² Harkins, Brown and Davies, *J. Amer. Chem. Soc.*, **39**, 354–64 (1917); Harkins, Davies and Clark, *Ibid.* 541–96, and later papers.
³ Langmuir, *Chem. Met. Eng.*, **15**, 468 (1916); *J. Amer. Chem. Soc.*, **39**, 1848 (1917).
⁴ Finkle, Draper and Hildebrand, *J. Amer. Chem. Soc.*, **45**, 2780 (1923).
⁵ Harkins and Keith, *Science*, **59**, 463–7 (1924).

POLYMOLECULAR AND MONOMOLECULAR FILMS

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The work of Harkins and Feldman[1] indicates that pure liquids may spread upon water to give films which are thicker than one molecule, and the writers have been able to find these films with such characteristics that accurate measurements may, and have been made of the variation of the force of compression with a change in area. Lord Rayleigh,[2] Devaux,[3] Marcelin,[4] Langmuir,[5] Harkins and King,[6] Adam,[7] Harkins and Grafton[8] and Harkins and McLaughlin[9] have made measurements upon monomolecular films.

Monomolecular Films.—The thickness of monomolecular films has not been measured, but a "mean"thickness has been calculated from the molecular area. The water film on an aqueous salt solution is thus found to be 4×10^{-8} cm. (4Å) thick for a tenth molal, and 2.4Å for a 5 molal concentration. Langmuir has found that a film of palmitic acid is 25, and of myricyl alcohol, 41Å thick. The molecules of this alcohol are very long, and contain a chain of 30 carbon atoms.
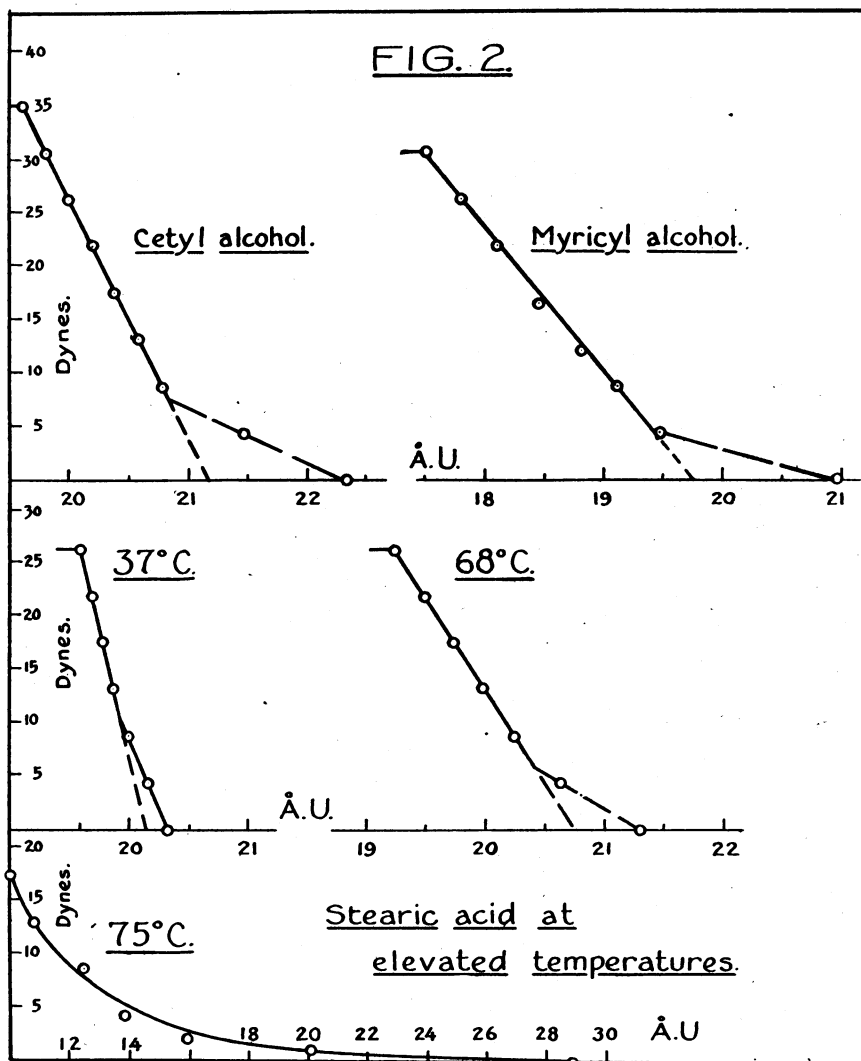
Phenanthrol (Fig. 1), with a polar hydroxyl group in each molecule when spread on an aqueous solution of calcium chloride, exhibits the characteristics of a monomolecular film. This substance and phenyl dibiphenyl methyl amine form films which are thinner than any others which have been measured directly. Both of these films were spread on a concentrated aqueous solution of calcium chloride. As the phenanthrol film is compressed, no force of compression is apparent until the area per molecule is decreased to 36.5×10^{-16} sq. cm. (36.5 A.U.). On further compression the increase of compressive force is linear to the molecular area up to 32 dynes per cm. and 21.5 A.U. molecular area. From this on the increase is again linear, but with a much steeper slope; that is, the film has become stronger. When the force reaches 44 dynes per cm. the film collapses and the force rises only very slightly higher as the film is still further compressed. The mean thickness of the film is 7Å at the point where the force first becomes apparent and 12Å at collapse. The next row in the

