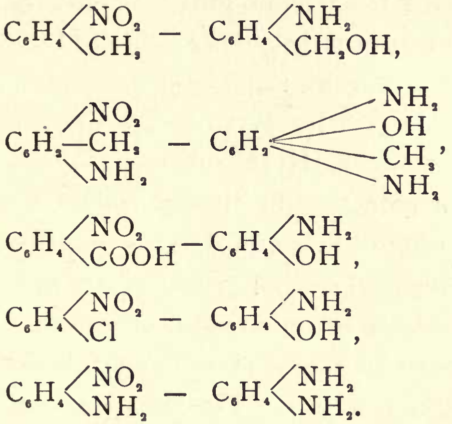
---

[1] German Patent, 79731.

[2] Chem. Ber., **28**, 2349.

from *p-nitraniline*, p-amido-phenol-sulphonic acid from *p-nitro-phenol*, and p-amido-phenol-sulphonic acid from *p-chlor-nitro-benzene*.

They explain the reactions in the following manner:



$$C_6H_4\left\langle\begin{array}{l}NO_2\\CH_3\end{array}\right. - C_6H_4\left\langle\begin{array}{l}NH_2\\CH_2OH\end{array}\right.,$$

$$C_6H_3\left\langle\begin{array}{l}NO_2\\CH_3\\NH_2\end{array}\right. - C_6H_2\left\langle\begin{array}{l}NH_2\\OH\\CH_3\\NH_2\end{array}\right.,$$

$$C_6H_4\left\langle\begin{array}{l}NO_2\\COOH\end{array}\right. - C_6H_4\left\langle\begin{array}{l}NH_2\\OH\end{array}\right.,$$

$$C_6H_4\left\langle\begin{array}{l}NO_2\\Cl\end{array}\right. - C_6H_4\left\langle\begin{array}{l}NH_2\\OH\end{array}\right.,$$

$$C_6H_4\left\langle\begin{array}{l}NO_2\\NH_2\end{array}\right. - C_6H_4\left\langle\begin{array}{l}NH_2\\NH_2\end{array}\right..$$

The phenomena of the reduction of nitro-compounds in alkaline solution have been investigated by Löb.[1] In his first experiments he used *nitro-benzoic acids* and *nitro-phenols*. It was found that m-nitro- and p-nitro-benzoic acid were smoothly reduced to the corresponding azo-acids, while the o-acid under similar conditions yielded o-azoxy-benzoic acid and o-hydrazo-benzoic acid. The nitro-phenols in alkaline solutions gave amido-phenols.

The fact that the reduction in an alkaline solution may be carried as far as the azo-phase has been made

---

[1] Zeitschr. f. Elektroch., **2**, 529: *ibid.*, **3**, 45.

use of by Löb[1] in performing a direct electrosynthesis of the mixed azo-bodies and azo-dyes. The components of the compounds desired, in exactly equimolecular proportions, are reduced under conditions which render the union of the two residues possible. In this way azo-compounds are obtained in which the substituents are in the meta-position—compounds which could not be prepared by the Griess method.

Kaufmann and Hof[2] subjected *m-nitro-benzaldehyde* to reduction in alkaline solution and thus obtained m-azo-benzoic acid as the principal product and m-azo-benzyl alcohol as a secondary product. By the electrolysis of m-nitro-benzaldehyde Löb[3] obtained m-azo-benzoic acid and m-azo-benzyl alcohol as secondary products. The chief product consisted of a mixed azo-body, azo-m-benzyl-alcohol-m-benzoic acid,

$$m - CH_2OH.C_6H_4.N:N.C_6H_4.COOH - m.$$

The Gesellschaft f. Chem. Industrie of Basel[4] prepare orange dyes by using as cathode fluid an alkaline solution of the yellow condensation products of *p-nitro-toluene-sulphonic acid*,

$$CH_3.C_6H_3\langle\begin{matrix}NO_2\\SO_3H\end{matrix}$$

---

[1] Ztschr. f. Elektroch., 4, 530.

[2] Chemiker Zeitung, 1896.

[3] Ztschr. f. Elektroch., 4.

[4] English Pat., 22482.

(namely, a mixture of azoxy-stilbene-disulphonic acid, azo-stilbene-disulphonic acid, and dinitro-stilbene-disulphonic acid).

The reduction, however, must not be continued until amido-compounds result. Other reduction processes are used by the Badische Aniline u. Sodafabrik[1] for making naphthazarine from $\alpha_1\alpha_4$-*dinitro-naphthalene* or $\alpha_1\alpha_3$-*dinitro-naphthalene*. In these cases intermediate products are first formed in the electrolytic reduction, and these are transformed into naphthazarine by heating.

The Basel company[2] mentioned above obtains triphenyl-methane dyes by the electrolytic reduction of *nitro-leuco-bodies* of the type $\underset{(4)}{NO_2}—C_6H_4.\underset{(1)}{CHR_2}$, which result in the formation of the carbinoles $\underset{(4)}{NH_2}—C_6H_4.\underset{(1)}{COH}.R_2$.[3]

Ahrens[4] accomplished the electrolytic reduction of *pyridine* and the derivatives of pyridine, and obtained piperidine from pyridine, and pipecoline from *picoline*. In these electrolyses lead cathodes and 10% solutions of sulphuric acid were employed.

If strong sulphuric acid and a platinum cathode

---

[1] German Pat., 79406.

[2] German Pat., 84607.

[3] In these formulæ R denotes aromatic radicals with primary, secondary, or tertiary amido-groups, or with hydroxyl-groups.

[4] Ztschr. f. Elektroch., **2**, 577, 580.

were used there was formed a substance containing nitrogen and sulphur, the chemical nature of which has not yet been determined.

Nitro-piperidines on electrolytical reduction give piperylhydrazines, ammonia is split off, and piperidine is in part regenerated.

Nitroso-α-pipecoline gives, in addition to ammonia, α-pipecoline and α-methyl-piperylhydrazine.

In a like manner from *nitroso-aldehyde-copellidine* ($CH_3.C_2H_5.C_5H_8:N.NO$) there is formed ammonia, a large proportion of copellidine ($CH_3.C_2H_5.C_5H_8:NH$), and also the corresponding methyl-ethyl-piperylhydrazine:

$$CH_3.C_2H_5.C_5H_8:N.NH_2.$$

Quinoline in 10% sulphuric-acid solution gave a polymeric dihydro-quinoline and tetrahydro-quinoline (Ahrens[1]).

Quinaldine, likewise in sulphuric-acid solution, gave dihydroquinaldine and tetrahydro-quinaldine.

6. Electrolytic Oxidation of Nitro-compounds.

The influence which the nitroso- and nitro-groups exert on the other substituents is especially shown in oxidation reactions, which here occur much more readily than in the case of compounds which have not

---

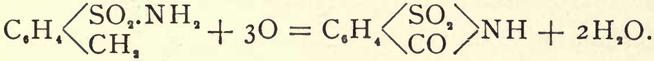
[1] Chem. Ber., 29, 1123.

been nitrated. By the electrolytic oxidation of *nitroso-piperidine* Ahrens[1] obtained dipiperidyl ($C_{10}H_{20}N_2$). Elbs[2] secured a satisfactory yield of p-nitro-benzyl alcohol from *p-nitro-toluene*.

