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# Problems of the Boundary State

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# PHILOSOPHICAL TRANSACTIONS.

## I. *Problems of the Boundary State.*

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### CONTENTS.

References in brackets are to the list of papers at the end, and to the page of the paper referred to. The friction referred to throughout is static friction.

1. *Introductory.*—Matter distributed as a thin layer between two continuous phases may fairly be said to be in a fourth state because the energy of every element is shared with those phases. This is not a distinctive character, the energy of any portion of matter in the universe is shared to a greater or less degree with every other portion by the operation of their mutual attractions. The energy of these films is, however, shared so overwhelmingly with the enveloping phases as to merit some distinctive term.

The numerical value of the influence of the enveloping phases depends upon the point of reference (*see* later, p. 13). One way of estimating it is by a comparison of the tensile strength of the matter in mass with its value when enclosed.

TABLE I.

| | $C_0$. | C.<br>$h = 0{\cdot}007$ mm. | C.<br>$h = 0{\cdot}0027$ mm. |
|---|---|---|---|
| Palmitic acid . . . . . | 449 | 15,853 | [31,000] |
| Stearic acid . . . . . | 636 | 18,397 | [36,000] |
| Eicosane . . . . . | 454 | 8,606 | [17,000] |
| Impure wax (M.P. 57–59°) . . . . . | 2,907 | Not observed. | |

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$C_0$ is the adhesion in grammes per square centimeter across an interface within the solid lubricant* in mass. It was obtained in the usual way by breaking a rod. Fracture in each occurred without tangential flow.

C the value when enclosed between plane faces of steel, the faces being $h$ apart.

The values in brackets were calculated from measurements made with myristic acid on the assumption that adhesion is always the same function of $h$.

There is real difficulty in the application of accepted terms to this fourth state of matter. The solid condition, as the microscope shows, is indubitably solid, but the fluid condition is not fluid because it will bear a tangential stress with finite deformation. When a fluid joint is surrounded by liquid it will not, however, bear a *normal* stress (X).† The word fluid therefore means no more in this paper than the formation of the joint between slider and plate with material which is fluid in mass.

It does not seem possible to evade this difficulty by calling the " fluid " joint plastic since the resistance to slip is " brittle." My own experiments show that a " fluid " joint will resist for days traction which is less than the static friction.

The experimental basis of this paper is narrow. Though over one hundred substances have been examined as lubricants and the general relations of chemical constitution to friction outlined (II) attention has been confined mainly to long chain compounds, namely, normal paraffins, acids and alcohols and carbinols. The following pages are based on observations made with chain compounds.

A cylinder, 1 cm. in diameter, with a plane face placed on a plate in a large pool of any fluid, air being one, sinks slowly until the capillary pressure between the faces is equal to its weight. If the cylinder be now pressed down or pulled up, it returns to its position of equilibrium when the added force ceases to act (XI, 225, IX, 9).

For each load there is therefore a value of $h$, the distance between cylinder and plate, at which the capillary pressure is equal to the loading, and this value is constant for all fluids including clean air, and for different solids when the solid faces are clean, but seems to be exceedingly sensitive to errors in the shape of the surface (XI, 274). The capillary pressure we have called the Leslie pressure (IX, 10).‡

The most difficult problem of the boundary state is offered by this fact that a solid cylinder will float in air over a plane solid surface at a distance which may be as much as 0·007 mm., is independent within the limits of accuracy of the method of measurement of the solids (steel and glass were tried), and is unchanged when air is replaced by a liquid (see also p. 36).

There must be either an excess of hydrostatic pressure between the faces to support the load or the support is furnished by solid particles adhering to the faces.

That the air gap is due to a true capillary pressure and not to solid particles is inferred from the following facts.

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* This word is retained throughout for the substance between the solid faces.

† *See* references, p. 37.

‡ LESLIE, ' Phil. Mag.,' vol. 14, 1802 ; MAXWELL, ' Encyc. Brit.,' 9th Edit. Art. Capillary Action.

When the cylinder is pressed down by increasing the loading it rises to the same height when the loading is removed. An attempt to destroy or at the least to deform possible particles by moving the cylinder about on the plate failed to alter the height. For the same loading the gap is the same. It follows from these that solid particles would have always to be perfectly elastic and of the same size.*

The crucial experiment however is the following. When a disc of glass or quartz is placed upon a plate in a high vacuum Newtonian colours appear and the colours persist in the vacuum but disappear when air is admitted.

It is not easy to get this result because the air must be dry. A trace of liquid acts as an adhesive, causing the surfaces to adhere as the following experiment shows. When the disc is pressed down in dry air until colours appear it rises at once when the excess pressure is removed, but the colours persist indefinitely if the surfaces are contaminated with a liquid. A trace will suffice. It is enough to press the disc down with the naked hand, the moisture given off forming the contaminant. But if the hand be covered with a dry cloth the disc rises. BURGESS found that steel faces would not adhere when dry (XIX).

When dry metal surfaces are pressed together until metallic contact is sufficient to scratch them, they separate in dry air when the excess pressure is removed.

Many experiments prove that surfaces held together with liquid will float apart in a liquid miscible with the lubricant. For this reason they will not separate in air.

Solid surfaces which have been wrung together so that they seize separate in a pool of liquid only if that liquid has a sensible vapour pressure (IX, 16).

All of the fluid between the faces cannot be forced out by any load which can be applied. There persists a limiting layer of great mechanical stability which resists pressure up to some million grammes per square centimeter. There are, therefore, two stages, a first in which the Leslie pressure is adjusted to the load by fluid flowing in or out from between the faces, and a second in which the reaction to the load is adjusted by the elastic forces between the atoms and molecules.

In the first stage comparable mechanical states are states of equal Leslie pressure. The proof lies in the fact that comparisons so limited yield surprisingly simple relations between the variables.

