

THE PROPERTIES OF SURFACE FILMS ON LIQUIDS

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EARLY OBSERVATIONS

It was not until about 1890, that systematic attempts were made to distinguish clearly between the properties of water surfaces when clean, and when covered by a film of contamination. It had been known that oil films on water diminish the surface tension, and also tend to calm wave motion; but there was not enough knowledge of the properties of surface for it to be easily ascertained whether a given surface of water was clean or not. In 1890 Rayleigh (1) measured the amount of olive oil necessary to check the motions of camphor, which take place on a clean surface, though not on a contaminated one; and he also measured the amount of the depression of the surface tension of water caused by the minimum quantity of oil required to stop the camphor movements (3,5). The diminution of surface tension at this point is about 16 dynes per centimeter; calculating from Rayleigh's determination, the area per molecule of the oil, at this point, was 100 sq. Å.U.,¹ assuming as is not far from the truth, that the oil consists wholly of triolein. This is in excellent agreement with the most recent measurements, which give 97 sq. Å.U. at this depression of surface tension, for triolein.

In the same year Rayleigh (2) found that Plateau's observation (4), that the surface viscosity of water is greater than the internal viscosity, is not true of a clean water surface, but that any excess viscosity is due to the presence of a surface film which can be cleaned away. In 1892 (6) he found that certain anomalies in the reflection of light from water surfaces were also due to surface films of contamination.

¹ 10^{-16} sq. cm.

Miss Pockels, in 1891 (7), showed that a film on a water surface may be mechanically removed, or rather concentrated in any desired part of the surface, leaving the remainder clean, in just the same manner that fallen leaves on a swimming bath may be swept up by a floating plank pulled from end to end. By the use of barriers working on the surface of water contained in a trough filled to the brim she was able to vary the surface available for a given amount of oil present as a film. She found that when the area available exceeded a certain amount, there was no perceptible diminution of surface tension, but as soon as the area was diminished below this, a rapid fall of surface tension began. The damping of wave-motion was closely connected with the area of the surface film; and the so-called solution currents from a solid body dipped into the liquid, the streams of matter leaving the solid and spreading out along the surface, made visible by dusting the surface with a light powder, might be stopped by reducing the area of the surface film.

THE CONCEPTION OF SURFACE PRESSURE, AND OF THE FILMS
AS ONE MOLECULE THICK

In 1899, Rayleigh (5) confirmed Pockels' observation on the manner of variation of the surface tension with the area of the film, and suggested that at the point of the first fall in surface tension, the molecules of the film were just crowded together into contact, to form a layer one molecule thick. He wrote:

. . . . at what point will an opposition to contraction arise? The answer must depend upon the forces supposed to be operative between the molecules of oil. If they behave like the smooth rigid spheres of gaseous theory, no forces will be called into play until they are closely packed. . . . If we accept this view, we conclude that the first drop in surface tension corresponds to a complete layer one molecule thick, and that the diameter of a molecule of oil is about $1.0\mu\mu$.
. . . . An essentially different result would seem to require a repulsive force between the molecules, resisting concentration long before the first layer is complete.

This suggestion involves two points of great importance; that the molecules of oil can be likened to small hard floating

bodies, and that the diminution of surface tension is nothing more than the force required to compress these floating molecules close together against the repulsive forces between them.

Rayleigh did not elaborate these points, but they have proved fundamental, and indispensable, to the further development of the theory. That the molecules of oil may be legitimately considered as floating objects follows from their insolubility in water. The surface pressure, or outward force exerted by a surface film upon a barrier bounding it, is of the same nature as the outward pressure which would be exerted by a "film" composed of visible floating objects. There must obviously be some such pressure caused by any floating objects which possess size and shape, on a barrier which allows the water molecules to pass, but not those of the film; and any float which blocks the whole surface must act as such a "two-dimensional semipermeable membrane." So far, this point of view seems obvious and legitimate. But some difficulty has been caused in its acceptance, by the very strong tendency which existed during last century, and still persists to some extent, to regard the resistance which the surface of a liquid offers to any increase of area, as due to a structure present in the surface, which has some of the properties of an elastic skin enclosing the liquid. The contractile force of such a skin is equal to the surface tension of the liquid, according to those who regard it as a reality; and since the films diminish the surface tension of the water, the molecules of oil, on that theory, must operate in some manner to impair the strength of the surface skin.

Are we to regard the force on a float bounding an area of the surface covered by a film, as due to the outward pressure of the film molecules, or to the difference between the outward tension of the clean water surface on one side, and the smaller inward tension of the dirty surface on the other? Apart from the predisposition to regard the surface of a liquid as in a "state of tension," which is a natural, but not a logical, result of the general use of the word "surface tension" to express the work which must be done per unit area of fresh surface formed, the idea of surface pressure has so much in common with other branches of

Physics that it appears unquestionably correct. It might be asked, how much progress should we have made, by regarding the force on the walls of a vessel containing gas, as the difference between the tension of the vacuum outside the vessel, and the diminished tension of the "contaminated vacuum" inside? Attempts to regard the force on the boundary of a film as due to the difference between two tensions, have not led to any tangible theory of the molecular structure of the films, whereas abandoning the idea of a contractile skin, and using the idea of an outward pressure of the film molecules—a two-dimensional osmotic pressure on the perfect semipermeable membrane which the float forms for the insoluble films—very complete analogies have been discovered between the arrangements of the molecules in the two dimensions of the films, and the ordinary forms of matter in bulk. The ideas of surface pressure, and of a contractile skin, are mutually exclusive; and if the contractile skin theory is wrong in the application to properties of surface films, it must also be wrong in its application to all other phenomena of Capillarity. Many writers have warned against the contractile skin theory; in a recent note (8) the author has attempted to show that the so-called proofs of the existence of such a skin are invalid, and that satisfactory explanations of the phenomena of Capillarity can always be obtained without its use; and also that the various forms assumed by the contractile skin theory in the literature are generally contradictory when applied to other phenomena than the single one for which they were invented. Much remains to be done, in developing the theory of Capillarity on the usual lines of molecular Physics; and the author is convinced that all remnants of the idea of a contractile skin in the surface of liquids must be cleared away before progress can be made in this direction.

The surface pressure is quantitatively equal to the diminution in the surface tension of the surface by the film, for if the barrier bounding a film which exerts a pressure F is moved inwards so as to diminish the area by 1 sq. cm., work F ergs must be done; but if the surface tension of the clean surface is γ and that of the film covered surface is γ' , the mechanical work is $\gamma - \gamma'$, since

the surface tension is only the work necessary to increase the area of a surface by 1 sq. cm. It is frequently necessary to determine the surface pressure by taking the difference between the surface tension of the film covered, and of the clean surfaces.

DEVELOPMENTS OF THE MONOMOLECULAR THEORY

The rise of surface pressure after the molecules first come into contact was soon found not to be always quite abrupt, and this caused some doubt as to the films being always 1 molecule thick. Marcelin (9) for a time considered that the area to which it is necessary to compress the films of several oils, to bring them into equilibrium with drops in bulk on the surface, is so nearly half the area of maximum extension of the film, at which the first surface pressure is developed, that the point of equilibrium with the drops is that at which the film is 2 molecules thick. Devaux (10) considered it possible that the films were more than 1 molecule thick, when compressed. The ratio of the areas at the first appearance of surface pressure, and at equilibrium with the drops, is not usually however two to one; figure 2 shows that for the saturated fatty acids it is not far from 1.01 to 1, and it would not be difficult to find substances in which it would be five to one or even more, according to the sensitivity of the means used to determine the first surface pressure.