same figures exhibits the relations for stearic acid on water, and on salt solutions. In either case the lower branch of the curve may be present or absent (Fig. 2). In the latter case only one straight line represents the compression up to the point of collapse, and the area at zero force is 19.3 A.U.
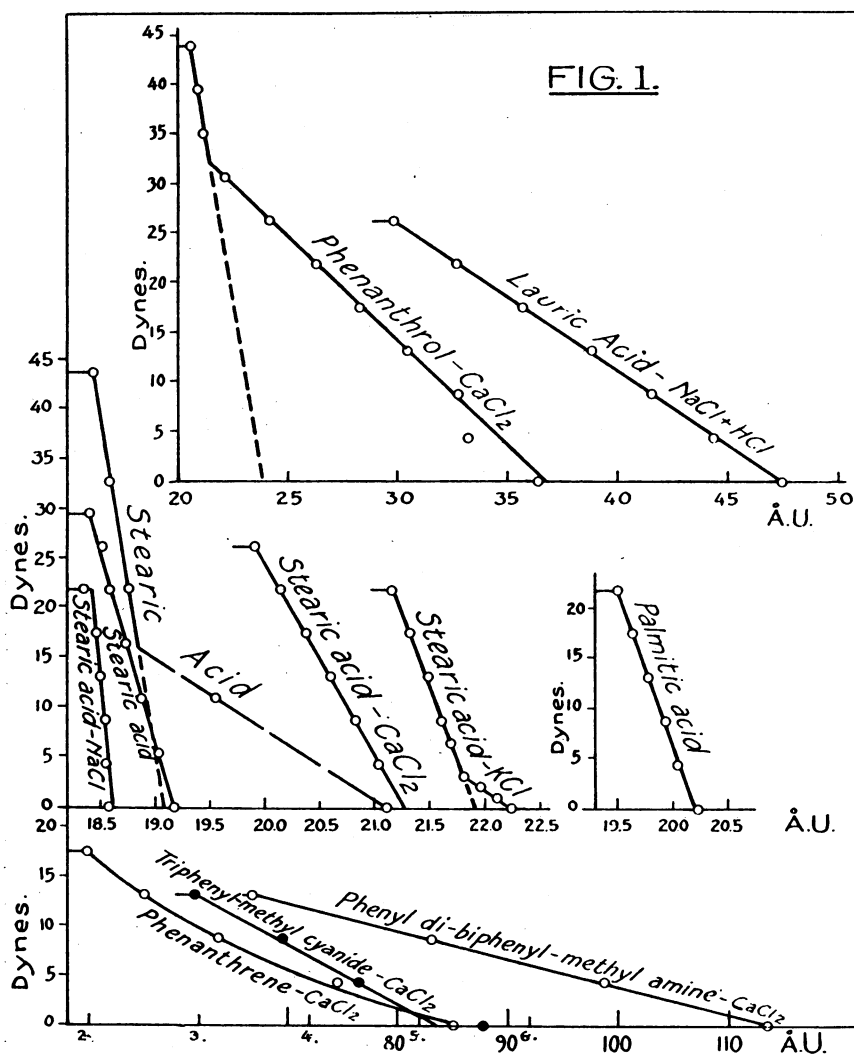
Polymolecular Films.—Phenanthrene spread on an aqueous calcium chloride solution gives a typical polymolecular film. Though this substance has a large molecule (14 carbon atoms and 10 hydrogen atoms), the zero area is very small: only 5.6 A.U., with a thickness of 47Å which