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* Actual measurements will be found on page 224 of XI. The following were obtained two years later:—

| | Load ÷ area. grs. | Lubricant. | Gap. mm. |
|---|---|---|---|
| Steel on steel . . . . . | 8·2 | air | 0·0039 |
| | | cetyl alcohol | 0·0038 |
| | | naphthalene | 0·0040 |
| | | | 0·0039 |
| Glass on steel . . . . . | 8·2 | air | 0·0039 |
| | | cetyl alcohol | 0·0042 |
| | | | 0.0041 |
| Glass on glass . . . . . | 8·2 | cetyl alcohol | 0·0042 |
| ,, ,, ,, . . . . . | 3·5 | air | 0.0057 |
| | | cetyl alcohol | 0·0058 |

On pages 224 and 225 of XI the load should have been, cylinder A 6·47 grs., cylinder B 6·48 grs., which give a loading of 8·3 grs./cm.².

In the second stage, the Leslie pressure ceases to carry the load and comparable states are simply states of equal loading—that is load ÷ area.

In the first stage the coefficient of friction ($\mu$ = friction ÷ load) varies with the load (IX). It is obvious why this is so. The load varies both $h$ and the Leslie pressure and therefore comparison is not between comparable states. In the second stage, however, $h$ is sensibly constant, the Leslie pressure unaffected, and $\mu$ is independent of the load. This is AMONTONS' law.

The limit of Boundary Lubrication is over-passed when the solid faces are so far apart that a portion of the lubricant is beyond the influence of either. Let $a'$ and $a''$ be the range of the influence of the two solids then $h = (a' + a'')$ is the limit of boundary lubrication.

This limit can be fixed with some precision from a curve of any variable and of $h$. The curve, fig. 5, for $h$ and the load in the paper of 1928 (XI, 226), already referred to, cuts the $h$ ordinate at 0·007 mm. and the curve for $h$ and friction in fig. 1 of this paper gives the same value. The most perfect plate and cylinder used gave 0·005 mm. for the limit. Either is a surprisingly high value. WATSON found the value of $h$ to be constant in air down to a pressure of 2 mm. Hg when it slowly and slightly decreased (XV).

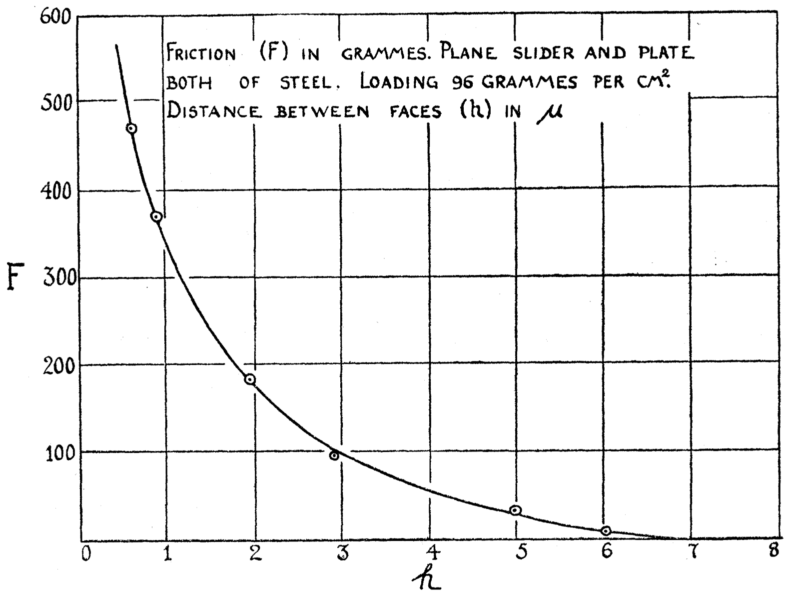

FIG. 1.

It will be convenient to have separate terms for the two ways in which the attraction field at the surface of a solid, or, indeed, of any phase, could affect matter in contact with it. It may do so either by *direct attraction* of relatively long range and of the sort contemplated in Laplacian theory of short range forces or by the spreading from molecule to molecule of a state of strain. Let us suppose that the range of direct cohesive attraction includes only molecules in contact with the face. These molecules will be both oriented and strained and they in their turn orient and strain molecules beyond them until the effect fades out by reason, for example, of the heat motions. Let us call the state of orientation and strain of the molecules " polarisation " and the spreading of polarisation from molecule to molecule *diachysis*. Polarisation and diachysis (διάχυσις) are the basis of the electrical theory of cohesion put forward by Sutherland in 1881 (XX).

The limiting layer mentioned earlier may be taken to be composed of two strongly adsorbed layers, the primary films with the surface of slip between them. Bad lubricants, however, seem to shift the surface of slip into the solids (I). Such lubricants might be distinguished as abrasives, but the same substance may apparently be a lubricant for some solids and an abrasive for others.

A primary film is of insensible thickness. It is completely invisible when deposited on to a clean metal face from vapour of the lubricant or when exposed by breaking a solid joint, yet in both cases the surfaces are as completely lubricated as they would be if the slider were sunk in a pool (N. 554).

The molecules in such a film are highly oriented (*see* especially VII, IX and XI). When the lubricant is a long chain acid alcohol or carbinol, there is a period called the Latent Period, during which friction or adhesion slowly reaches its steady value. The latent period may be due either to the slider rising or sinking in a pool of lubricant until the loading is equal to the Leslie pressure or to the orientation of the molecules of the lubricant by the attraction field of the solids. It is easy to distinguish between the two causes by, *e.g.*, the use of a spherical slider, which, owing to its form, cuts through the lubricant at once until the limiting layer is reached (IX, 12). The latent period of orientation is then found to be exhibited only by lubricants, the ends of whose molecules are unlike such as long chain acids which have at one end the carboxyl group —COOH and at the other the group —$CH_3$ (VII).

Normal paraffins whose molecules end for end are symmetrical show no such latent period. This is sufficient evidence that the molecules are oriented. It is also sufficient evidence that the molecules are oriented with the long axis at right angles to the face for, if the molecules were flat on the face, there would be no reason for the long latent period of orientation of molecules of acids or alcohols, sixty minutes and forty minutes respectively, and the insensible latent period of paraffins.

Each molecule of lubricant in a primary film exerts its influence independently of the others. This follows from the fact that the friction varies directly with the density of the vapour of the lubricant when the primary films on the surface are deposited from vapour (IV, 556).