In about five thousand experiments on films of long chain aliphatic substances, the author has never found a case of a film more than one molecule in thickness. When the molecules leave the surface, to mount on one another, as they must do when the area is sufficiently reduced, they pile up into aggregates many thousands of molecules thick, which are usually visible to the eye. That this is likely to be the case is shown, when the forces on individual molecules are considered. They are anchored to the water by an attraction perpendicular to the surface, and the film, in the closer stages of packing, is further stabilized by the lateral attractions between the long chains, which are often packed closely side by side. For a single molecule to leave the film, and lie on the top, would require the overcoming

of both the perpendicular and side by side attractions; but if a number are expelled together, the side by side cohesions are not disturbed, and even the work of overcoming the perpendicular attractions is diminished by the attractions which the molecules exert on one another as they come together outside the film.

LANGMUIR'S WORK

The next considerable advance in our knowledge of the structure of surface films was made by Langmuir in 1917 (11). He accepted the monomolecular idea completely; making numerous experiments, measuring surface pressure directly by observing the outward pressure on a float in the surface, and also the area per molecule by measuring the area of the films and the quantity of substance put on, concluded that the films of insoluble fatty substances with long chains are fairly closely packed on the surface, in some cases so closely packed as to have the properties of a solid substance on the surface. With the closest packings, the area of the film was independent of the length of the molecule in any one homologous series of compounds. The area per molecule in this closest packing was about 21 sq. Å.u., a value fairly close to that obtained by assuming the film to be of the same density as the material in bulk, the long chains oriented vertically and the distance of the carbon atoms above each other 1.5 Å.u., the distance apart of the carbon atoms in the diamond. The independence of area and length of the chain alone points very strongly to a vertical orientation of the chains. There were some complications, the area of some of the films being roughly double that of the closest packing; Langmuir did not elucidate these, but later work has shown that they can be explained without conflicting with the essentials of his view.

Langmuir also dealt with the structure of the films adsorbed at the water-air surfaces of slightly soluble fatty acids, and many other substances. Direct measurement of the outward pressure of the film molecules cannot be made by a float in the surface in this case, as the film molecules can pass under the float by dissolving in the water. But the surface pressure is the dif-

ference between the surface tension of the solution with the adsorbed layer formed, and that of the pure solvent, or more strictly that of the solution if it were possible to measure surface tension so rapidly that the adsorbed layer had not been formed. Measurements of the surface tension of the solution therefore provide a measure of the surface pressure of the adsorbed film.

The area per molecule may be found from Gibbs' adsorption equation, when the surface tensions are known over a sufficient range of concentration of solution. The equation may be exactly written in any of the following forms (Γ is the number of molecules adsorbed per sq. Å.u., A the area per molecule, γ the surface tension, F the surface pressure, μ the potential of the solute, a the activity, c the mol fraction or concentration, R , is 1.372):

$$\frac{1}{A} = \Gamma = - \frac{d\gamma}{d\mu} = \frac{dF}{d\mu} = \frac{dF}{RTd \ln a} \quad (1)$$

and approximately in the form

$$\frac{1}{A} = \frac{dF}{RTd \ln c} \quad (2)$$

The variation of $\log c$ or $\log a$ with F is determined experimentally by measuring the surface tensions of the solutions at various concentrations, and the area per molecule found from the slope of the curve relating these quantities.

Langmuir reviewed a large amount of data in the literature on the surface tensions of aqueous solutions, using the approximate form of Gibbs' equation. When the solutions were sufficiently dilute, the relation $FA = RT$ holds. This is precisely analogous to the relation between pressure and volume in an ideal gas or ideal solution. Indeed this is to be expected, since the surface is a solution in two dimensions, and any float which could prevent the surface film molecules passing, allowing the water molecules to pass freely, would be an ideal two-dimensional semipermeable membrane. We have seen that such a float, or perfect barrier to film molecules, is realisable experimentally in the case of the insoluble and non-volatile films, so that the surface pressure F is clearly a surface osmotic pressure.

When the solutions become more concentrated, the relation $FA = RT$ does not hold, but the adsorption increases until with large concentrations it is nearly constant, at 31 sq. Å.u. per molecule.

Langmuir considered that the insoluble films which he investigated by the float method were analogous to two-dimensional solids and liquids, and the adsorbed films in the dilute state to two dimensional gases. He predicted a series of phenomena completely analogous to evaporation, as a connecting link between these two states. This prediction has been fully verified, quite recently. Langmuir also applied the theorem of kinetic theory, which gives the relation between the concentrations of a gas in two regions differing in potential energy, to the equilibrium between the surface and interior of the solutions, and obtained information as to the orientation of the molecules in the gaseous condition of the films. This will be explained later.

THE PRESENT POSITION. GASEOUS FILMS

Owing to the small size of the molecules, the normal state of the films is one in which the thermal agitation plays a predominant part. The pressure on a barrier, when the floating objects are small enough, will be a series of impacts from the moving objects, not a steady pressure. With the longer chain compounds studied by Rayleigh and Langmuir, there was much cohesion in the films, so that sometimes the effect of the thermal motions could be neglected, and the size and shape of the molecules were the predominant factors in determining the properties of the films.

When there is a negligible cohesion between the film molecules, and the molecules are small in comparison with the area available in the surface, the average kinetic energy in each degree of freedom of the surface, $\frac{1}{2} RT$ for each molecule, operates wholly to produce pressure on the barriers, that is, the surface pressure. Then it may be shown by the methods of kinetic theory that $FA = RT$. The same equation may be deduced thermodynamically by a combination of Gibbs' adsorption equation, with Langmuir's kinetic theory of adsorption, or some equivalent theory

which will account for the fact first observed by Traube (12), that in dilute solutions the surface pressure is proportional to the concentration in the bulk of the solution.²

Films in which the relation $FA = RT$ is approximately obeyed are called "gaseous" films. Figure 1, which is compiled from direct measurements by Jessop and the author (19), in the case of the acids from C_{12} upwards, and from Schofield and Rideal's calculations, using Gibbs' equation in its exact form and v. Szyszkowski's (24) and Frumkin's (25) measurements of the surface tension of the aqueous solutions of the normal acids from C_4 to C_{12} , shows the variation of the product FA with F . As with gases and vapors, this method of plotting emphasizes the departure from the perfect gaseous state. The equation $FA = RT$ is represented on the diagram with sufficient accuracy by the horizontal line $FA = 400$, since all the measurements are within 10° of 18° . All the acids approach the perfect gaseous condition at very low pressures; but in the case of the acids above C_8 , they do not approach closely to this condition above pressures of one dyne.³ The curves are dotted where the absence of experimental data at the present time makes their actual course a matter of extrapolation. The curves resemble so closely the PV - P isothermals of a gas-liquid system at different temperatures, that it is reasonable to continue the extrapolation down to zero pressure along the line $FA = 400$, when this line has already been reached at higher pressures. At present the direct method of measuring surface pressures, by recording the actual force on a float, is much more accurate than the deduction of surface pressures by subtracting the surface tension of the film-covered surface from that of the clean surface; the direct and the indirect methods have both been applied to the C_{12} acid, almost identical results being obtained on the rising portion of the curve.⁴

² For an elaboration of this theory, the reader should consult (19, p. 424, footnote) and Schofield and Rideal (22).