The introduction of hydroxyl-groups into azo-benzene, which Heilpern[3] succeeded in accomplishing, can also be regarded as an oxidation process. If azo-benzene be dissolved in as small a quantity of conc. sulphuric acid as possible and this solution be subjected to electrolytic action at the anode, chiefly tetra-oxy-azo-benzene is formed:

$$C_{12}H_{10}O_4N_2 = (OH)_2C_6H_3N : NC_6H_3(OH)_2.$$

According to a patent[4] benzoyl-sulphone-imides can be prepared by the electrolytic oxidation of *toluene-sulphone-amides;* for example, o-benzoyl-sulphone-imide, or saccharine, from *o-toluene-sulphone-amide:*



$$C_6H_4\left\langle\begin{matrix}SO_2.NH_2\\CH_3\end{matrix}\right. + 3O = C_6H_4\left\langle\begin{matrix}SO_2\\CO\end{matrix}\right\rangle NH + 2H_2O.$$

The corresponding p-compound, and *p-nitro-o-toluene-sulphone-amide*,

$$NO_2.CH_3.C_6H_3.SO_2NH,$$

show a similar behavior.

Yellow mordant dyes are obtained by the Badische Aniline u. Sodafabrik[5] by the oxidation of *aromatic*

---

[1] Ztschr. f. Elektroch., 2, 579.

[2] *Ibid.*, 2, 522.

[3] *Ibid.*, 4, 89.

[4] F. v. Heyden's Nachfolger, German Pat., 85491.

[5] German Pat., 85390.

oxycarboxylic acids in sulphuric acid solution, by the use of ammonium persulphate or by electrolysis. A whole series of acids have been investigated: *m-dioxybenzoic acid*, *gallic acid*, *tannin*, the *ethyl ester of gallic acid*, *gallamide* ($(OH)_3C_6H_2CO.NH_2$), *o-*, *m-*, and *p-oxy-benzoic acids*, *cresotinic acid*, etc.

7. Electrolysis of Alkaloids.[1]

Caffeïne, Theïne, $C_8H_{10}N_4O_2$.—On permitting the electric current to act for several days on a solution of caffeïne acidified with sulphuric acid Pommerehne[2] obtained amalic acid, formic acid, ammonia, and methylamine.

Atropine, $C_{17}H_{23}NO_3$.—From the neutral sulphate of atropine crystallized atropine is gradually precipitated at the cathode, while at the anode carbon dioxide, carbon monoxide, oxygen, and nitrogen are evolved. The acid sulphate behaves in a similar manner, but the evolution of nitrogen was not observed.

Opium.—If opium is subjected to the action of the electric current the acid goes to the cathode and the base to the anode. Thus meconic acid (oxy-pyrone-dicarboxylic acid) was found at the positive pole and morphine ($C_{17}H_{17}NO(OH)_2$) at the negative pole.

---

[1] Donato Tommasi: Traité d'Electrochimie, Théorique et Practique, Part 4, 788.

[2] Arch. f. Pharm., **235**, 364.

Bourgoin, however, showed that the reaction does not take place smoothly, but is always accompanied by secondary reactions.

Morphine.—Pommerehne,[1] by the electrolysis of a solution of morphine acidified with sulphuric acid, obtained, after a few days, crystals of oxy-dimorphine sulphate. The solution became dark-colored.

Codeïne (methyl-morphine), $C_{17}H_{17}NO(OH)O.CH_3$.—On the electrolysis of the neutral sulphate hydrogen is evolved, codeïne is precipitated, and the solution turns brown. The acid sulphate undergoes more complete decomposition, and carbon dioxide, carbon monoxide, oxygen, and nitrogen are split off.

Cotarnine,[2] $C_{12}H_{15}NO_4$.—This compound is converted by the electrolytic hydrogen quantitatively into pure hydro-cotarnine,

$$(C_{12}H_{15}NO_3)_2.H_2O.$$

Quinine, $C_{20}H_{24}N_2O_2$.—Although the neutral sulphate is a very poor conductor, the acid sulphate is readily decomposed into carbon dioxide, carbon monoxide, and nitrogen. The color of the solution changes to a dark brown.

Cinchonine,[3] $C_{19}H_{22}N_2O$.—On the electrolysis of the nitrate of this compound an oil-like body appears at the anode.

---

[1] Arch. f. Pharm., **235**, 364.

[2] German Pat., 94949.

[3] Journ. prakt. Chem., 72, 73.

Strychnine,[1] $C_{21}H_{22}N_2O_2$. — The neutral sulphate suffers but little change. The solution becomes slightly colored, hydrogen and oxygen are given off, and crystals of strychnine collect on the cathode.

The acid sulphate behaves in a like manner, except that in its case the formation of carbon dioxide and carbon monoxide as well as oxygen and nitrogen shows that a part of the substance undergoes complete decomposition. In strongly acid solutions the splitting off of nitrogen does not occur.

Brucine,[1] $C_{23}H_{26}N_2O_4$.—A solution of the neutral sulphate turns red and the sulphate is decomposed. Hydrogen is evolved at the negative pole, but the brucine completely absorbs the oxygen at the positive pole. The acid salt is very energetically decomposed, becoming first red and then brown. At the anode carbonic-acid gas, carbon monoxide, oxygen, and nitrogen escape.

Besides the gases mentioned, the above alkaloids break up into other products, principally complicated compounds containing nitrogen.

8. Camphor and Glucosides.

Terpentine hydrochloride.—This compound on electrolysis in the melted condition or in an alcoholic acetic-acid solution gave camphor, $C_{10}H_{16}O$ (Richardson[2]).

---

[1] Bull. soc. chim., 12, 400.

[2] English patent, 3555.

Salicine, $C_{13}H_{18}O_7$.—Salicine on electrolysis yielded salicylic aldehyde and salicylic acid (Tichanowitsch[1]).

9. Electrolysis of Blood.

The defibrinated blood of a dog was submitted to electrolysis by Becquerel. He made use of platinum electrodes and a current furnished by a battery of three Daniel cells. At the negative pole he observed the following phenomena:

The blood became brown and alkaline, and contained neither white nor red corpuscles; it possessed the property of gradually dissolving blood-corpuscles and had the odor of putrid meat.

At the positive pole undecomposed and partially decomposed blood-corpuscles were present in large quantities. The fluid gave a precipitate of albumen with nitric acid, mercuric chloride, and lead acetate.

10. Electrolysis of Albumen.

When an albumen solution was electrolyzed by Dumas and Prevost, under conditions similar to those used by Becquerel for blood, the alkali metal went to the negative pole, hydrogen was evolved, and acetic and phosphoric acids appeared at the positive pole. The result of this is that the albumen is coagulated

---

[1] Chem. Centralblatt, 1861, p. 613.

at the negative pole (by the alkali present), while at the positive pole the solution remains clear.

As Lassaigne has shown, pure albumen in aqueous solution is a non-conductor of electricity; the addition of salts or acids is therefore necessary in its electrolysis.