The properties of primary films are easily studied by the use of a spherical slider, and the fact that the friction is the same when such a slider stands in a large pool of lubricant as it is when the faces of slider and plate are covered only by an insensible primary film deposited from saturated vapour proves that the molecular configuration of such films is the same in both cases (*see* especially IV, 554, and VII, 28).

A primary film is there, even when a solid lubricant has been deposited from solution in a volatile solvent, and may be reached by moving a spherical slider about. When this is done the friction rises as the slider cuts through until it reaches a value unchanged by further movement *and identical with the value for the same* lubricant when fluid.*

In IX, 7, the fact that the coefficient of friction varies with the load and that a latent period of rising friction and falling coefficient followed an increase in the load when the surfaces were lubricated only by a primary film deposited from saturated vapour and the slider was plane was taken to prove that a primary film is more than one molecule in thickness and is capable of being squeezed out from between the faces. That inference was unwarranted. It was drawn before the fact that air is condensed between the faces was discovered (XI, 222).

The later knowledge makes it certain that the cylinder was separated from the plate by a layer of condensed vapour and air, about 0·002 mm. in thickness and the change in friction and latent period following a variation in the load were due to the variation in the depth of this condensed layer.

When the layer of lubricant between the faces is thicker than the limiting layer but yet within the limits of boundary lubrication, the primary films are separated by what we will call the median plate.

If, after the joint has been formed by running fluid between the faces, the temperature be lowered enough to freeze the lubricant in position the median plate is seen under the microscope on breaking the joint to be crystalline (XI, 214). It will be seen from what follows that the crystals throughout are polarised, but nothing is known directly of their structure.

Nothing is known directly of the structure of a fluid joint, but TRILLAT and BRAGG, by X-ray analysis, have found long chain molecules to be disposed on a plane solid face in layers with the long axis at right angles to the face. It is probable, therefore, that such a disposition exists in an enclosed layer of fluid lubricant. There are, therefore, not an infinite number of possible surfaces of slip or break to be considered, but only a relatively small number placed between the layers of oriented molecules because, within each such layer, the limit of resistance to either normal or tangential forces may be taken to be infinite. There are in a fluid joint an infinite number of mathematical tangential surfaces, but only a finite and small number of " *significant* " surfaces.

In a solid joint the number of significant surfaces is reduced to two, namely, those between the primary films and the median crystalline plate (*cf*. p. 26).

Throughout this paper the condition referred to, save when the contrary is stated, is the steady state of equilibrium between lubricant and solids. The length of the latent period needed to reach the steady state depends upon whether the slider or cylinder is spherical or plane, on how the lubricant is applied, and on the chemical

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* The reader may be reminded here of the absence of a temperature coefficient.

composition of the lubricant. Simple relations between the variables appear only when the state is steady and when " comparable " states are compared.

Measurements were made with solid faces previously cleaned and in an atmosphere cleared from impurities, especially from water.

There is no intention here to consider critically observations made by others. The conditions are defined in order to give point to the remark that they are necessary if a disorderly presentation of values is to be avoided. The simplest most fundamental relations of the values appear only when the lubricant is composed of one pure chemical substance. For example, no indications of true metastable values (WATSON and MENOR, XV, 195) were found, save when the lubricant was complex (VII, 31). The want of agreement between dielectric strength and friction noticed by these authors might well give way to agreement under more rigid conditions.

*Section* 2.—The following values have been measured :—

1. The static friction between solid surfaces, either clean or separately coated with solid lubricant (value $F_1$).
2. The static friction of clean surfaces joined by fluid lubricant (value $F_2$).
3. The tangential force needed to produce slip in a solid joint between a cylinder and a plate (value S).
4. The normal force needed to break a fluid joint between a cylinder and a plate (value A).
5. The normal force needed to break the same joint when solid (value B).

An attempt to find the relation between these values meets with curious anomalies. Value $F_1$ obviously is external friction, that is, the friction between readily separable portions of matter. Value $F_2$ on the other hand, since slip occurs within the lubricant, is internal friction, yet it is completely different from viscosity, which is the internal friction of a fluid in mass, but identical with value $F_1$. The viscosity of a chemical series, such as the paraffins, increases with molecular weight; values $F_1$ and $F_2$, on the other hand, decrease.

$F_1 = F_2$ when the lubricant and solids are the same and the curve connecting friction with molecular weight of a chemical series shows no break where the change from fluid to solid occurs. The orientation of the molecules in a fluid joint must, therefore, be such as to form an internal tangential surface where the discontinuity of structure is so complete as to give to it the properties of an external surface so far as slip is concerned. But the portions of matter are not readily separable at this surface. The position of the surface offers no difficulty. The only measurements available for comparison of the friction with solid and fluid lubricants were made with a spherical slider which in both cases cuts through to the limiting layer. The lubricant therefore consisted in both cases of two primary layers probably monomolecular with the surfaces of slip between them at $h_2$. (*See* especially IX, 20.)

Though value $F_2$ has all the characters of external friction, it is neither more nor less than the strength of a fluid joint in shear and therefore akin to value S. But it differs completely from value S in magnitude and in its relations to chemical constitution. Taking the paraffin $C_{22}H_{46}$ as an example $S/F = 1200$ as a round number.

The real relation of the values one to another appears when their derivation from the fundamental mechanical properties of surfaces, namely, their normal and tangential reactions, is traced. Let the traction on a surface of slip grow from nothing. It is balanced by the tangential reaction until the latter reaches the greatest value of which the surface is capable. This value is a true characteristic of the surface because it is defined by the chemical nature and configuration of the molecules in the capillary layers which enclose the surface.

A second true characteristic is the greatest value of the normal reaction to an external force tending to separate the portions of matter on each side of the surface. Let us enquire into the relation of these two values to the observed values. Here we are helped by two identities. The resistance to a normal force can be identified simply with the normal reaction only when there is no tangential flow of the material under normal stress such, for example, as the flow which causes a rod of metal to narrow before it is broken by a longitudinal pull. Since no sign of tangential flow could be detected, even under the microscope, when a solid joint was broken, value B may be directly identified with the normal reaction, and the tangential reaction T can be safely identified with external friction.