³ Pressures will be recorded as so many "dynes," meaning dynes per centimeter.

⁴ The points determined from surface tension measurements and Gibbs' equation are marked Δ , and those by measuring the force on a float X . With the C_{12} acid, both methods are working under unfavorable conditions, owing to the slight solubility of the acid. The agreement is better than could be expected. Probably

The good agreement between the two methods is an excellent verification of Gibbs' equation, and the fact that the change in the curves, as the hydrocarbon chains are lengthened, is gradual and without any unusual feature where the direct method of determining surface pressure and area is substituted for that based on Gibbs' equation, is striking evidence of the equivalence

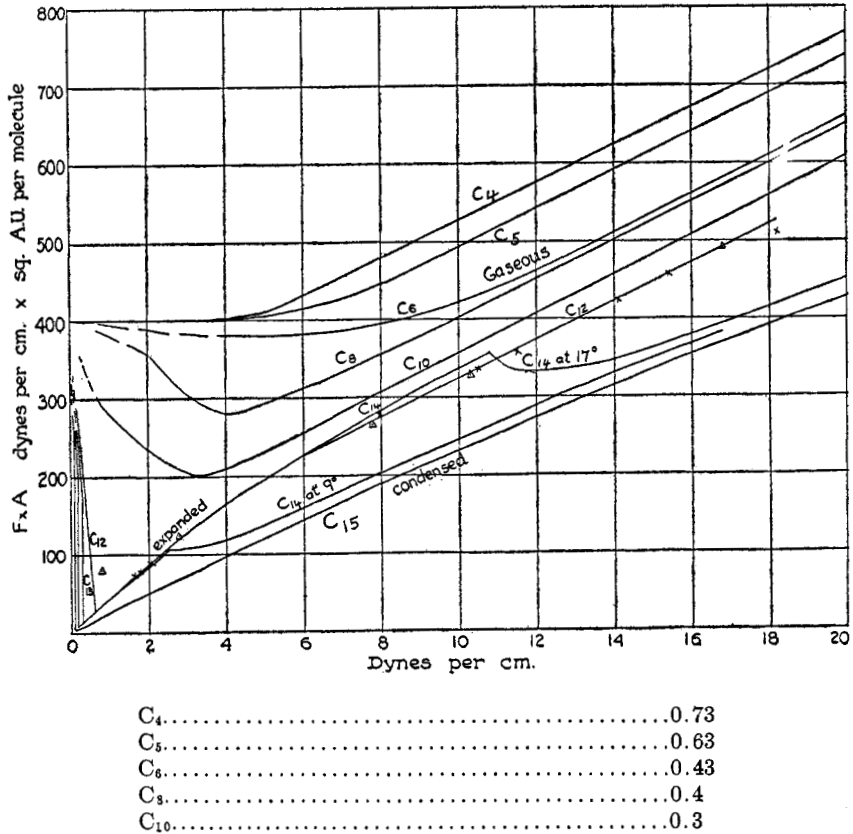


FIG. 1. GASEOUS FILMS

the curve for the C₁₄ acid is more accurate than that for the C₁₂, and it was to be expected that the C₁₂ curve would lie, if anything, slightly above that for the C₁₄ acid.

The experimental methods are described at the end of this paper.

of the two methods; it also proves that the adsorbed films, like the insoluble films, are 1 molecule thick.

The films of all the acids shorter than C_{12} are quite definitely gaseous in character; that is, their F - A isothermals correspond to the P - V isothermals of actual gases. For the acids shorter than C_6 , above 10 dynes per centimeter, the principal deviation from the perfect gas laws is due to the size of the molecules; an equation of the same form as Amagat's equation of state for gases under high pressures holding within the accuracy of experiment.

$$FA = FB + RTx \quad (3)$$

B is a constant, equal to 25 sq. Å.u. practically the same for all the acids C_4 to C_{10} ; it is the limiting area to which the films can be compressed. x has the following values; it decreases with increasing cohesion between the molecules.

At lower pressures, and especially with the longer chains, phenomena due to strong cohesion between the molecules appear. The curves of C_{10} , C_{12} , and C_{14} follow very closely the isothermals for carbon dioxide at various temperatures on either side of the critical point. The C_{12} curve is just above the critical point; this region is better seen in the curves of (19), figure 1. C_{13} is the first acid which shows a definite vapor pressure, and all the acids above this also show a vapor pressure, which becomes very small above C_{15} . The vapor pressures of the fatty acids, on dilute HCl (which is used as more reproducible results are obtained, and less trouble experienced from solubility, than on distilled water) are, C_{13} , 0.30; C_{14} , 0.18; C_{15} , 0.10; C_{16} , 0.04 dynes.

Similar evaporation phenomena have also been studied in the series of ethyl esters, primary alcohols, and nitriles, the main features being the same in all cases. The "critical pressures" are never greater than a few tenths of a dyne, and there are some differences between the films on the liquid side of the vapor pressure region, which will be discussed later.

WORK OF ADSORPTION. ORIENTATION OF MOLECULES IN
GASEOUS FILMS

It is possible, as Langmuir showed, to calculate the work done in bringing a molecule from the adsorbed film into the interior of the solution against the surface forces, when the solution and the adsorbed film are both dilute. Considering the adsorbed layer, and the interior of the solution, as two separate solutions of different concentration, then Boltzmann's theorem of the relation between the concentration of the molecules in two different regions, where their potential energies differ by λ , states that

$$\frac{k\Gamma}{c} = e^{\frac{\lambda}{RT}} \quad (4)^5$$

$k\Gamma$ is the concentration in the adsorbed layer, and c that in the bulk of the solution. This equation is accurate only in the limiting case of infinite dilution, when the volume filled by the molecules is negligible in comparison with that of the region under consideration.

By Gibbs' equation

$$\frac{\Gamma}{c} = \frac{1}{RT} \frac{dF}{dc} \quad (5)$$

hence

$$\lambda = RT \ln \frac{k}{RT} \left(\frac{dF}{dc} \right)_0 \quad (6)$$

$\left(\frac{dF}{dc} \right)_0$ being the limiting slope of the surface tension—concentration curves at extreme dilution. We have seen already that the ratio $\frac{F}{c}$ becomes constant or nearly so at attainable dilutions.

⁵ This equation may be more familiar under the form

$$\lambda = RT \ln \frac{k\Gamma}{c}$$

λ is the maximum work obtainable in taking a mol of the substance from the solution to the surface layer.

If an assumption is made as to the thickness of the surface layer, the concentration of the solute in the adsorbed film may be calculated and the constant k found. This is a rather arbitrary proceeding in our present state of knowledge; but in the case of any one homologous series we may assume as a first approximation that the thickness of this layer is the same, and therefore k the same, for each member of the series. It then becomes possible to calculate the increase in the work of adsorption as one CH_2 group is added to the chain of the molecule. By (4), in this case, when λ_n and λ_{n-1} are the energies of adsorption of successive members of the series, with n and $n-1$ carbon atoms,

$$\lambda_n - \lambda_{n-1} = RT \ln \frac{\left(\frac{\Gamma}{c}\right)_n}{\left(\frac{\Gamma}{c}\right)_{n-1}} \quad (7)$$

Szyszkowski (24) found that the surface pressure of solutions of the fatty acids from C_3 to C_6 could be approximately represented by the equation.

$$F = B\gamma_0 \log_{10} \left(1 + \frac{c}{\alpha}\right)$$

B being a constant having the value 0.411 for all the acids, and α a constant for each acid, for C_3 , 0.165; C_4 , 0.051; C_5 , 0.015; C_6 , 0.0043. The ratio of the values of α for successive members of the series is very close to 3.4 in each case. γ_0 is the surface tension of water, 72.8 dynes at 20° .