11. Electrolysis and Electrosynthesis with Alternating Currents.

If the polarity of the current does not change altogether too rapidly, since oxidation and reduction occur successively at each pole, it is possible to accomplish electrolyses and electrosyntheses with alternating currents. Experiments with this end in view have been made by Drechsel.[1] Dehydration is a case of simultaneous reduction and oxidation. The supposition that in living organisms carbamide is produced from *ammonium carbamate* by the splitting off of water prompted Drechsel to make experiments in this direction.[2]

If an aqueous solution of ammonium carbamate was electrolyzed with a current from a battery of 4–6 Grove elements and platinum electrodes were used, carbamide was obtained independently of the elec-

---

[1] Journ. prakt. Chem., **22**, 476.

[2] *Ibid.*

trode material when alternating currents were employed. The reactions are supposed to be either

I. $NH_2.COONH_4 + O = NH_2.CO.ONH_2 + H_2O$,

II. $NH_2.CO.ONH_2 + 2H = NH_2.CO.NH_2 + H_2O$,

or

I. $NH_2.COONH_4 + 2H = NH_2.CONH_4 + H_2O$,

II. $NH_2.CO.NH_4 + O = NH_2.CO.NH_2 + H_2O$.

The fact that the platinum electrodes were strongly attacked, with the formation of platinum salts, caused Gerdes[1] to investigate the platinum bases. As the principal product he found a compound to which he gave the following formula:

$$\mathrm{CO}\begin{matrix}\diagup\\\diagdown\end{matrix}\begin{matrix}\mathrm{ONH_3}\\\mathrm{ONH_3}\end{matrix}\Big\}\,\mathrm{Pt}\begin{matrix}\diagup\\\diagdown\end{matrix}\begin{matrix}\mathrm{NH_3}\\\mathrm{NH_3}\end{matrix}\quad\begin{matrix}\mathrm{NH_3O}\\\mathrm{NH_3O}\end{matrix}\begin{matrix}\diagdown\\\diagup\end{matrix}\mathrm{CO},$$

and the chloride of which is said to have the composition

$$\begin{matrix}\mathrm{ClNH_3}\\\mathrm{ClNH_3}\end{matrix}\begin{matrix}\diagdown\\\diagup\end{matrix}\mathrm{Pt}\begin{matrix}\diagup\\\diagdown\end{matrix}\begin{matrix}\mathrm{NH_3}\\\mathrm{NH_3}\end{matrix}\quad\begin{matrix}\mathrm{NH_3Cl}\\\mathrm{NH_3Cl}\end{matrix},\ \mathrm{PtCl_4} + 2\mathrm{H_2O}.$$

Gerdes also examined the nitrate and sulphate of this base.

In the course of further researches[2] Drechsel found that when alkaline solutions were used platinum was present in the electrolyzed fluid. Copper when used as electrode showed a similar behavior; lead was less

---

[1] Journ. prakt. Chem., **26**, 257.

[2] *Ibid.*, **29**, 229.

attacked, gold but very slightly, and palladium not at all.

The formation of the phenol ester of sulphuric acid in living organisms is supposed, like carbamide, to be the result of dehydration. Taking this into consideration, Drechsel carried out the following experiment:

A saturated solution of acid magnesium carbonate was mixed with an equal volume of a solution of magnesium sulphate and the mixture was saturated with commercial *carbolic acid*.[1]

When this solution was electrolyzed for thirty hours with alternating currents and platinum electrodes were used, the following products were obtained:

1. γ-Diphenol.
2. Pyrocatechin.
3. Hydroquinone.
4. Phenol ester of sulphuric acid.
5. Oxalic acid.
6. Formic acid.
7. Succinic acid.
8. Malonic acid (?).
9. n-Valeric acid (?).
10. n-Butyric acid (?).
11. Some cyclohexanone,[2] $C_6H_{10}O$.

According to Drechsel the formation of the phenol ester of sulphuric acid is probably represented by the following equations:

$$\text{I. } C_6H_5OH + HO.SO_2H + O = C_6H_5.OOSO_2H + H_2O,$$

$$\text{II. } C_6H_5.OOSO_2H + 2H = C_6H_5.SO_3H + H_2O.$$

---

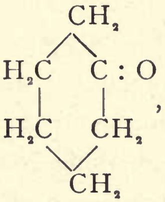
[1] Journ. prakt. Chem., [2] **29**, 229.

[2] *Ibib.*, [2] **38**, 67.

Later Drechsel[1] electrolyzed *normal capronic acid* with alternating currents. The electrolytic solution contained, in a volume of 3 liters, 200 g. of capronic acid as magnesium salt and was nearly saturated with acid magnesium carbonate. Platinum electrodes were used. At the end of the experiment the following compounds could be identified in the solution:

1. Valeric acid.
2. Butyric acid.
3. Oxalic acid.
4. Succinic acid.
5. Adipic acid.
6. Oxy-capronic acid.
7. Glutaric acid.

In a still later research on the electrolysis of *pheno* with alternating currents Drechsel[2] detected phenyl-sulphuric acid, dioxy-benzenes, a number of acids of the fatty acid series, and in addition to these an oil which he identified as hydro-pheno-ketone,



and whose phenylhydrazine compound he was able to isolate. Drechsel regards the hydro-pheno-ketone as the origin of the fatty compounds formed. By the

---

[1] Journ. prakt. Chem., 34, 135.

[2] *Ibid.*. 38, 65.

direct addition of water to this compound capronic acid results, and this then breaks up into the acids and other decomposition products mentioned above.

A critical review of the subject-matter which has here been presented will bring out, concerning the electrolysis and electrosynthesis of organic compounds, several important points which promise to be of great assistance, at no very distant date, in connection with future research in the field of organic chemistry. These points may be summarized as follows: the oxidation reactions which occur in the electrolysis of acids of the aliphatic series, the reduction reactions in the case of the aromatic series, and, lastly, the reactions involving substitutions, concerning which but few researches have been published. Of these the first is apparently the most promising.

Since in all the experiments which have thus far been made the dependence of all reactions upon current density, temperature, and concentration is clearly evident, the attention of experimenters is again called to the importance of exact data concerning the conditions of experiment.

AUTHORS.

INDEX.

SHORT-TITLE CATALOGUE

OF THE

PUBLICATIONS

OF

JOHN WILEY & SONS,

NEW YORK.

LONDON: CHAPMAN & HALL, LIMITED.

ARRANGED UNDER SUBJECTS.

Descriptive circulars sent on application.

Books marked with an asterisk are sold at *net* prices only.

All books are bound in cloth unless otherwise stated.

AGRICULTURE.

CATTLE FEEDING—DAIRY PRACTICE—DISEASES OF ANIMALS—GARDENING, ETC.

Armsby's Manual of Cattle Feeding	12mo,	$1 75
Downing's Fruit and Fruit Trees	8vo,	5 00
Grotenfelt's The Principles of Modern Dairy Practice. (Woll.)	12mo,	2 00
Kemp's Landscape Gardening	12mo,	2 50
Lloyd's Science of Agriculture	8vo,	4 00
Loudon's Gardening for Ladies. (Downing.)	12mo,	1 50
Steel's Treatise on the Diseases of the Dog	8vo,	3 50
" Treatise on the Diseases of the Ox	8vo,	6 00
Stockbridge's Rocks and Soils	8vo,	2 50
Woll's Handbook for Farmers and Dairymen	12mo,	1 50

ARCHITECTURE.

BUILDING—CARPENTRY—STAIRS—VENTILATION, ETC.