We have, therefore, if N be the normal reaction and T the tangential reaction, the two identities,

$$N = B \text{ and } T = F_1 = F_2$$

and these two identities furnish criteria of the two reactions. Before turning to these, however, it will be well to define the quantities more closely.

Let us consider a tangential surface drawn anywhere within the lubricant. The maximal normal reaction of this surface will depend upon where it is drawn and the adhesion value B is the least of these values. A surface possessing this least value is a surface of break and direct observation shows that there is one, or at most two, of these surfaces of break when the lubricant is solid, the number being determined by the nature of the enclosing solids (XI). The quantity B therefore is equal to the maximum normal reaction of a surface of break.

Since solids contract and expand with changes of temperature they are subject to an internal or intrinsic pressure I, which is a function of temperature. When an external longitudinal force of magnitude E is applied tending to break a solid joint, we have at any tangential surface, since there is no viscous flow, the simple condition of equilibrium.

$$E = C - I.$$

C is, of course, the cohesive attraction per unit area across the surface, and B is the greatest value of (C — I) which a surface of break is capable of exhibiting. A solid joint breaks when at the surface of break,

$$\frac{d\,(\mathrm{C}-\mathrm{I})}{d\mathrm{E}} = 0,$$

or, if $h$ be the distance separating the surfaces of the enclosing solids, namely, the cylinder and plate in the particular experiments, when

$$\frac{d\,(\mathrm{E}-\mathrm{C}+\mathrm{I})}{dh} > 0.$$

When friction is external the surface of slip is identifiable if there be no seizing and the value $\mathrm{F}_1$ is the greatest value of the tangential reaction of which this surface is capable. It is also less than the similar value for any surface drawn parallel to the surface of slip. Both B and $\mathrm{F}_1$, therefore, are the least of a series of maxima, and the quantities N and T respectively represent the value of the maximal normal reaction of a surface of break and the maximal tangential reaction of a surface of slip.

The distinctive characters of the normal and tangential reactions now appear when we consider the relation of B and F to the variables, which are the number and chemical constitution of the substances composing the lubricant, the composition of the enclosing solids (the cylinder and plate or the slider and plate as may be), the distance $h$ separating the enclosing solids, the normal pressure (that is, load ÷ area), and temperature.

In dealing with the effect of the composition of the lubricant it is necessary for reasons already given to consider only chain compounds, and, to discover the simplest relation, comparison must be confined to lubricants composed only of one chemical substance. The effect of chemical constitution is then found to include two variables, namely, the chemical series (paraffin, acid, alcohol or carbinol, as the case may be), and for a given series the number of carbon atoms in the chain.

Any of the variables can be used to define features peculiar to B or F, but the one most easily apprehended is the number of carbon atoms in the chain. Call this number $n$, then if the signs + or — indicate whether the coefficient is positive or negative, we have from experiment

$$\frac{d\mathrm{B}}{dn} \text{ is } + \text{ and } \frac{d\mathrm{F}}{dn} \text{ is } - .$$

The evidence is to be found in earlier papers. This relation also holds for the external friction of lubricants in mass as the following figures show :—

Friction of a clean spherical glass slider on solid blocks of—

| | | | | | |
|---|---|---|---|---|---|
| Lauric acid .. | .. | Mol. Wt. | 200 | $n = 12$ | $\mu = 0{\cdot}039$ |
| Palmitic acid | .. | ,, ,, | 256 | 16 | 0·033 |
| Stearic acid .. | .. | ,, ,, | 284 | 18 | 0·028 |

By the identities given earlier we have, therefore, as characteristics of the normal and tangential reactions

$$\frac{(dN)}{(dn)} \text{ always positive } \frac{(dT)}{(dn)} \text{ always negative,}$$

when the coefficients refer to the same chemical series. A second character is the surprisingly great difference in magnitude for the same load. As an example :

Lubricant solid, steel on steel.

| | | |
|---|---|---|
| Paraffin $C_{22}H_{46}$ | Spherical slider | F = 7·3 gr. |
| | Cylinder or plate | B = 9441 gr. |
| Palmitic acid | *ibid.* | F = 0·0 gr. |
| | *ibid.* | B = 15853 gr. |

None of the many measurements lend themselves readily to a comparison of traction (F per unit area) and B value (adhesion per unit area), at the same pressure (load per unit area), but the following figures are sufficiently accurate :—

Nonadecane pressure, 7·15 grs., steel on steel.

| | |
|---|---|
| Plane slider | Traction (about) 10 grs. |
| Cylinder | B value, 8200 grs. |

A third character is the absence of a temperature coefficient for both value F in the second stage of boundary lubrication when the lubricant is reduced by pressure to two primary layers, and for value B.

When the lubricant is fluid and more than two primary layers in thickness, both friction and adhesion (value A) vary with temperature, but this may be due to a variation in viscosity which allows the slider or cylinder to rise or fall in the lubricant. Comparison then would not be between comparable states. *It is tempting to suppose that both* Amontons' *law and the absence of any effect of temperature are fundamental characters of every significant surface.*

*Value S* is the tangential force needed to produce slip in a solid joint made by running fluid beneath a cylinder with plane ends resting on a plate and freezing the lubricant *in situ* (XI, 228). The microscope shows that slip occurs at the interface between a primary film and the median crystal plate. This interface is also a surface of break when the joint is broken by a normal force.

The coefficient $dS/dn$ is positive and the magnitude large, value S therefore has the characters of a normal reaction.

A remarkable feature is the sudden fall in resistance to slip to that of simple friction, caused by the slightest tangential displacement. The joint in short is just as effectively broken by what seems to be tangential motion as it is by normal motion—the fields of force acting across the interface must be completely unlocked in both.

Why did cohesion practically vanish when the lateral displacement was so small as to leave the area in contact sensibly unchanged ? It is possible, of course, that contact was not maintained but was interrupted by a film of air drawn in by capillary attraction. JOFFE, KERPECTEWA and LEWITSKY have drawn attention to the influence upon the breaking stress of a crystal of minute fissures on its surface.* When a fresh surface was formed on a crystal of salt by solution in water the breaking stress per square centimeter was raised from 440 grammes to 5000 grammes, and as the surface aged the value fell again. If the fracture of brittle joints begins by the formation of a minute fissure, as it might well do when the applied force is tangential, air would be drawn in and the Leslie pressure of the air within it would help to deepen the fissure. Joffe and Lewitsky found the breaking stress of rock salt greater in a vacuum than in air.†

If the air be not drawn in and contact be actually maintained, then either the fracture must be accompanied by a re-orientation of the molecules of the lubricant, or the range of cohesive attraction is vanishingly small. The second of these possibilities would make it necessary to refer the influence which each enclosing solid has upon the whole of the lubricant solely to diachysis.