Differentiating,

$$dF = 0.434 B\gamma_0 \frac{dc}{c + \alpha}$$

and combining with Gibbs' equation in its approximate form (2),

$$\Gamma = \frac{0.434 B\gamma_0}{RT} \frac{c}{c + \alpha} = \frac{13 \cdot 0}{RT} \frac{c}{c + \alpha} \quad (8)$$

For very dilute solutions, when c is small compared with α , this becomes

$$\frac{\Gamma}{c} = \frac{13.0}{RT\alpha} \quad (9)$$

Hence for the acids C_3 to C_6 , the ratio $(\Gamma/c)_n \div (\Gamma/c)_{n-1}$ is 3.4, and from (7),

$$\lambda_n - \lambda_{n-1} = 2.303 RT \log_{10} 3.4 = 4.91 \times 10^{-14} \text{ ergs per molecule or 710 calories per gram molecule}$$

The significance of the experimental fact that the ratio of the α 's in Szyszkowski's equation for successive members of the series is always 3.4, is that the energy of adsorption of each successive CH_2 in the chain of the molecule is constant and equal to 710 calories per mol. This constancy can only mean that each CH_2 group occupies a similar position in relation to the surface as all the others, and this can only be the case if the chains are lying flat on the surface.⁶

The proof that the chains are lying flat in the gaseous films only exists for the C_3 to C_6 acids, but the curves of figure 1 form such a continuous series that probably *in all gaseous films, the chains lie flat on the surface.*

By assuming the thickness of the surface adsorbed layer to be 6 Å.u., Langmuir calculated the work of adsorption for a large number of compounds. This could be expressed by the formula

$$\lambda = \lambda_0 + 625n \quad (\text{calories per mol})$$

λ_0 being constant for each homologous series, depending on the

⁶ The assumption that the thickness of the adsorbed layer is the same for successive members of the homologous series may of course be incorrect, but any possible error does not seriously impair the above argument that the chains are lying flat. Suppose that the layers are proportional in thickness to the length of the molecule; then the k 's in equation (4) will be inversely proportional to the lengths of the molecules, and the difference between the energies of adsorption will be less than those calculated from equation (7) by $RT \ln \frac{n}{n-1}$. The difference between $RT \ln \frac{4}{3}$ and $RT \ln \frac{5}{4}$ is negligible in comparison with the difference in the work of adsorption, $RT \ln 3.4$.

nature of the end group, and n the number of carbon atoms in the molecule. The values of λ_0 were

	END GROUP	λ_0
Monobasic acid.....	-COOH	437
Primary alcohol.....	-CH ₂ OH	575
Primary amine.....	-CH ₂ NH ₂	600
Ester.....	-COOR	470
Amide.....	-CONH ₂	-510
Ketone.....	RCOR'	295
Dibasic acid.....		-700

A double bond in the molecule decreases λ_0 by about 400 and every additional hydroxyl group in an acid decreases it by about 800. The value 625 for the coefficient of n is fairly near that of 710 previously obtained for the work of adsorption of a CH₂ group in the fatty acids, and indicates that the CH₂ groups in all cases lie in the surface, long chains lying flat; of course all these films are of the "gaseous" type.

Much further information might be gained by an accurate study of the influence of chemical constitution on the value of λ . The chief desiderata are a more accurate means of measuring small depressions of surface tension, and more data as to the assumptions made in assigning values to the thickness of the surface layer; the latter may be difficult to obtain, λ being the decrease in potential energy when a mol passes from the interior to the surface of the solution, a small value indicates high polarity, or tendency to dissolve in water. Langmuir pointed out that although hydroxyl and carboxyl groups increase the polarity, the polar character does not appear strictly additive, but two adjacent active groups enhance each other's polarity.

CONDENSED FILMS

When the cohesion between the molecules is great enough, and the temperature low enough, the molecules pack very closely, into "condensed" films. In these, the thermal agitation of the molecules is insufficient to permit them to have independent translatory motion along the surface, and the film

behaves as a coherent whole. This does not mean that experimentally it is possible to apply a tension to such a film along the surface; at least no attempt to do so has yet resulted in evidence that the film could support a tension. But it frequently happens that the film can resist a shearing stress in the plane of the surface, thus possessing surface rigidity. Condensed films, even those of the closest packing, may be either solid or liquid, or highly viscous but still liquid. Quantitative work on the surface rigidity of films is at present lacking. From qualitative observations, there is no doubt that there is sometimes a genuine rigidity; the author has sometimes had a film strong enough to resist a pressure of 2 or 3 dynes per centimeter, uniformly applied at one end, when there was no support at the other, the film being merely supported by the friction against the sides of the trough, 14 cm. wide. It is rare to find a definite "melting point" in the films, when the solid film suddenly loses rigidity and becomes liquid. One such case is known, with the acetamides (18). As a rule it appears as if there is considerable resistance to complete solidification, and possibly considerable "supercooling" even when parts of the film are solid. The molecules can only move to their equilibrium positions in the two dimensions of the surface.

The characteristics of condensed films are close packing, small compressibility, and negligible variation of area with temperature. When one chain is present in the molecule, the area is almost always between 20 and 30 sq. Å.u. per molecule. There are however wide variations among condensed films in area and compressibility, as the F - A curves of figure 2 show. These curves are of the following substances; the lower portions below about 2 dynes are dotted, as most of the data were obtained with the apparatus in which air jets disturb the equilibrium of the balance slightly (see the final section of this paper), and the lowest portions so determined were not reliable.

- I. Acids on distilled water (final curve); amides; di- and tri-glycerides (areas per chain, not per molecule); ureas above the transition temperature; acetamides below transition temperature.

- II. Ethyl, methyl, and allyl esters of saturated acids.
- III. Alcohols.
- IV. Acids on dilute HCl or H₂SO₄.
- V. Iso-oleic acid on dilute HCl.
- VI. Ethyl iso-oleate.
- VII. Hexadecyl phenol and allied substances.
- VIII. Ureas below the transition temperature.
- IX. Nitriles.
- X. Final curves of the longer chain α bromo-acids, on dilute HCl.
- XI. Bromo-palmitic and bromo-margaric acids on HCl.
- XII. Acetamides above the transition temperature.

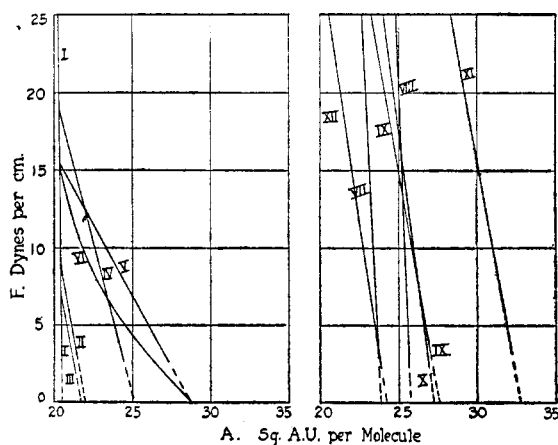


FIG. 2. CONDENSED FILMS

The data for these curves and some additional information is in (13-18).