Berg's Buildings and Structures of American Railroads	4to,	7 50
Birkmire's American Theatres—Planning and Construction	8vo,	3 00
" Architectural Iron and Steel	8vo,	3 50
" Compound Riveted Girders	8vo,	2 00
" Skeleton Construction in Buildings	8vo,	3 00
" Planning and Construction of High Office Buildings.	8vo,	3 50

Carpenter's Heating and Ventilating of Buildings	8vo,	$3 00
Downing, Cottages	8vo,	2 50
" Hints to Architects	8vo,	2 00
Freitag's Architectural Engineering	8vo,	2 50
Gerhard's Sanitary House Inspection	16mo,	1 00
" Theatre Fires and Panics	12mo,	1 50
Hatfield's American House Carpenter	8vo,	5 00
Holly's Carpenter and Joiner	18mo,	75
Kidder's Architect and Builder's Pocket-book	Morocco flap,	4 00
Merrill's Stones for Building and Decoration	8vo,	5 00
Monckton's Stair Building—Wood, Iron, and Stone	4to,	4 00
Wait's Engineering and Architectural Jurisprudence	8vo,	6 00
	Sheep,	6 50
Worcester's Small Hospitals—Establishment and Maintenance, including Atkinson's Suggestions for Hospital Architecture	12mo,	1 25
World's Columbian Exposition of 1893	4to,	2 50

ARMY, NAVY, Etc.

MILITARY ENGINEERING—ORDNANCE—PORT CHARGES—LAW, ETC.

Bourne's Screw Propellers	4to,	5 00
Bruff's Ordnance and Gunnery	8vo,	6 00
Bucknill's Submarine Mines and Torpedoes	8vo,	4 00
Chase's Screw Propellers	8vo,	3 00
Cooke's Naval Ordnance	8vo,	12 50
Cronkhite's Gunnery for Non-com. Officers	18mo, morocco,	2 00
Davis's Treatise on Military Law	8vo,	7 00
	Sheep,	7 50
" Elements of Law	8vo,	2 50
De Brack's Cavalry Outpost Duties. (Carr.)	18mo, morocco,	2 00
Dietz's Soldier's First Aid	12mo, morocco,	1 25
* Dredge's Modern French Artillery	4to, half morocco,	15 00
" Record of the Transportation Exhibits Building, World's Columbian Exposition of 1893	4to, half morocco,	10 00
Durand's Resistance and Propulsion of Ships	8vo,	5 00
Dyer's Light Artillery	12mo,	3 00
Hoff's Naval Tactics	8vo,	1 50
Hunter's Port Charges	8vo, half morocco,	13 00

Ingalls's Ballistic Tables	8vo,	$1 50
“ Handbook of Problems in Direct Fire	8vo,	4 00
Mahan's Advanced Guard	18mo,	1 50
“ Permanent Fortifications. (Mercur.)	8vo, half morocco,	7 50
Mercur's Attack of Fortified Places	12mo,	2 00
“ Elements of the Art of War	8vo,	4 00
Metcalfe's Ordnance and Gunnery	12mo, with Atlas,	5 00
Murray's A Manual for Courts-Martial	18mo, morocco,	1 50
“ Infantry Drill Regulations adapted to the Springfield Rifle, Caliber .45	18mo, paper,	15
Phelps's Practical Marine Surveying	8vo,	2 50
Powell's Army Officer's Examiner	12mo,	4 00
Reed's Signal Service		50
Sharpe's Subsisting Armies	18mo, morocco,	1 50
Very's Navies of the World	8vo, half morocco,	3 50
Wheeler's Siege Operations	8vo,	2 00
Winthrop's Abridgment of Military Law	12mo,	2 50
Woodhull's Notes on Military Hygiene	12mo,	1 50
Young's Simple Elements of Navigation	12mo, morocco flaps,	2 00
“ “ “ “ “	first edition	1 00

ASSAYING.

SMELTING—ORE DRESSING—ALLOYS, ETC.

Fletcher's Quant. Assaying with the Blowpipe	12mo, morocco,	1 50
Furman's Practical Assaying	8vo,	3 00
Kunhardt's Ore Dressing	8vo,	1 50
* Mitchell's Practical Assaying. (Crookes.)	8vo,	10 00
O'Driscoll's Treatment of Gold Ores	8vo,	2 00
Ricketts and Miller's Notes on Assaying	8vo,	3 00
Thurston's Alloys, Brasses, and Bronzes	8vo,	2 50
Wilson's Cyanide Processes	12mo,	1 50
“ The Chlorination Process	12mo,	1 50

ASTRONOMY.

PRACTICAL, THEORETICAL, AND DESCRIPTIVE.

Craig's Azimuth	4to,	3 50
Doolittle's Practical Astronomy	8vo,	4 00
Gore's Elements of Geodesy	8vo,	2 50

Hayford's Text-book of Geodetic Astronomy	8vo.	
Michie and Harlow's Practical Astronomy	8vo,	$3 00
White's Theoretical and Descriptive Astronomy	12mo,	2 00

BOTANY.

Gardening for Ladies, Etc.

Baldwin's Orchids of New England	8vo,	1 50
Loudon's Gardening for Ladies. (Downing.)	12mo,	1 50
Thomé's Structural Botany	18mo,	2 25
Westermaier's General Botany. (Schneider.)	8vo,	2 00

BRIDGES, ROOFS, Etc.

Cantilever—Draw—Highway—Suspension.

(*See also* Engineering, p. 6.)

Boller's Highway Bridges	8vo,	2 00
* " The Thames River Bridge	4to, paper,	5 00
Burr's Stresses in Bridges	8vo,	3 50
Crehore's Mechanics of the Girder	8vo,	5 00
Dredge's Thames Bridges	7 parts, per part,	1 25
Du Bois's Stresses in Framed Structures	4to,	10 00
Foster's Wooden Trestle Bridges	4to,	5 00
Greene's Arches in Wood, etc.	8vo,	2 50
" Bridge Trusses	8vo,	2 50
" Roof Trusses	8vo,	1 25
Howe's Treatise on Arches	8vo,	4 00
Johnson's Modern Framed Structures	4to,	10 00
Merriman & Jacoby's Text-book of Roofs and Bridges. Part I., Stresses	8vo,	2 50
Merriman & Jacoby's Text-book of Roofs and Bridges. Part II., Graphic Statics	8vo.	2 50
Merriman & Jacoby's Text-book of Roofs and Bridges. Part III., Bridge Design	8vo,	2 50
Merriman & Jacoby's Text-book of Roofs and Bridges. Part IV., Continuous, Draw, Cantilever, Suspension, and Arched Bridges	8vo,	2 50
* Morison's The Memphis Bridge	Oblong 4to,	10 00

Waddell's Iron Highway Bridges	8vo,	$4 00
" De Pontibus (a Pocket-book for Bridge Engineers).		
Wood's Construction of Bridges and Roofs	8vo,	2 00
Wright's Designing of Draw Spans	8vo,	2 50

CHEMISTRY.

QUALITATIVE—QUANTITATIVE– ORGANIC—INORGANIC, ETC.