The effect of air is of critical significance and little understood. Any fluid, whether liquid or gas, which surrounds the base of a cylinder is drawn in until the Leslie pressure carries the load.

For example, if a cylinder be wrung down on to a proof plane of glass, Newtonian colours appear. When the pressure is taken off the colours persist unchanged if there be the least moisture present in the air, but if air and surfaces be dry, the blue and yellow at once change to red and green, which, in turn, slowly vanish. This is true, for clean faces and for faces contaminated with a solid film. Air will not displace a liquid, for if a cylinder be wrung down on to a plate covered only by an insensible film of liquid lubricant it remains adherent in air, but floats up in a liquid miscible with the lubricant.

BURGESS noticed the adhesive quality of water and he found the adhesion of two metal plates joined by lubricant to be increased in a vacuum. This increase probably was not due to the hydrostatic pressure of the atmosphere, but to the operation of short range forces. Air drawn into an insensible superficial cleft gave a Leslie pressure and the adhesion was diminished thereby.

*Value A* gives the adhesion of a fluid joint (VI). Its magnitude is of the order of friction, though the sign of the coefficient ($d/dn$) is that of adhesion. By these tests, therefore, this type of adhesion is of mixed origin, including both normal and tangential reactions.

The A value is certainly not merely a measure of the viscosity of the lubricant, for not only is it a linear function of molecular weight like the value B, which certainly gives the

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[*] 'Nature,' vol. 113, p. 424 (1924).

[†] 'Z. Physik.,' vol. 31, p. 576 (1925).

normal reaction of a solid lubricant, but it is not related in any simple fashion to viscosity, as the following figures show (X, 69) :—

| | Steel on Steel. $\eta$ 18°. | Load, 259·6 grs. A value, 18°. grs. |
|---|---|---|
| Octane .. .. .. .. | 0·005 | 3·3 |
| Octyl alcohol .. .. .. | 0·064 | 50·9 |
| Capryllic acid .. .. .. | 0·057 | 97·9 |

On the other hand, it differs from the B value in the fact that it varies with temperature whilst the B value does not so vary over the range explored, namely, from 4° to 56° C. Temperature may, however, alter the distance $h$ between the enclosing solids, the cylinder and the plate, in which event comparison at different temperatures would not be made between comparable states.

An attempt was made to get the normal reaction of a fluid joint uncomplicated by tangential flow by supplying the necessary lateral support. Osborn Reynold's principle of dilatancy suggested the method. A thin skin was applied to the edge of a joint of *solid* lubricant by varnishing with Necol, or a strong solution of gelatine, and allowing the varnish to dry. The lubricant was then melted by raising the temperature and the joint broken. The value of adhesion was now much greater than value A. The capacity which impurities possess for penetrating a fluid joint make it certain, however, that the full value of the normal reaction was far from being reached.

Steel on Steel.

| | Value A. grs. | Value B. grs. | Value A, but edge coated with Necol. grs. |
|---|---|---|---|
| Lauric acid .. .. .. | 70 | 10,683 | 4,070 |
| Palmitic acid .. .. | 120 | 15,858 | 5,370 |

It would appear from these experiments that the A value as measured did not give the complete normal reaction of the fluid joint, but the increase in value caused by a skin of Necol may be due to something other than simple restraint of tangential flow. When the A value was measured, the joint was sunk always in a pool of lubricant. Before applying the skin of Necol, this pool was removed, the conditions were therefore completely changed, for whilst the joint was sunk in the pool, the lubricant would be the seat of the Leslie pressure. Removal of the pool and the presence of the skin of Necol would reduce this pressure to zero (*see* Section 3), we therefore have, when the quantities are reckoned at the moment of break :—

$$\text{value A} = \text{N} - \text{L},$$

when L is the Leslie pressure and

$$\text{value B} \doteq \text{N.}$$

The broad conclusion is that the A value is not the normal reaction per unit area, but that reaction reduced in value by that flow inwards of fluid from the pool which peels the layers of oriented molecules apart and by the operation of the Leslie pressure.

Worthington's method of measuring the tensile strength of a continuous column of liquid provides the necessary lateral support and probably gives its normal reaction. He found the tensile strength of ethyl alcohol to be 8,165 grs./cm.$^2$ and, for reasons just given, this is probably its normal reaction in the fluid state. The value for the solid alcohol is not known and we have not measured it for any other alcohol. If alcohols resemble the related acids and paraffins the normal reaction in the solid state is only a few hundred grammes.

The normal reaction of ethyl alcohol in the fourth state, that is as a lubricant, can be computed roughly from the value for cetyl alcohol 15,860 (XI, 214), by assuming that the effect of molecular weight is about the same as it is for paraffins. The assumption is justified by the form of the curves for friction and it gives—

$$\text{B (ethyl alcohol in steel)} = 10,160, \text{ when } h \text{ is of the order } 0\cdot007 \text{ mm.}$$

The normal reaction of a substance in the solid state in mass is the tensile strength of the weakest planes in the crystal lattice, or of the interface between crystals. That of the liquid in mass is the sum of the reactions across an internal surface of molecules presented to each other in every kind of orientation. On the other hand, the normal reaction of the fluid or solid joint is that of molecules oriented by the attraction fields of the steel.

In estimating the effect of the enclosing phases, it would appear natural to compare a solid joint with the solid lubricant as was done on page 1, but it is now obvious that comparison with the fluid lubricant would yield a very different result.