There is practically no effect in most of the films, due to the length of the hydrocarbon chain, provided it is long enough to provide sufficient cohesion to keep the molecules in the condensed film. In the case of the bromo-acids there is however a definite difference in area between the 16 and 17 carbon acids, and the 18 and 21 carbon acids. The pair with the longer chains pack more closely than the pair with the shorter. In the aldoximes (17) and possibly also in the alcohols, there is a slight al-

teration in the curves, with length of chain. But these are minor differences, of which the different packings possible through the lower ends of the molecules being larger in cross section than the upper, may be the cause. The broad fact remains that the area is independent of the length of the molecules; in the case of the acids and alcohols, this has been verified for lengths from 14 to over 30 carbon atoms. The molecules are therefore oriented perpendicular to the surface.

The evidence that the polar group at the end of the molecule is the one directed downwards is as follows. It is only those long chain compounds with a water soluble group, that is a group which with a very short chain confers solubility on the molecule, which form stable films. The hydrocarbons, alkyl bromides and iodides, and the methyl ethers, do not form films at all, but the molecules remain in aggregates on the surface. Also if a large group is attached to the polar group, the adhesion of the film to the surface is destroyed; e.g., benzyl palmitate, palmitic anilide, cetyl palmitate, do not form films, simply because the polar group is prevented from approaching the water closely enough (16).

The curve of figure 1 is found with a large number of different types of compounds which have nothing in common except the long hydrocarbon chains. Some of these compounds only reach this curve at fairly high compressions, showing a definite lower portion, which is in all cases except that of ethyl iso-oleate a straight line. Areas smaller than those of curve I have never been found. It is obvious that the long chain compounds cannot pack together side by side to a smaller area than that of the long chains packed closely, therefore the curve I indicates that the long chains are touching each other in the closest packing. Where, as with curves II to VI, there is a definite lower portion of the curve, which cuts the abscissa at a greater area than curve I, the area at the foot of this lower portion is the cross section of the molecule at the widest point of the end group. This cross section is nearly always completely determined when the end group is given, hence we may take the areas at the foot of the curves as being the maximum cross sections of the end groups of the molecules, under the packing conditions in the film.

In curves II to VI, it is found that mere compression of the films forces the molecules eventually into the state of close-packed chains. It is necessary to account for the possibility of diminishing the area by compression, as at no compression we have supposed that the cross section of the head (end-group) is large enough to prevent close packing. Either the heads of the molecules are compressible, or they can be tucked away into recesses in the neighbouring chains, probably by a slight movement up or down of neighboring molecules. It seems likely that the second alternative is the correct explanation. The re-arrangement by forcing the heads into recesses in neighbouring chains could not occur if the end groups were too long vertically to fit into the recesses; and if the zigzags in the hydrocarbon chain are formed with the bonds between successive carbon atoms set at the tetrahedral angle of stereochemistry, it would not be possible to accommodate bulges on the molecules, which extended over more than two carbon atoms distance vertically, into the adjacent chains and still allow the chains to be closely packed. Curve VII shows that the benzene ring cannot be tucked away. Actually the compressibility of this curve, calculated in diminution of volume for a given increase in lateral pressure, assuming that the thickness of the part of the film which resists the lateral pressure, is 6 Å.u. or approximately the length of the benzene ring, is of the same order of magnitude as the compressibility of benzene; this is corroborative evidence that the resistance to compression is wholly provided in the case of these benzene derivatives by the close packed benzene rings, and it shows that the heads of the molecules are not more compressible in the films than are the same atomic groupings in matter in bulk. Another head which cannot be compressed in films is the urea group, $\text{NH}\cdot\text{CO}\cdot\text{NH}_2$, curve VIII.

Thus two main states of the condensed films can be distinguished, that of close-packed chains, and that of close-packed heads. The films with close-packed heads can be further subdivided into those which can undergo considerable re-arrangement by compression, probably by a vertical rearrangement of the molecules, the widest portions packing into recesses in the chains,

and sometimes being wholly accommodated in these, so that the chains can pack closely; and those where the heads of the molecules form of themselves a stable structure which cannot be compressed laterally (except to the extent that all matter can be compressed in bulk) into any other packing. The compressibility of curve I, the close packed chains, is of the same order of magnitude as that of liquid paraffins in bulk, if one takes the thickness of the film resisting the compression as the length of the molecules, the length being estimated on the assumption that the density of packing in the film is the same as in the substance in bulk.

The results on surface films are too frequently quoted as if they gave direct information as to the length of the molecules. The actual measurements are of cross section, and only the order of magnitude of the length can be obtained, by an assumption as to the density of the films; but that the density in the condensed films is of the same order of magnitude as that in the substances in bulk is clear, since the area per molecule calculated on the assumptions that the volume of a CH_2 group in the films is 29.4 cub. Å.u., the same as in organic compounds at their melting points, and that the vertical height of this group in the films is 1.5 Å.u., or the distance apart of the centres of carbon atoms in the diamond, is 19.6 sq. Å.u., the observed area of curve I, being 20.4 sq. Å.u.

The principal areas of groups as packed in the films, are

	<i>sq. Å. u.</i>
Hydrocarbon chains.....	20.4
- $\text{CH}_2\text{CH}_2\text{COOH}$	25.1
- CH_2OH	21.7
- $\text{CH}_2\text{CH}_2\text{COOR}^*$	22
- $\text{CH}=\text{CHCOOH}$	28.7
- $\text{CH}=\text{CHCOOR}$	28.7
- CONH_2	less than 21
- CN	27.5
- $\text{C}_6\text{H}_4-\text{OH}$, - OCH_3 , or - NH_2	23.8
- $\text{C}_6\text{H}_4\text{NHCOCH}_3$	23.2 or 25.8
- NHCONH_2 -.....	26
- NHCOCH_3	24.2
- $\text{CHBr}\cdot\text{COOH}$	26 to 32
- $\text{CH}_2\text{CH}=\text{NOH}$	25

Hydrolecithin.....	52
Cholesterol.....	39
Triglycerides.....	63
Glycol dipalmitate.....	42

* R may be methyl, ethyl, or allyl.

SHAPE OF THE MOLECULES

It is evident that the length of the molecules must be much greater than the thickness; assuming the density in the films to be the same as in bulk, the length of the molecule of stearic acid, or the thickness of the condensed film, is 26 Å.u.; the square root of the cross section is only 4.5 Å.u. Bulky groups such as bromine increase the cross section of the head of the molecule; even a double bond, as in the iso-oleic acid which has a double bond in the α - β position, greatly increases the area of packing. When however the double bond is in the middle of the chain, in elaidic and erucic acids, there is no enlargement of the cross section. The double bond may be a kink in the molecule, rather than a local swelling. These measurements are exactly what would be expected from the organic structural formulae, proving that it is legitimate to regard these formulae as models, at any rate approximately accurate, of the molecules.

CHANGES OF STATE IN THE CONDENSED FILMS. ALLOTROPY

Figure 2 gives two curves for the ureas, RNHCONH₂. The curve I is obtained above a transition temperature; it shows that the chains are closely packed. The curve VIII is obtained below this temperature. The transition was been observed on the C₁₆, C₁₇, C₁₈, and C₂₀ ureas (14, 18), the only effect of increasing the length of the chain being to raise the transition temperature slightly. The low temperature curve is that of close packed heads, area 26 at no compression; the film is solid, and compression does not re-arrange the molecules. It appears that below the transition temperature the packing of the heads alone determines the area and gives strength to the film. The transition temperature is therefore a melting of the structure formed by

the heads of the molecules; when this is destroyed, it is possible to pack the molecules closer together, till the chains are in contact. Increase of pressure lowers the transition temperature slightly, as it should, since the high temperature packing has a smaller area than the low. Near the transition temperature, if the pressure is raised so that the close packed chains becomes the stable formation, the change from the close packed heads to this is not instantaneous but takes some minutes; and the expansion to the state of close packed heads on reducing the pressure in this region may also be delayed. There is therefore a possibility of much hysteresis in the films (18).