Adriance's Laboratory Calculations	12mo,	1 25
Allen's Tables for Iron Analysis	8vo,	3 00
Austen's Notes for Chemical Students	12mo,	1 50
Bolton's Student's Guide in Quantitative Analysis	8vo,	1 50
Classen's Analysis by Electrolysis. (Herrick and Boltwood.)	8vo,	3 00
Crafts's Qualitative Analysis. (Schaeffer.)	12mo,	1 50
Drechsel's Chemical Reactions. (Merrill.)	12mo,	1 25
Fresenius's Quantitative Chemical Analysis. (Allen.)	8vo,	6 00
" Qualitative " " (Johnson.)	8vo,	3 00
" " " " (Wells) Trans. 16th. German Edition	8vo,	5 00
Fuerte's Water and Public Health	12mo,	1 50
Gill's Gas and Fuel Analysis	12mo,	1 25
Hammarsten's Physiological Chemistry. (Mandel.)	8vo,	4 00
Helm's Principles of Mathematical Chemistry. (Morgan).	12mo,	1 50
Kolbe's Inorganic Chemistry	12mo,	1 50
Ladd's Quantitative Chemical Analysis	12mo,	1 00
Landauer's Spectrum Analysis. (Tingle.)	8vo,	3 00
Mandel's Bio-chemical Laboratory	12mo,	1 50
Mason's Water-supply	8vo,	5 00
" Analysis of Potable Water. (*In the press.*)		
Miller's Chemical Physics	8vo,	2 00
Mixter's Elementary Text-book of Chemistry	12mo,	1 50
Morgan's The Theory of Solutions and its Results	12mo,	1 00
Nichols's Water-supply (Chemical and Sanitary)	8vo,	2 50
O'Brine's Laboratory Guide to Chemical Analysis	8vo,	2 00
Perkins's Qualitative Analysis	12mo,	1 00
Pinner's Organic Chemistry. (Austen.)	12mo,	1 50
Poole's Calorific Power of Fuels	8vo,	3 00
Ricketts and Russell's Notes on Inorganic Chemistry (Non-metallic)	Oblong 8vo, morocco,	75

Ruddiman's Incompatibilities in Prescriptions	8vo,	$2 00
Schimpf's Volumetric Analysis	12mo,	2 50
Spencer's Sugar Manufacturer's Handbook.	12mo, morocco flaps,	2 00
" Handbook for Chemists of Beet Sugar House.	12mo, morocco,	3 00
Stockbridge's Rocks and Soils	8vo,	2 50
Troilius's Chemistry of Iron	8vo,	2 00
Wells's Inorganic Qualitative Analysis	12mo,	1 50
" Laboratory Guide in Qualitative Chemical Analysis,	8vo,	1 50
Wiechmann's Chemical Lecture Notes	12mo,	3 00
" Sugar Analysis	8vo,	2 50
Wulling's Inorganic Phar. and Med. Chemistry	12mo,	2 00

DRAWING.

Elementary—Geometrical—Topographical.

Hill's Shades and Shadows and Perspective	8vo,	2 00
MacCord's Descriptive Geometry	8vo,	3 00
" Kinematics	8vo,	5 00
" Mechanical Drawing	8vo,	4 00
Mahan's Industrial Drawing. (Thompson.)	2 vols., 8vo,	3 50
Reed's Topographical Drawing. (H. A.)	4to,	5 00
Reid's A Course in Mechanical Drawing	8vo.	2 00
" Mechanical Drawing and Elementary Machine Design.	8vo.	
Smith's Topographical Drawing. (Macmillan.)	8vo,	2 50
Warren's Descriptive Geometry	2 vols., 8vo,	3 50
" Drafting Instruments	12mo,	1 25
" Free-hand Drawing	12mo,	1 00
" Higher Linear Perspective	8vo,	3 50
" Linear Perspective	12mo,	1 00
" Machine Construction	2 vols., 8vo,	7 50
" Plane Problems	12mo,	1 25
" Primary Geometry	12mo,	75
" Problems and Theorems	8vo,	2 50
" Projection Drawing	12mo,	1 50
" Shades and Shadows	8vo,	3 00
" Stereotomy—Stone Cutting	8vo,	2 50
Whelpley's Letter Engraving	12mo,	2 00

ELECTRICITY AND MAGNETISM.

ILLUMINATION—BATTERIES—PHYSICS.

Anthony and Brackett's Text-book of Physics (Magie).	8vo,	$4 00
Barker's Deep-sea Soundings	8vo,	2 00
Benjamin's Voltaic Cell	8vo,	3 00
" History of Electricity	8vo	3 00
Cosmic Law of Thermal Repulsion	18mo,	75
Crehore and Squier's Experiments with a New Polarizing Photo-Chronograph	8vo,	3 00
* Dredge's Electric Illuminations	2 vols., 4to, half morocco,	25 00
" " " Vol. II	4to,	7 50
Gilbert's De magnete. (Mottelay.)	8vo,	2 50
Holman's Precision of Measurements	8vo,	2 00
Michie's Wave Motion Relating to Sound and Light,	8vo,	4 00
Morgan's The Theory of Solutions and its Results	12mo,	1 00
Niaudet's Electric Batteries. (Fishback.)	12mo,	2 50
Reagan's Steam and Electrical Locomotives	12mo,	2 00
Thurston's Stationary Steam Engines for Electric Lighting Purposes	12mo,	1 50
Tillman's Heat	8vo,	1 50

ENGINEERING.

CIVIL—MECHANICAL—SANITARY, ETC.

(*See also* BRIDGES, p. 4; HYDRAULICS, p. 8; MATERIALS OF ENGINEERING, p. 9; MECHANICS AND MACHINERY, p. 11; STEAM ENGINES AND BOILERS, p. 14.)

Baker's Masonry Construction	8vo,	5 00
" Surveying Instruments	12mo,	3 00
Black's U. S. Public Works	4to,	5 00
Brook's Street Railway Location	12mo, morocco,	1 50
Butts's Engineer's Field-book	12mo, morocco,	2 50
Byrne's Highway Construction	8vo,	7 50
" Inspection of Materials and Workmanship.	12mo, mor.	
Carpenter's Experimental Engineering	8vo,	6 00
Church's Mechanics of Engineering—Solids and Fluids	8vo,	6 00
" Notes and Examples in Mechanics	8vo,	2 00
Crandall's Earthwork Tables	8vo,	1 50
" The Transition Curve	12mo, morocco,	1 50