is entirely too thick for the film to be monomolecular, since the molecule has a ring structure and is only about 12Å long.   The film collapses when the force of compression is still low; 17.5 dynes per cm. with a mean thickness of 132 A.U.   The line of compression is not linear, and the slope of

FIG. 2.

Cetyl alcohol.

Myricyl alcohol.

37°C.

68°C.

75°C.

Stearic acid at elevated temperatures.

the curve shows that the film is extremely weak.   It should be mentioned that the value of the compressive force at collapse depends somewhat upon the rapidity of compression.

Other films which are certainly polymolecular in thickness are those

formed by 9–10 dibromoanthracene (Fig. 3), triphenyl methyl cyanide, di-β-naphthylamine, α-brom-naphthalene and hexachloro-benzene. The compression of triphenyl methyl cyanide is represented by a straight line, that of the dibromo anthracene by a curve and a straight line. If it were

FIG. 3.
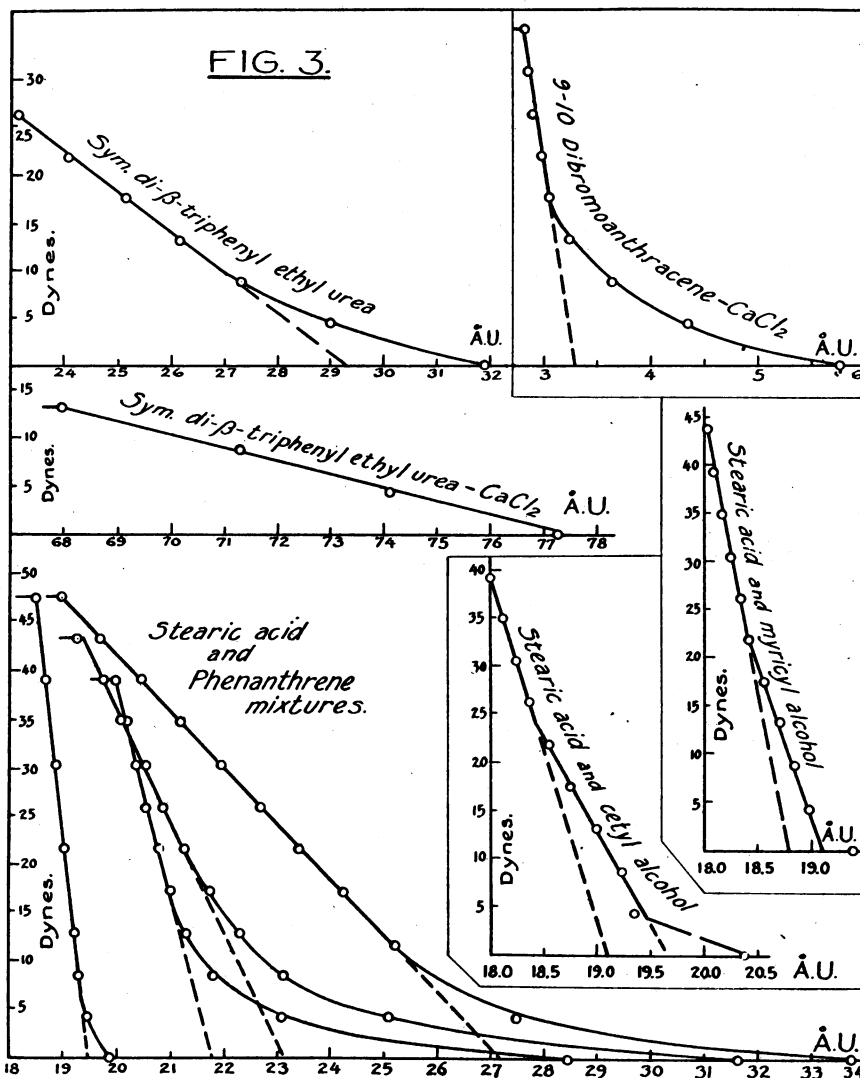
not for the fact that the mean thickness of the film of triphenyl methyl cyanide is too great, its line of compression might be mistaken for that of a monomolecular film. Some of the characteristics of a few of the films measured are given in table 1. The substances are arranged in order of increas-