The same kind of change between two allotropic forms of the films occurs with hexadecyl acetanilide $R\langle\text{hexagon}\rangle\text{NHCOCH}_3$ (18). Here the low temperature packing has the greater area; but the high temperature packing is not that of close packed chains, nor even that of close packed benzene rings, but has a larger area than either.

The acetamides, RNHCOCH_3 , show a different change, the low temperature film being solid, and having the close packed chain formation; the high temperature film is liquid and has a larger area. It may be that below the transition temperature or melting point, which is in this case a sharply marked point, there is a cohesion which keeps the heads of the molecules tucked away in the chains; at a certain temperature this breaks down, and the molecules begin to rotate about a vertical axis, at once destroying the solid structure of the film and sweeping out an area greater than that of the closest packing.

SPONTANEOUS CHANGES IN AREA OF THE FILMS

With condensed films, the pressure equilibrium is not always attained instantaneously. This is sometimes due to slowness of the molecules in attaining their final packing, as in the case of the urea derivatives near the transition temperature. Hydrolecithin seems to be another such case; at room temperature this film, if suddenly compressed, takes some minutes to reach the final area, the pressure falling in the interval; if suddenly

allowed more space on the surface, after being compressed, the pressure falls below the equilibrium value and then rises. The complicated constitution of the molecule may account for its slowness in settling down to the most stable packing (21). In other cases, it is possible that a slow change in the film is due to chemical reaction altering the size of a part of the molecule; the amine hydrochlorides on distilled water form films which increase slowly in area for about ten minutes. In other cases, a change in area may be due to an easily recognizable chemical change in the film; the lactone of γ hydroxystearic acid is hydrolyzed on a normal aqueous solution of caustic soda to the acid; the lactone is a condensed film, and the hydroxyacid, on this solution, a very strongly expanded film, so that the change can be followed by the rate of increase of pressure or area. These reactions of the films need further investigation, which has been delayed until the main facts of the structure could be ascertained.

INFLUENCE OF TEMPERATURE

Condensed films show little if any change of area with temperature. As the temperature is raised, and the thermal agitations of the molecules made more intense, the structure of the condensed films may break down in one of two ways. The principal forces stabilising the condensed films are the lateral attractions between the hydrocarbon chains, and the vertical attraction of the polar heads to the water. In some cases, as with the long chain phenol methyl ethers (16), rise of temperature causes the anchorage to the water to break down first; then the films collapse spontaneously to form masses on the surface.⁷

EXPANDED FILMS

In nearly all cases, however, it is the lateral adhesion which is overcome before the vertical. At a certain temperature the

⁷ Cary and Rideal (27) bring evidence to show that many of the films which can be examined at leisure, once spread by the aid of a solvent, are thermodynamically unstable. The action of heat in causing the collapse is therefore probably one of accelerating the attainment of equilibrium.

area begins to increase, then increases rapidly with further rise, until about ten degrees above the temperature of first increase of area the rate of expansion with rising temperature drops abruptly to an amount about the same as the coefficient of thermal expansion of a gas. This expansion was first recorded by Labrouste (29), and has been studied mainly by the author. Figure 3 shows the F - A curves for myristic acid on dilute HCl, at various temperatures from 2.5° up to 34° . The curve at 2.5° is the condensed curve. That at 34° is the fully expanded curve; further rise of temperature merely moves it nearly parallel to

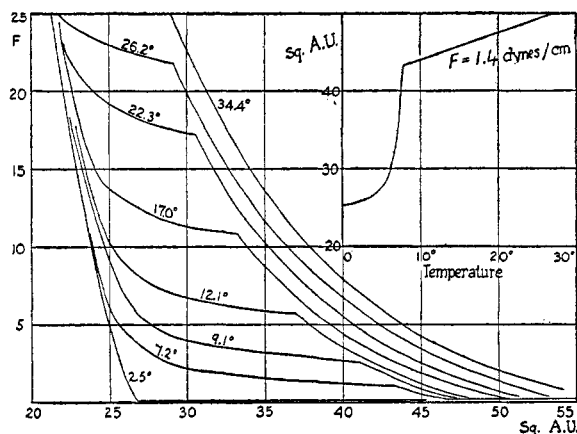


FIG. 3. EXPANSION OF MYRISTIC ACID

itself to the right and upwards. The intermediate curves show that there is always a well defined point at which pressure causes the expanded film to begin to condense; this point is found at a higher pressure, the higher the temperature. The effect of pressure after the condensation has commenced is not exactly that of a pressure on a change of state, for the transition portions of the curves between the condensed and expanded states are not horizontal. In fact at the condensed end of the transition curve there is only a very gradual change of area.

There are two classes of expanded film, those which pass into the gaseous film with a definite discontinuity and show a con-

stant vapor pressure region, and those which show no discontinuity or surface vapor pressure; cases of the first are the higher fatty acids (above C_{13}) as seen in figure 1, the bromo-acids, the unsaturated acids oleic, elaidic, and erucic, and probably palmitic nitrile. The fatty acids such as lauric, which is seen from figure 1 (or better from 19, fig. 1) to be above the "critical evaporation temperature," and the ethyl esters, do not show this constant vapor pressure, and the curves pass continuously into the gaseous curves.

The first class of expanded films tend to a definite area at no compression, which can be fairly accurately estimated by extrapolation, since the expanded curves continue down to the commencement of the vapor pressure, which is not greater than a few tenths of a dyne. It is a curious fact that the area of these expanded films at no compression is always, when one chain is present in the molecule, about 50 sq. Å.u. per molecule. There is evidently much cohesion in the films in this condition, but the structure is not yet clear. The area is much too great for the molecules to be vertical and closely packed; it is also much too small for the molecules to be lying flat. It is possible that the long chains are coiled down in a helical form, with vertical axis; alternatively the chains may be oscillating through a variety of orientations, passing through horizontal and vertical positions. To account fully for the complicated phenomena shown in the curves of figure 3 seems no easy task; it is however an important one, since the expanded state of the films is very common.

The esters belong to the second class of expanded films, and reach larger areas (about 60 or 70 Å.u. at 1.4 dynes per centimeter) than the preceding; there is no discontinuity between them and the gaseous state. The F - A isothermals of the esters (19, fig. 2) show something approaching a discontinuity for ethyl palmitate, though there is no horizontal vapor pressure region; as the chain is shortened there is no sign of a discontinuity, but the curves pass smoothly into the gaseous condition, from areas below 100 sq. Å.u. It appears that the same kind of forces are operating, in the case of those ethyl esters not far removed from their expansion temperature, which cause

the expanded films of the first class to have a definite limit on their expansion; there is in the case of the esters, some peculiarity which prevents the cohesion being as strong as with the fatty acids. Further work is being done on these expanded films, but the solution does not seem close at hand yet.