The values observed can now be arranged in a more rational manner :—

| | |
|---|---|
| Tangential Reaction .. .. .. .. | The Friction F. |
| Normal Reaction .. .. .. .. .. | The Adhesion B.<br>The Slip S. |
| Mixed Reaction .. .. .. .. .. | The Adhesion A. |

Tomlinson's theory of friction (XVIII) suggests that the reason for the difference in magnitude between the tangential and normal reactions may be sought in the fact that the former is the resistance to traction when the attractive and repulsive forces acting across the surface of slip are in equilibrium with the load whilst the latter is the greatest resistance offered by the attractive forces to a tension. This, however, would leave the anomalous S value unaccounted for.

The fact that the sign of the effect of the number of carbon atoms in the chain is different for T and N shows that the difference between them does not consist merely in an extinction of the forces of repulsion. It might indeed be taken to mean that the portion of the molecular field involved is different. This would explain why the sign is the same for the viscosity $\eta$ of a fluid in mass as it is for the normal reaction, because during flow, owing to the heat motions, the molecules must be presented in every spatial way to the shearing stress.

The difference between the normal and tangential reactions appears in a new and striking way when the adhesion and friction of lubricants composed of two pure chemical substances are contrasted.

Consider a pair of miscible substances such that chemical action between them is not possible at ordinary temperatures. A normal long chain acid and a normal paraffin form such a pair. The curves for friction (ABC), adhesion (DEF), and melting point in mass of the mixture (GHI) are given in the diagram, fig. 2 (VII, 32; XII, 610). The curve for friction is a simple adsorption curve. The polar molecules of the acid have complete possession of the adsorbed layer until the concentration has fallen almost to the vanishing point where there is a sharp inflection when the non-polar molecules manage to invade the layer. The linear form of the portion AB is according to expectation, for it can be proved by experiment that the effect of a substance on friction is directly proportional to the number of molecules adsorbed by the solid surfaces (IV, 556). The curve ABC has no obvious relation to the melting points of the mixture.

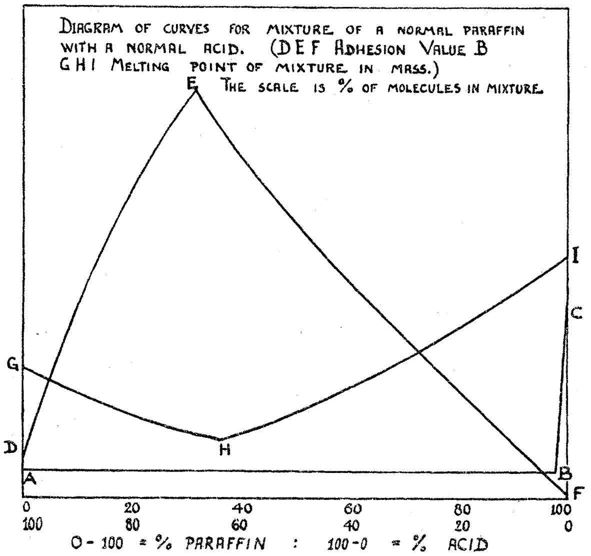

FIG. 2.

On the other hand, the curve DEF of adhesion has none of the features of an adsorption curve, but is related in simple fashion to the melting point (curve GHI).

The melting point of a mixture is a mass phenomenon, or better a volume phenomenon, and when we remember that the normal reaction N is equal to (C — I) and that a solid melts when the intrinsic pressure overpowers the cohesion of the parts of the crystal, the connection between them is obvious. Both value B and the melting point measure a limiting value of (C — I). The absence of any obvious relation to adsorption is, however, paradoxical because the surface of break in these mixtures, sometimes, but not always (XII), lies between the adsorbed layer (primary film) and the median crystal plate (*see* Section 4).

The facts suggest that, though a surface of slip may be defined as a plane surface separating two portions of matter moving in opposite directions, a surface of break may sometimes be far from plane because long molecules with their long axes oriented in the direction of stress are, at the break, pulled apart, like teeth out of their sockets.

The study of complex mixtures of substances such as are commercial lubricating oils presents other aspects of the relation of friction to adsorption (*cf.* XIII).

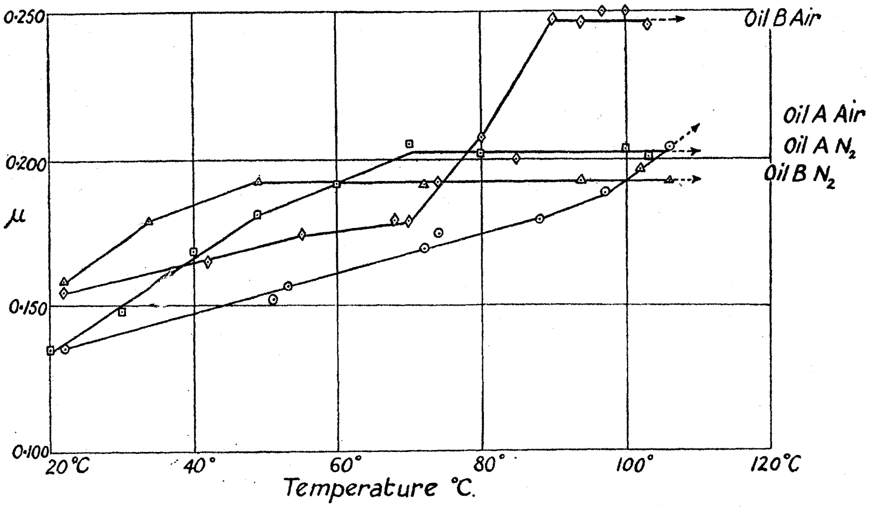

Fig. 3.

Friction-temperature curves of a commercial lubricating oil are shown in fig. 3. Such curves commonly consist of horizontal portions or plateaux where the temperature coefficient is zero joined by ascending or descending limbs. All the evidence goes to show that the composition of the adsorbed layers is constant throughout a plateau. It is, for instance, possible by percolating the oil through glass beads to remove by adsorption the more active polar constituents which form only about 3 per cent. The percolated oil now has no temperature coefficient (XIII, 33). It is now adsorbed not selectively, but as a whole, so that further percolation does not alter its qualities as a lubricant.