ing mean thickness at collapse, so that the monomolecular films are given at the top, and the polymolecular at the bottom of the table.

TABLE 1

FILMS ARRANGED IN ORDER OF INCREASING THICKNESS AT COLLAPSE

(Monomolecular Films above and Polymolecular below: Dimensions in Angstrom units. CaCl₂ represents an aqueous solution of the salt.)

SUBSTANCE OF FILM	On	AT ZERO AREA	FORCE THICKNESS	AT COLLAPSE AREA	THICKNESS
Phenyl dibiphenyl methyl amine	CaCl₂	112	6	80	8.4
Phenanthrol	CaCl₂	36.5	7	21.3	12
Stearic acid	H₂O	19.3	28.5	18.4	30
Symmetrical di-β-triphenyl ethyl }	CaCl₂	77.5	12.2	68	14
urea (polymolecular on water) }	H₂O	28.3	33.4	22.6	42
POLYMOLECULAR FILMS					
9,10-Dibromo anthracene	CaCl₂	5.9	47	2.5	111
Triphenyl methyl cyanide	CaCl₂	5.2	70	5	120
Phenanthrene	CaCl₂	5.6	47	2	132
Di-β-naphthylamine	H₂O	2.7	125.6	2.15	158
Hexachlorobenzene	CaCl₂	5.2	45	0.95	248
α-Bromonaphthalene	CaCl₂	1.5	187	0.6	405

It may be noted that the urea listed in the table occupies about three times the molecular area on the calcium chloride solution that it does on water; so the film is very much thinner on the salt solution. This illustrates a phenomenon which is quite general. Thus phenanthrene will not spread at all on water, but will on a concentrated calcium chloride solution, to form a polymolecular film. Harkins and Feldman[1] have shown that the spreading or nonspreading of a substance depends upon the value of the spreading coefficient S in the expression

$$S = F_a - (F_b + F_{ab}) = T_a - (T_b + T_{ab}).$$

In this case F_a represents the free surface energy and T_a the numerically equal surface tension of the water or the salt solution. The subscript b refers to the substance which may spread and ab refers to the interface between the two. By a change from water to the calcium chloride solution, T and F are increased from 72.8 to more than 100 dynes per cm., which increases the value of S unless the free interfacial energy (F_{ab}) increases by this much or more, which is not usually the case since F_{ab} is relatively small and a large relative increase may occur without such a large numerical increase. The solution of a large amount of a salt in the water causes many substances to spread which have negative values of S on water and therefore will not spread on water alone.

It may be noted (Table 1) that all of the polymolecular films are very thin, even at collapse. Thus the thickest of all is only about one-tenth of the shortest wave-length of visible light. The film of dibromoanthracene

is visible in a strong light almost parallel with the surface, which suggests that the film is crystalline and that many points rise far above the general level. This is also true of di-β-naphthylamine on water and of anthracene on the calcium chloride solution. In some cases the film seems to consist of transparent flakes, which may be photographed.

Strength of Films.—Young's modulus for steel is about 12,000. For a monomolecular film, stearic acid on water, it is 39 and on a calcium chloride solution less than this. A polymolecular is in general much weaker than a monomolecular film. Thus the value for dibromoanthracene is less than 2.