A regularity has been established connecting the temperature of expansion from the condensed to the expanded films, with the length of the chain. The temperature of expansion rises by about 10° near 0° , and about 7° near 60° , when one carbon atom is added to the chain. This has been found with every one of ten homologous series, although the absolute temperature of expansion depends greatly both on the chemical nature of the end group, and the composition of the solution. This influence of the length of the chain shows that it is the lateral attraction between the parallel, close packed molecules in the condensed state, which is being overcome in the change to the expanded state; this attraction is naturally longer, the greater the length of the hydrocarbon chains.

INFLUENCE OF CHOLESTEROL

Leathes (30) found that cholesterol, mixed with myristic or other fatty acids in the films, has the property of reducing the area of the acid in the film, from the expanded, to the condensed value. It has been found (21) that very few other substances have this property; tripalmitin and one or two other very bulky molecules have some condensing action, though not to the same extent as cholesterol.

INFLUENCE OF PERMANGANATE IN THE WATER

Potassium permanganate in the water on which the films are formed has practically no effect on most films with a saturated chain; but it changes a condensed, or expanded film, of an unsaturated substance with a double bond in the middle of the chain, into a gaseous film, increasing enormously the pressure at a given area. Doubtless this is due to the attraction of the of the permanganate on the middle of the chain assisting the molecule to lie flat, thus causing it to assume the characteristic

orientation of the gaseous film, and diminishing the opportunity for the action of the lateral cohesion between the molecules.

EQUILIBRIUM BETWEEN CRYSTALS OR DROPS, AND THE FILMS

Cary and Rideal (26-28) have studied the equilibrium between long chain substances in bulk on the surface, and the monomolecular films, and also the rate of spreading from crystals to form films. There is a definite maximum surface pressure in the film which stops further spreading the equilibrium pressure; the molecules leave the crystal at a rate which is at any temperature proportional to the difference between the equilibrium pressure and the actual pressure at any moment in the film, and also to the perimeter of the crystal. The rate of spreading increases rapidly with the temperature; the equilibrium pressure increases also with the temperature, the rate of this increase being linear. In the curves relating equilibrium pressure to temperature, there are some curious discontinuities, the meaning of which is not yet clear. The measurements were of the surface tension of the contaminated surfaces, by observing the force needed to withdraw a ring; as the substances were insoluble, the direct measurement of surface pressure would have been applicable and perhaps more convenient. Adam and Jessop (20) continued the observations down to very low pressures on myristic acid, obtaining complete agreement with the above theory of the mechanism.

Hardy (31), Wilson Taylor (32), and others, have shown that when a liquid spreads on a water surface, it is first drawn out into a more or less uniform thin sheet, which then undergoes disruption until it consists of a thin, almost certainly monomolecular, film, in equilibrium with numerous drops of liquid. The author regards the mechanism of this spreading, as due to the action of the tangential components of the thermal agitation of the water molecules at the surface, dragging out the oil molecules rapidly along the surface. Owing to the viscosity of the oil, the lowest layer of oil molecules drags the remainder of the drop out along the surface; when the lowest layer is spread over the whole surface and becomes quiet, the upper

layer adjusts itself as rapidly as possible to the position of equilibrium, which is of course that of large drops in equilibrium with a mono-molecular film. This phenomenon is sometimes quoted as due to a squeezing action, the attraction exerted by the water on layers of the oil remote from the water squeezing out the lowest layer along the surface; and hence as proof that the attraction of the water extends to several molecules distance into the oil; but if the thermal motions of the water are taken into account, the phenomenon does not require that the molecular attractions should extend over more than infinitesimal distances.

THE OPTICAL PROPERTIES OF SURFACE FILMS

A surface film makes an appreciable difference to the reflection of light at a solid or liquid surface. Fresnel's law of reflection requires that if the transition between air and a material of refractive index n is sudden, the light reflected when the angle of incidence is the Brewsterian angle ($\tan^{-1} n$) will be completely plane polarized, and that light polarized perpendicularly to the plane of incidence will not be reflected at all at this angle. Jamin and others found that as a rule the polarization was not perfect, the residual light being elliptically polarized, from liquid surfaces. Drude found that Fresnel's laws were often obeyed by freshly cleaved surfaces of crystals, but if these were left in the air for a time, elliptical polarization of the reflected light was the rule. Rayleigh (6) cleaned the water surface carefully, and found that it then reflected as if the transition was abrupt; a film of olive oil, only one fifth of the density needed to stop the movement of camphor on the surface, made an obvious difference, causing ellipticity. He did not succeed in tracing a definite relation between the degree of ellipticity of polarization of the reflected light, and the surface pressure.

Raman and Ramdas (33) have recently found that the surface scattering of light from a water surface, which is appreciable in the case of clean water, may be increased 100 per cent by a film of oleic acid sufficiently dense to stop movements of camphor. Less dense films had no perceptible effect, so that it appears

that an amount which causes noticeable deviation from Frensel's laws does not necessarily affect the surface scattering of light.

FILMS ON MERCURY

The difficulties in obtaining a clean surface of mercury have so far prevented much information being obtained on the properties of the films which can undoubtedly form on this liquid. Optical methods have been employed by Fischer (34), Haak and Sissingh (35), Haak (36), and Reeser (37). Air appears to condense on the surface of mercury, in a film which affects the reflection of light; its thickness is estimated as of the order 20 Å.u., or several molecules thick. The proof that the mercury surface was really clean, when supposed to be so, does not appear complete, and possibly the result attributed to air is due to some other cause. Fischer gave the thickness of oil layers on mercury as less than 50 Å.u., and Reeser as of the order 20 Å.u.

Iredale (38) has investigated the variation of surface tension of mercury with the partial pressure of various organic vapors. This is equivalent to the investigation of the film at a liquid-air surface, by measuring the surface tensions of solutions of different concentrations, the vapor phase being of course the solution in which the concentration is varied. The course of the surface tension—partial pressure curves shows the films to be of the gaseous type, in the cases of methyl acetate and benzene. At partial pressures approaching saturation, the area per molecule becomes of the order 20 to 30 sq. Å.u.

A mere numerical coincidence, in order of magnitude, between the area per molecule in an adsorbed film, at the maximum observed adsorption, with the area of a condensed film, does not justify the conclusion that the film is condensed, for as Langmuir found, most gaseous films tend towards a minimum area of about 25 Å.u. at high compressions. Such conclusions have been drawn mistakenly. It is necessary to observe not only the area per molecule, but the whole course of the $F - A$ isothermals, before drawing conclusions as to the structure. Goard and Rideal's measurement (39) of the minimum area per mole-

cule, in the adsorbed layer of phenol on water was 23.8 sq. Å.u.; this is probably a merely accidental agreement with the author's measurement of the cross section of the tightly packed phenol groups in a condensed film (see table, p. 182). These adsorbed films are gaseous and obey equation (3).

Burdon has recently described a method of obtaining a clean mercury surface, which may be very useful in the study of surface films. He has also obtained much interesting information on the spreading of various liquids on mercury (40).

THE EFFECT OF A SURFACE FILM ON THE EVAPORATION OF WATER

Rideal (41) has shown that surface films of fatty acids have a retarding effect on the evaporation of water. The retardation, though considerable in that the film offers a serious resistance to the passage of water molecules through the surface, is not easy to detect, as under ordinary conditions of evaporation what is measured as the "rate of evaporation" is merely the rate at which the vapor diffuses away from the layer of saturated vapor near the surface. By evacuating the space over the water until it was on the point of boiling, rates of evaporation up to 0.4 per cent of the theoretical were obtained; and these were slowed down by 20 to 50 per cent if either a condensed or an expanded film was present. Increasing the surface pressure increased the retardation of evaporation. Evidently a film very greatly retards the real rate of the molecules leaving the surface; it will be difficult to make quantitative measurements until the retarding effect of the slow diffusion away from the surface can be still further eliminated.