* Dredge's Penn. Railroad Construction, etc.	Folio, half mor.,	$20 00
* Drinker's Tunnelling	4to, half morocco,	25 00
Eissler's Explosives—Nitroglycerine and Dynamite	8vo,	4 00
Fowler's Coffer-dam Process for Piers	8vo.	
Gerhard's Sanitary House Inspection	16mo,	1 00
Godwin's Railroad Engineer's Field-book.	12mo, pocket-bk. form,	2 50
Gore's Elements of Geodesy	8vo,	2 50
Howard's Transition Curve Field-book	12mo, morocco flap,	1 50
Howe's Retaining Walls (New Edition.)	12mo,	1 25
Hudson's Excavation Tables. Vol. II.	8vo,	1 00
Hutton's Mechanical Engineering of Power Plants	8vo,	5 00
Johnson's Materials of Construction	8vo,	6 00
“ Stadia Reduction Diagram	Sheet, 22½ × 28½ inches,	50
“ Theory and Practice of Surveying	8vo,	4 00
Kent's Mechanical Engineer's Pocket-book	12mo, morocco,	5 00
Kiersted's Sewage Disposal	12mo,	1 25
Kirkwood's Lead Pipe for Service Pipe	8vo,	1 50
Mahan's Civil Engineering. (Wood.)	8vo,	5 00
Merriman and Brook's Handbook for Surveyors	12mo, mor.,	2 00
Merriman's Geodetic Surveying	8vo,	2 00
“ Retaining Walls and Masonry Dams	8vo,	2 00
Mosely's Mechanical Engineering. (Mahan.)	8vo,	5 00
Nagle's Manual for Railroad Engineers	12mo, morocco,	3 00
Patton's Civil Engineering	8vo,	7 50
“ Foundations	8vo,	5 00
Rockwell's Roads and Pavements in France	12mo,	1 25
Ruffner's Non-tidal Rivers	8vo,	1 25
Searles's Field Engineering	12mo, morocco flaps,	3 00
“ Railroad Spiral	12mo, morocco flaps,	1 50
Siebert and Biggin's Modern Stone Cutting and Masonry	8vo,	1 50
Smith's Cable Tramways	4to,	2 50
“ Wire Manufacture and Uses	4to,	3 00
Spalding's Roads and Pavements	12mo,	2 00
“ Hydraulic Cement	12mo,	2 00
Thurston's Materials of Construction	8vo,	5 00
* Trautwine's Civil Engineer's Pocket-book	12mo, mor. flaps,	5 00
* “ Cross-section	Sheet,	25
* “ Excavations and Embankments	8vo,	2 00

* Trautwine's Laying Out Curves.............12mo, morocco,	$2 50
Waddell's De Pontibus (A Pocket-book for Bridge Engineers). 12mo, morocco,	3 00
Wait's Engineering and Architectural Jurisprudence.......8vo,	6 00
Sheep,	6 50
" Law of Field Operation in Engineering, etc........8vo.	
Warren's Stereotomy—Stone Cutting.....................8vo,	2 50
Webb's Engineering Instruments..............12mo, morocco,	1 00
Wegmann's Construction of Masonry Dams...............4to,	5 00
Wellington's Location of Railways.......................8vo,	5 00
Wheeler's Civil Engineering..............................8vo,	4 00
Wolff's Windmill as a Prime Mover......................8vo,	3 00

HYDRAULICS.

WATER-WHEELS—WINDMILLS—SERVICE PIPE—DRAINAGE, ETC.

(*See also* ENGINEERING, p. 6.)

Bazin's Experiments upon the Contraction of the Liquid Vein (Trautwine)......................................8vo,	2 00
Bovey's Treatise on Hydraulics..........................8vo,	4 00
Coffin's Graphical Solution of Hydraulic Problems.......12mo,	2 50
Ferrel's Treatise on the Winds, Cyclones, and Tornadoes...8vo,	4 00
Fuerte's Water and Public Health......................12mo,	1 50
Ganguillet & Kutter's Flow of Water. (Hering & Trautwine.).8vo,	4 00
Hazen's Filtration of Public Water Supply................8vo,	2 00
Herschel's 115 Experiments 8vo,	2 00
Kiersted's Sewage Disposal..........................12mo,	1 25
Kirkwood's Lead Pipe for Service Pipe 8vo,	1 50
Mason's Water Supply...................................8vo,	5 00
Merriman's Treatise on Hydraulics.....................8vo,	4 00
Nichols's Water Supply (Chemical and Sanitary)..........8vo,	2 50
Ruffner's Improvement for Non-tidal Rivers..............8vo,	1 25
Wegmann's Water Supply of the City of New York 4to,	10 00
Weisbach's Hydraulics. (Du Bois.)......................8vo,	5 00
Wilson's Irrigation Engineering..........................8vo,	4 00
" Hydraulic and Placer Mining.................12mo,	2 00
Wolff's Windmill as a Prime Mover......................8vo,	3 00
Wood's Theory of Turbines...............................8vo,	2 50

MANUFACTURES.

ANILINE—BOILERS—EXPLOSIVES—IRON—SUGAR—WATCHES—WOOLLENS, ETC.

Allen's Tables for Iron Analysis 8vo,	3 00
Beaumont's Woollen and Worsted Manufacture..........12mo,	1 50
Bolland's Encyclopædia of Founding Terms..............12mo,	3 00

Bolland's The Iron Founder	12mo,	2 50
" " " " Supplement	12mo,	2 50
Booth's Clock and Watch Maker's Manual	12mo,	2 00
Bouvier's Handbook on Oil Painting	12mo,	2 00
Eissler's Explosives, Nitroglycerine and Dynamite	8vo,	4 00
Ford's Boiler Making for Boiler Makers	18mo,	1 00
Metcalfe's Cost of Manufactures	8vo,	5 00
Metcalf's Steel—A Manual for Steel Users	12mo,	$2 00
Reimann's Aniline Colors. (Crookes.)	8vo,	2 50
* Reisig's Guide to Piece Dyeing	8vo,	25 00
Spencer's Sugar Manufacturer's Handbook	12mo, mor. flap,	2 00
" Handbook for Chemists of Beet Houses.	12mo, mor. flap,	3 00
Svedelius's Handbook for Charcoal Burners	12mo,	1 50
The Lathe and Its Uses	8vo,	6 00
Thurston's Manual of Steam Boilers	8vo,	5 00
Walke's Lectures on Explosives	8vo,	4 00
West's American Foundry Practice	12mo,	2 50
" Moulder's Text-book	12mo,	2 50
Wiechmann's Sugar Analysis	8vo,	2 50
Woodbury's Fire Protection of Mills	8vo,	2 50

MATERIALS OF ENGINEERING.

STRENGTH—ELASTICITY—RESISTANCE, ETC.

(*See also* ENGINEERING, p. 6.)

Baker's Masonry Construction	8vo,	5 00
Beardslee and Kent's Strength of Wrought Iron	8vo,	1 50
Bovey's Strength of Materials	8vo,	7 50
Burr's Elasticity and Resistance of Materials	8vo,	5 00
Byrne's Highway Construction	8vo,	5 00
Carpenter's Testing Machines and Methods of Testing Materials.		
Church's Mechanics of Engineering—Solids and Fluids	8vo,	6 00
Du Bois's Stresses in Framed Structures	4to,	10 00
Hatfield's Transverse Strains	8vo,	5 00
Johnson's Materials of Construction	8vo,	6 00
Lanza's Applied Mechanics	8vo,	7 50
Merrill's Stones for Building and Decoration	8vo,	5 00
Merriman's Mechanics of Materials	8vo,	4 00
" Strength of Materials	12mo,	1 00
Patton's Treatise on Foundations	8vo,	5 00
Rockwell's Roads and Pavements in France	12mo,	1 25
Spalding's Roads and Pavements	12mo,	2 00
Thurston's Materials of Construction	8vo,	5 00

Thurston's Materials of Engineering	3 vols., 8vo,	$8 00
Vol. I., Non-metallic	8vo,	2 00
Vol. II., Iron and Steel	8vo,	3 50
Vol. III., Alloys, Brasses, and Bronzes	8vo,	2 50
Weyrauch's Strength of Iron and Steel. (Du Bois.)	8vo,	1 50
Wood's Resistance of Materials	8vo,	2 00

MATHEMATICS.