The medicinal paraffin (Oil, B.P.) of the pharmacopœia is a fully percolated oil. It has no temperature coefficient of static friction over the range 10° to 115° C. There is no certainty that it is a chemical individual, but it appears to be an "adsorption individual " which may be defined as one which is adsorbed without selection of molecular species and has no temperature coefficient of friction.

Solution of a new molecular species in such an adsorption individual reveals two new principles in adsorption, namely, " availability " and " accessibility." The state of the substance in solution may be such that its molecules are not able to displace the molecules of the solvent, or *diluent*, in the adsorption layers. They are not " available." On the other hand, the state of the adsorption layer may be such as to prevent access of available molecules. It is not easy to discriminate between availability and accessibility, but the behaviour of solutions containing highly polar acids and paraffins show the need for admitting the existence of both. When the temperature is rising, the friction shows that the paraffins have access to the adsorbed layer, but when the friction is falling, the more polar molecules which have obtained access at the higher temperature are not displaced by the non-polar molecules though the state in solution of the latter must be a pure function of temperature (XIII).

An unusually simple example of the operation of availability is furnished by a solution of any paraffin in medicinal " paraffin " (Oil, B.P.).

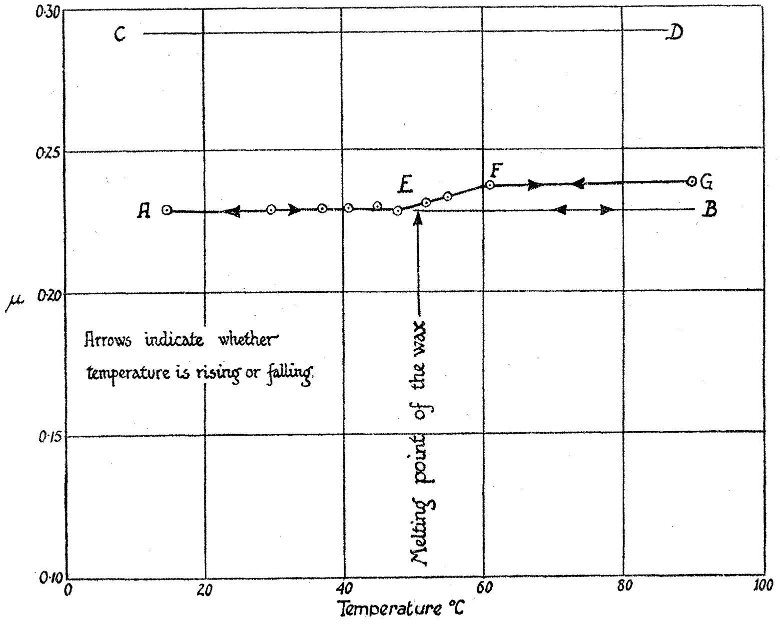

FIG. 4.

The curves AB and CD in fig. 4 are respectively the temperature curves of B.P. Oil, and of a normal paraffin. In the oil, 0·52 per cent. of the paraffin, whose melting point was 56° C., was dissolved to form a clear solution. The temperature curve of this solution now shows a sharp gradient between E (48°) and F (62°), and the gradient separates two plateaux. The curve is exactly reversible, that is to say, it has the same form, whether plotted with rising or falling temperatures.

From A to E the molecules of paraffin are not present in the adsorbed layers, either because they are not available for adsorption or because they are denied access. It is almost certainly the former, because the melting point of the paraffin lies always in the region of varying friction. Near its melting point the degree of dispersion of the paraffin increases and it is a fair inference from this and other similar cases that only unassociated molecules of the solute are capable of adsorption. The associated molecules are not "available." Four different paraffins were tried and with each the region of varying friction included the melting point.

Over the plateau AE, fig. 4, the solvent molecules are "dominant." Over the plateau FG both solvent and solute molecules occur in the adsorbed layers in a proportion which is independent of temperature.

The absence of a coefficient of temperature is not, however, proof that a complex oil is an adsorption individual, since it may be due to some constituent or molecular species with high polarity having secured possession of the adsorbed layer. Palmitic acid has highly polar molecules. When this acid is dissolved in oil, B.P., the friction curve for rising temperature falls as the polar molecules obtain admission to the adsorbed layers until equilibrium is reached when the curve changes to a plateau whose level depends

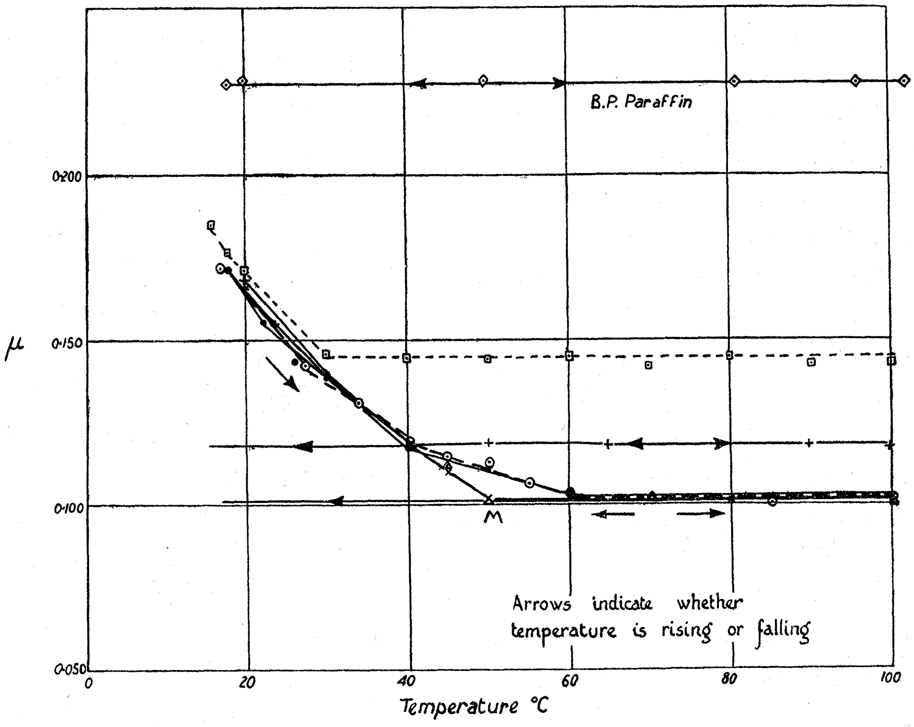

FIG. 5.

upon the percentage of acid in solution up to a limit of about 1 per cent. when at M the layers are fully saturated. The curve changes to a plateau, not because the mixture is adsorbed without selection, but because the polar molecules become "dominant" in the adsorbed layer. This appears in the curve for a falling temperature which now shows no coefficient of temperature over the whole range explored. The curve for caprylic acid and undecane offers another example. The plateau AB, fig. 2, is due to the " dominance " of the polar molecules of acid.