CATAPHORESIS OF SURFACE FILMS

Some recent experiments (21) have failed to detect any force on a film on water, caused by applying a fall of potential of about 70 volts per centimeter along a water surface. The film was about 130 sq. cm. in area, on water in a trough 4 mm. deep, made of ebonite, and a force of 0.005 dyne per centimeter could have

been detected. Films of fatty acids and of amine hydrochlorides were used, and at present no explanation can be given of the negative result.

ADSORPTION OF WATER ON SALT SOLUTIONS

If the surface tension increases with increasing concentration, then there is less of the solute in the surface layers than in the bulk of the solution. The amount of the deficiency of solute in the surface, or "negative adsorption" may be calculated by Gibbs' equation, if the surface tensions and activities of a series of different concentrations of solution are known. Interesting results have been obtained on the assumption that the excess of water at the surface is present in the form of a thin layer of pure water spread on the top of the solution, which is supposed to remain of the same concentration as in the interior, right up to the boundary of this water layer. If $-\Gamma$ be the deficiency in the solute per square centimeter of the surface, calculated from Gibbs' equation, τ the thickness of the superficial layer of water, m the molality of the solution (mols per 1000 grams), then
$$\tau = -\frac{1000\Gamma}{m}.$$
 Langmuir (11) calculated the thickness of the adsorbed water layer in this way, using the approximate form of Gibbs' equation, finding values of τ from 3.3 to 4.2 Å.u. The length of the side of a water molecule, assuming it to be a cube and that these cubes are close packed in liquid water, is 3.1 Å.u., so that these figures lend some support to the view that the surface of the salt solutions which show negative adsorption are covered by a layer of water without salt, 1 molecule thick.

More recent work by Goard (42) and Harkins and others (43, 44) shows that in all cases the thickness τ of the water layer, calculated on these assumptions, diminishes with increasing concentration of the solution; from about 5 Å.u. at low concentrations to about 2 Å.u. in strong solution. The most probable explanation of this variation is that the surface of the solution is not quite free from salt, in the stronger solutions at any rate; there is a tendency to form a layer of pure water at the surface, but the diffusion pressure of the solute in the stronger solutions

tends to force some salt molecules to the surface. The forces at the surface of a liquid are an inward attraction exerted on those molecules which are in the surface layer; owing to the residual affinity of the salt being higher than that of the water, these forces are strongest on the salt molecules and therefore the surface is richer in water than the rest of the solution; unless however the difference in residual affinity between the water and the salt is very great, the tendency of the diffusion forces to keep the concentration uniform is not entirely masked even in the surface layer. The fact that the amount of adsorbed water is so nearly equal to a monomolecular layer of pure water spread on the surface is evidence of the very small range over which the surface attractive forces are operative, under ordinary conditions.

THE NATURE OF THE ABSORBED FILMS IN STRONG SOLUTIONS OF CAPILLARY ACTIVE SUBSTANCES

Schofield and Rideal (22) find that both with ethyl alcohol and water at a liquid-air interface, and with pyridine and water, at a water-mercury interface, the adsorption calculated from the exact form of Gibbs' equation rises from zero to a maximum as the concentration of the more strongly adsorbed component increased, and then falls off. In each case the maximum occurs at a mol fraction of about 0.3 and an area per molecule of 24 Å.u.

The apparent adsorption then *decreases* fairly rapidly with increasing concentration, falling to less than half of its maximum value at a mol fraction of 0.7. The maximum adsorption is a layer practically closely packed, of the alcohol and pyridine; it is unlikely that this layer will be disturbed by further increase in the concentration, and therefore it is undesirable to attempt to explain the apparent falling off in adsorption by assuming the adsorbed layer to become less dense. But if as the alcohol or pyridine concentration increases, there is a tendency to commence the formation of a second layer of *water*, adsorbed underneath the outermost layer of alcohol or pyridine, the net effect on the surface layer will be to diminish Γ . The formation of a double adsorbed layer, consisting of the most easily adsorbed constituent outside, and the less easily adsorbed one immediately

underneath it, appears the best explanation possible at present of this apparent falling off in adsorption in strong solutions.

THE METHODS OF INVESTIGATION OF INSOLUBLE SURFACE
FILMS

For full details the reader must refer to the original papers, especially (14, 19). Some points are important as affecting the design of any instrument to be used with the films, and may be mentioned here.

Reliable methods of cleaning the surface are essential, as well as of frequently ascertaining its cleanliness. Far the best method is to use heavy barriers working on a trough filled to the brim with the liquid, the top of the sides being about 1 cm. wide. The barriers must be coated with paraffin wax, and the top of the sides of the trough also. Ordinary high melting commercial wax is quite satisfactory. Its function is to prevent the water spreading over the trough, and so escaping under the barriers outside the trough and carrying the films with it; the wax does not cause appreciable contamination of the water surfaces, up to about 30°, and approximate measurements can be made above the melting point of the wax.

With these barriers, tests of the cleanliness can be made simply by reducing the area of the surface and noting whether any surface pressure is developed. The films being invisible, frequent tests must be made.

For some purposes an adequate method of cleaning a water surface is to have a vessel of any shape, with a level brim and a means of introducing water at the bottom; an ordinary funnel serves well. The water is allowed to run in from the bottom for a minute or two, and any contamination is swept over the top, the surface remaining clean for a long time after stopping the flow. This method does not require any special cleanliness in the vessel.

To measure the surface pressure, it is necessary to have a float freely moving in the surface, which nevertheless does not allow the film to leak past the ends; and to apply a measured force to this float. Various devices have been used to prevent leaks

past the ends of the float. Langmuir and the author have used a float about 1 mm. from the sides of the trough at each end, and blocked the gaps by blasts of air from jets directed at a suitable angle on the surface of the water. These unfortunately disturb the force on the float to some extent, the error possibly reaching 0.5 dyne per centimeter when blasts strong enough to prevent leaks under high pressures are used. With this arrangement, a simple balance on the bell-crank principle has been used for measuring the forces.

A more satisfactory method, used by the author and Jessop (19), is to end the float about 1 cm. away from the sides of the trough, and block the gaps with fine gold ribbon, bent into an S shape, placed vertically in the water surface, and soldered to the ends of the float and to blocks pressed tightly against the sides of the trough. This arrangement allows of measurement down to 0.01 dyne, and is leak proof up to the highest pressures. Combined with an optical lever to record the position of the float, and a torsion wire system to measure the forces (19) it is probably the most satisfactory method available now.

Marcelin (45) describes two pieces of apparatus; a sensitive one with a vertical torsion wire, but without any means of blocking the gaps at the ends of the float. The author has shown (46) that the results obtained with this are probably seriously in error. The other instrument is on the principle of a two dimensional aneroid; it consists of a frame in the surface, one side of which is a thin, flexible piece of mica, attached to a sensitive lever system. The water in the interior of the frame is supposed to be clean, and the pressure of the film outside moves the mica and the lever system. There is however no means provided of cleaning the surface inside of the frame.

The experiments are not difficult, with proper arrangements, but a constant watch must be kept for leaks, and accidental contamination, or inexplicable results are liable to occur.

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