Calculus—Geometry—Trigonometry, Etc.

Baker's Elliptic Functions	8vo,	1 50
Ballard's Pyramid Problem	8vo,	1 50
Barnard's Pyramid Problem	8vo,	1 50
Bass's Differential Calculus	12mo,	4 00
Brigg's Plane Analytical Geometry	12mo,	1 00
Chapman's Theory of Equations	12mo,	1 50
Chessin's Elements of the Theory of Functions.		
Compton's Logarithmic Computations	12mo,	1 50
Craig's Linear Differential Equations	8vo,	5 00
Davis's Introduction to the Logic of Algebra	8vo,	1 50
Halsted's Elements of Geometry	8vo,	1 75
" Synthetic Geometry	8vo,	1 50
Johnson's Curve Tracing	12mo,	1 00
" Differential Equations—Ordinary and Partial	8vo,	3 50
" Integral Calculus	12mo,	1 50
" " " Unabridged.		
" Least Squares	12mo,	1 50
Ludlow's Logarithmic and Other Tables. (Bass.)	8vo,	2 00
" Trigonometry with Tables. (Bass.)	8vo,	3 00
Mahan's Descriptive Geometry (Stone Cutting)	8vo,	1 50
Merriman and Woodward's Higher Mathematics	8vo,	5 00
Merriman's Method of Least Squares	8vo,	2 00
Parker's Quadrature of the Circle	8vo,	2 50
Rice and Johnson's Differential and Integral Calculus,	2 vols. in 1, 12mo,	2 50
" Differential Calculus	8vo,	3 00
" Abridgment of Differential Calculus	8vo,	1 50
Searles's Elements of Geometry	8vo,	1 50
Totten's Metrology	8vo,	2 50
Warren's Descriptive Geometry	2 vols., 8vo,	3 50
" Drafting Instruments	12mo,	1 25
" Free-hand Drawing	12mo,	1 00
" Higher Linear Perspective	8vo,	3 50
" Linear Perspective	12mo,	1 00
" Primary Geometry	12mo,	75

Warren's Plane Problems	12mo,	$1 25
" Problems and Theorems	8vo,	2 50
" Projection Drawing	12mo,	1 50
Wood's Co-ordinate Geometry	8vo,	2 00
" Trigonometry	12mo,	1 00
Woolf's Descriptive Geometry	Royal 8vo,	3 00

MECHANICS—MACHINERY.

Text-books and Practical Works.

(*See also* Engineering, p. 6.)

Baldwin's Steam Heating for Buildings	12mo,	2 50
Benjamin's Wrinkles and Recipes	12mo,	2 00
Carpenter's Testing Machines and Methods of Testing Materials	8vo.	
Chordal's Letters to Mechanics	12mo,	2 00
Church's Mechanics of Engineering	8vo,	6 00
" Notes and Examples in Mechanics	8vo,	2 00
Crehore's Mechanics of the Girder	8vo,	5 00
Cromwell's Belts and Pulleys	12mo,	1 50
" Toothed Gearing	12mo,	1 50
Compton's First Lessons in Metal Working	12mo,	1 50
Dana's Elementary Mechanics	12mo,	1 50
Dingey's Machinery Pattern Making	12mo,	2 00
Dredge's Trans. Exhibits Building, World Exposition,	4to, half morocco,	10 00
Du Bois's Mechanics. Vol. I., Kinematics	8vo,	3 50
" " Vol. II., Statics	8vo,	4 00
" " Vol. III., Kinetics	8vo,	3 50
Fitzgerald's Boston Machinist	18mo,	1 00
Flather's Dynamometers	12mo,	2 00
" Rope Driving	12mo,	2 00
Hall's Car Lubrication	12mo,	1 00
Holly's Saw Filing	18mo,	75
Johnson's Theoretical Mechanics. An Elementary Treatise. (*In the press.*)		
Jones Machine Design. Part I., Kinematics	8vo,	1 50
" " " Part II., Strength and Proportion of Machine Parts.		
Lanza's Applied Mechanics	8vo,	7 50
MacCord's Kinematics	8vo,	5 00
Merriman's Mechanics of Materials	8vo,	4 00
Metcalfe's Cost of Manufactures	8vo,	5 00
Michie's Analytical Mechanics	8vo,	4 00
Mosely's Mechanical Engineering. (Mahan.)	8vo,	5 00

Richards's Compressed Air	12mo,	$1 50
Robinson's Principles of Mechanism	8vo,	3 00
Smith's Press-working of Metals	8vo,	3 00
The Lathe and Its Uses	8vo,	6 00
Thurston's Friction and Lost Work	8vo,	3 00
" The Animal as a Machine	12mo,	1 00
Warren's Machine Construction	2 vols., 8vo,	7 50
Weisbach's Hydraulics and Hydraulic Motors. (Du Bois.)	8vo,	5 00
" Mechanics of Engineering. Vol. III., Part I., Sec. I. (Klein.)...	8vo,	5 00
Weisbach's Mechanics of Engineering Vol. III., Part I., Sec. II (Klein.)	8vo,	5 00
Weisbach's Steam Engines. (Du Bois.)	8vo,	5 00
Wood's Analytical Mechanics	8vo,	3 00
" Elementary Mechanics	12mo,	1 25
" " " Supplement and Key		1 25

METALLURGY.

Iron—Gold—Silver—Alloys, Etc.

Allen's Tables for Iron Analysis	8vo,	3 00
Egleston's Gold and Mercury	8vo,	7 50
" Metallurgy of Silver	8vo,	7 50
* Kerl's Metallurgy—Copper and Iron	8vo,	15 00
* " " Steel, Fuel. etc	8vo,	15 00
Kunhardt's Ore Dressing in Europe	8vo,	1 50
Metcalf's Steel—A Manual for Steel Users	12mo,	2 00
O'Driscoll's Treatment of Gold Ores	8vo,	2 00
Thurston's Iron and Steel	8vo,	3 50
" Alloys	8vo,	2 50
Wilson's Cyanide Processes	12mo,	1 50

MINERALOGY AND MINING.

Mine Accidents—Ventilation—Ore Dressing, Etc.

Barringer's Minerals of Commercial Value	oblong morocco,	2 50
Beard's Ventilation of Mines	12mo,	2 50
Boyd's Resources of South Western Virginia	8vo,	3 00
" Map of South Western Virginia	Pocket-book form,	2 00
Brush and Penfield's Determinative Mineralogy	8vo,	3 50
Chester's Catalogue of Minerals	8vo,	1 25
" " " "	paper,	50
" Dictionary of the Names of Minerals	8vo,	3 00
Dana's American Localities of Minerals	8vo,	1 00

Dana's Descriptive Mineralogy. (E. S.)	8vo, half morocco,	$12 50
" Mineralogy and Petrography (J.D.)	12mo,	2 00
" Minerals and How to Study Them. (E. S.)	12mo,	1 50
" Text-book of Mineralogy. (E. S.)	8vo,	3 50
*Drinker's Tunnelling, Explosives, Compounds, and Rock Drills.	4to, half morocco,	25 00
Egleston's Catalogue of Minerals and Synonyms	8vo,	2 50
Eissler's Explosives—Nitroglycerine and Dynamite	8vo,	4 00
Goodyear's Coal Mines of the Western Coast	12mo,	2 50
Hussak's Rock-forming Minerals. (Smith.)	8vo,	2 00
Ihlseng's Manual of Mining	8vo,	4 00
Kunhardt's Ore Dressing in Europe	8vo,	1 50
O'Driscoll's Treatment of Gold Ores	8vo,	2 00
Rosenbusch's Microscopical Physiography of Minerals and Rocks. (Iddings.)	8vo,	5 00
Sawyer's Accidents in Mines	8vo,	7 00
Stockbridge's Rocks and Soils	8vo	2 50
Walke's Lectures on Explosives	8vo,	4 00
Williams's Lithology	8vo,	3 00
Wilson's Mine Ventilation	16mo,	1 25
" Hydraulic and Placer Mining	12mo.	