Films of Mixed Substances.—If two substances, each of which forms a monomolecular film, are mixed, the mixture forms a monomolecular film. The behavior of two such "mixed" films of stearic acid with either cetyl alcohol or myricyl alcohol, is illustrated at the bottom of figure 3.

Mixtures of stearic acid and phenanthrene give polymolecular films. Thus with 1 molecule of phenanthrene to 2.58 of stearic acid the area per molecule of the latter is practically the same as when it is alone. With 3.7 parts of the former to 1 of the latter the zero area per molecule of acid is increased only very slightly, from 19.3 to 21.7. The curves at the bottom of figure 3 (left side) are arranged in order of increasing percentage of phenanthrene and the area plotted is that per molecule of stearic acid. With 6.4 molecules of phenanthrene the extrapolated zero area is increased only to 23, and with 16.4 to 1 to 27. It is thus evident that when the relation between force of compression and area is linear, as it is over a considerable range, almost all of the phenanthrene is piled up over the stearic acid, which forms a monomolecular layer underneath it.

Strenth of Mixed Films.—The film which consists of 1 molecule of phenanthrene to 2.58 of stearic acid is as strong or stronger than a film of the acid alone, but the strength decreases if much more phenanthrene is present, as shown below.

TABLE 2

STRENGTH OF MIXED FILMS

PHENANTHRENE	STEARIC ACID	YOUNG'S MODULUS
0	Pure	35.83
1	2.58	37.5
3.7	1	6.7
6.4	1	2.64
16.4	1	0.9 cloudy film
Pure	0	1.45 at collapse
		0.04 at zero

All of these mixtures exhibit a curved lower portion, but with 16.4 molecules of phenanthrene to one of stearic acid there is no apparent force required to compress the film until the area per molecule of the latter has been decreased to 34 A.U., or the area per molecule in the film has de-

creased to 1.95 A.U. Thus this film has attained a mean thickness of about 135Å before the force needed to compress it becomes apparent. At collapse this film is about 240Å thick, which is much thicker than with phenanthrene alone. It is evident that the collapse of such a film occurs only when the stearic acid is torn away from the water, since the area per molecule of stearic acid at collapse in these mixed films is almost the same as with the acid alone. The addition of phenanthrene, which contains no polar group, changes considerably the actual zero area, has a smaller effect upon the extrapolated (from the straight line) zero area and almost no effect upon the area of collapse.

[1] Harkins and Feldman, *J. Amer. Chem. Soc.*, **43**, 1921 (2665).

[2] Rayleigh, *Phil. Mag.*, **48**, 1899 (331).

[3] Devaux, Papers 1903–13 reviewed in *Ann. Report Smithsonian Inst.*, **1913**, pp. 261–73.

[4] Marcelin, *Ann. Physique*, **1914** (19).

[5] Langmuir, *J. Amer. Chem. Soc.*, **39**, 1917 (1848).

[6] Harkins and King, *Ibid.*, **41**, 1919 (970).

[7] Adam, N. K., *Proc. Roy. Soc.*, **A101**, 1921 (452), and later papers.

[8] Harkins and Grafton, *J. Am. Chem. Soc.*, **44**.

[9] Harkins and McLaughlin, *Ibid.*, **44**.

THE ISOTOPIC COMPOSITION OF THE ELEMENT CHLORINE IN THE METEORITES: THE ATOMIC WEIGHT OF METEORIC AND TERRESTRIAL CHLORINE

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Introduction.—The element chlorine consists of two isotopes of atomic weights 35 and 37. If it is assumed that these whole numbers are exact, it is possible to calculate the isotopic composition of ordinary chlorine from its atomic weight which is 35.457. This indicates that the element consists of 77.15% of the lighter and 22.85% of the heavier isotope. A determination of the atomic weight of the chlorine obtained from a meteorite indicates that it has exactly the same atomic weight and therefore the same composition as the ordinary chlorine found on earth. It is found, too, that this element is the same in rocks of non-marine origin, such as Wernerite, apatite and sodalite.

The above results have a bearing upon the history of the earth and the meteorites and upon the stability of the atoms of the two isotopes. It is now commonly assumed that meteorites are fragments from small