STEAM AND ELECTRICAL ENGINES, BOILERS, Etc.

STATIONARY—MARINE—LOCOMOTIVE—GAS ENGINES, ETC.

(*See also* ENGINEERING, p. 6.)

Baldwin's Steam Heating for Buildings	12mo,	2 50
Clerk's Gas Engine	12mo,	4 00
Ford's Boiler Making for Boiler Makers	18mo,	1 00
Hemenway's Indicator Practice	12mo.	2 00
Hoadley's Warm-blast Furnace	8vo,	1 50
Kneass's Practice and Theory of the Injector	8vo,	1 50
MacCord's Slide Valve	8vo,	2 00
* Maw's Marine Engines	Folio, half morocco,	18 00
Meyer's Modern Locomotive Construction	4to,	10 00
Peabody and Miller's Steam Boilers	8vo,	4 00
Peabody's Tables of Saturated Steam	8vo,	1 00
" Thermodynamics of the Steam Engine	8vo,	5 00
" Valve Gears for the Steam Engine	8vo,	2 50
Pray's Twenty Years with the Indicator	Royal 8vo,	2 50
Pupin and Osterberg's Thermodynamics	12mo,	1 25
Reagan's Steam and Electrical Locomotives	12mo,	2 00
Röntgen's Thermodynamics. (Du Bois.)	8vo,	5 00
Sinclair's Locomotive Running	12mo,	2 00
Thurston's Boiler Explosion	12mo,	1 50

Thurston's Engine and Boiler Trials	8vo,	$5 00
" Manual of the Steam Engine. Part I., Structure and Theory	8vo,	7 50
" Manual of the Steam Engine. Part II., Design, Construction, and Operation	8vo,	7 50
	2 parts,	12 00
" Philosophy of the Steam Engine	12mo,	75
" Reflection on the Motive Power of Heat. (Carnot.)	12mo,	1 50
" Stationary Steam Engines	12mo,	1 50
" Steam-boiler Construction and Operation	8vo,	5 00
Spangler's Valve Gears	8vo,	2 50
Trowbridge's Stationary Steam Engines	4to, boards,	2 50
Weisbach's Steam Engine. (Du Bois.)	8vo,	5 00
Whitham's Constructive Steam Engineering	8vo,	10 00
" Steam-engine Design	8vo,	5 00
Wilson's Steam Boilers. (Flather.)	12mo,	2 50
Wood's Thermodynamics, Heat Motors, etc.	8vo,	4 00

TABLES, WEIGHTS, AND MEASURES.

For Actuaries, Chemists, Engineers, Mechanics—Metric Tables, Etc.

Adriance's Laboratory Calculations	12mo,	1 25
Allen's Tables for Iron Analysis	8vo,	3 00
Bixby's Graphical Computing Tables	Sheet,	25
Compton's Logarithms	12mo,	1 50
Crandall's Railway and Earthwork Tables	8vo,	1 50
Egleston's Weights and Measures	18mo,	75
Fisher's Table of Cubic Yards	Cardboard,	25
Hudson's Excavation Tables. Vol. II	8vo,	1 00
Johnson's Stadia and Earthwork Tables	8vo,	1 25
Ludlow's Logarithmic and Other Tables. (Bass.)	12mo,	2 00
Thurston's Conversion Tables	8vo,	1 00
Totten's Metrology	8vo,	2 50

VENTILATION.

Steam Heating—House Inspection—Mine Ventilation.

Baldwin's Steam Heating	12mo,	2 50
Beard's Ventilation of Mines	12mo,	2 50
Carpenter's Heating and Ventilating of Buildings	8vo,	3 00
Gerhard's Sanitary House Inspection	Square 16mo,	1 00
Mott's The Air We Breathe, and Ventilation	16mo,	1 00
Reid's Ventilation of American Dwellings	12mo,	1 50
Wilson's Mine Ventilation	16mo,	1 25

MISCELLANEOUS PUBLICATIONS.

Alcott's Gems, Sentiment, Language	Gilt edges,	$5 00
Bailey's The New Tale of a Tub	8vo,	75
Ballard's Solution of the Pyramid Problem	8vo,	1 50
Barnard's The Metrological System of the Great Pyramid	8vo,	1 50
Davis's Elements of Law	8vo,	2 00
Emmon's Geological Guide-book of the Rocky Mountains	8vo,	1 50
Ferrel's Treatise on the Winds	8vo,	4 00
Haines's Addresses Delivered before the Am. Ry. Assn	12mo.	2 50
Mott's The Fallacy of the Present Theory of Sound	Sq. 16mo,	1 00
Perkins's Cornell University	Oblong 4to,	1 50
Ricketts's History of Rensselaer Polytechnic Institute	8vo,	3 00
Rotherham's The New Testament Critically Emphasized.	12mo,	1 50
" The Emphasized New Test. A new translation.	Large 8vo,	2 00
Totten's An Important Question in Metrology	8vo,	2 50
Whitehouse's Lake Mœris	Paper,	25
* Wiley's Yosemite, Alaska, and Yellowstone	4to,	3 00

HEBREW AND CHALDEE TEXT-BOOKS.

For Schools and Theological Seminaries.

Gesenius's Hebrew and Chaldee Lexicon to Old Testament. (Tregelles.)	Small 4to, half morocco,	5 00
Green's Elementary Hebrew Grammar	12mo,	1 25
" Grammar of the Hebrew Language (New Edition).	8vo,	3 00
" Hebrew Chrestomathy	8vo,	2 00
Letteris's Hebrew Bible (Massoretic Notes in English).	8vo, arabesque,	2 25
Luzzato's Grammar of the Biblical Chaldaic Language and the Talmud Babli Idioms	12mo,	1 50

MEDICAL.

Bull's Maternal Management in Health and Disease	12mo,	1 00
Hammarsten's Physiological Chemistry. (Mandel.)	8vo,	4 00
Mott's Composition, Digestibility, and Nutritive Value of Food.	Large mounted chart,	1 25
Ruddiman's Incompatibilities in Prescriptions	8vo,	2 00
Steel's Treatise on the Diseases of the Ox	8vo,	6 00
" Treatise on the Diseases of the Dog	8vo,	3 50
Woodhull's Military Hygiene	12mo,	1 50
Worcester's Small Hospitals—Establishment and Maintenance, including Atkinson's Suggestions for Hospital Architecture	12mo,	1 25

rd
2 8th
30