Simple inspection of the curve, fig. 5, will show that the adsorbed layers cannot be simply taken to be in equilibrium with the overlying fluid when the latter contains more than one molecular species, even when steady states alone are contemplated. Any ordinate between the temperatures of 0° and 50° can cut a curve in two places, yet it can be proved that the state of the solution depends only upon temperature. It is rare to find a simple equilibrium between the adsorbed layer and the fluid, like that shown by a solution of paraffin in B.P. oil. Such an equilibrium can occur only when the work of adding a molecule to, or removing a molecule from, an adsorbed layer does not differ greatly as between the different molecular species present. When polar molecules are present " dominance " obscures the relations, and little can be predicted of the state of the adsorbed layers without a knowledge of the previous history. Something more than simple hysteresis is involved, for there is no certainty that the two paths of change meet at both ends.

A theory which has won general acceptance postulates the existence on an adsorbing surface of " active " patches where the absorptive attraction is much in excess of that at other parts of the surface. I am strongly of opinion that the evidence needs reconsideration in the light of the principles of availability, accessibility and dominance.

Leaving steady states, the latent period of orientation is affected in an unexpected way by the polarity of the molecule. So long as only one kind of open-chain molecule is present, so long, that is to say, as the lubricant is composed of only one hydrocarbon, the latent period is always a period of rising adhesion and falling friction, and, as might be expected, its duration increases as the length of the carbon chain or the degree of polarity increases.

*It is important, however, to note here that the only two ring compounds studied, naphthalene and phrenanthrene, gave latent periods of falling adhesion of* 35 *to* 40 *minutes* (XII, 615).

When the lubricant is composed of even as few as two components, the relations are much more complex. Friction and adhesion may now rise or fall in the latent period, and no exception has been found to the rule that the latent period is longer the higher the concentration of polar molecules. This is illustrated in fig. 6, which shows the curves relating friction and the duration of the latent period to the composition of two mixtures, namely, lactic acid and water, and undecane and caprylic acid. In fig. 2, the adhesion curve is reproduced for a mixture of palmitic acid and the paraffin $C_{30}H_{62}$. In the limb DE the latent period was one of rising adhesion, and in the limb EF of falling adhesion, the duration being respectively about 50 and 30 minutes. The form of these curves seems to show that a polar molecule, once in place, cannot be removed from the adsorbed layer by the impact of a non-polar molecule, and that, as the concentration of polar molecules increases, they crowd at each metal face in such a way as actually to delay the attainment of a steady state of orientation.

It was assumed in the first paper of this series (I) that friction of the kind directly

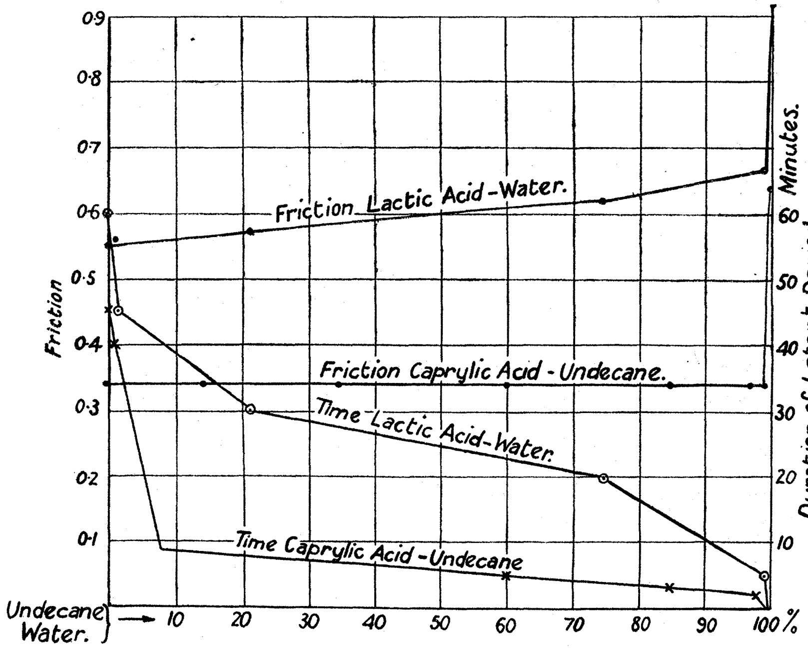

FIG. 6.

identifiable with the tangential reaction was some direct function of cohesion. This assumption certainly is not proven, for what is known of the tangential and normal reactions presents a striking picture of contrasts.

| | |
|---|---|
| Number of carbon atoms $n$ in the Chain. | Relation linear in both, but N.R. increases with $n$, T.R. decreases. |
| End group of molecule .. .. | N.R. paraffins < alcohols < acids.<br>T.R. paraffins > alcohols > acids. |
| Magnitude .. .. .. .. | N.R. much greater than T.R. |
| Temperature coefficient .. .. | Zero for both. |

Values in grammes per cm. square ; steel on steel.

*A. Value.*—For eight carbon atoms. Steel on steel.

| | Octane. | Octyl alcohol. | Caprylic acid. |
|---|---|---|---|
| Pressure, 7·15 .. .. .. | 1·4 | 23·8 | 24·1 |
| 147 .. .. .. | 3·6 | 46·1 | 94·1 |
| 331 .. .. .. | 4·2 | 64·8 | 124·7 |

*B. Value.*—Sixteen carbon atoms.

| | $C_{16}H_{34}$. | Cetyl alcohol. | Palmitic acid. |
|---|---|---|---|
| Pressure, 7·15 .. .. .. | 7,000 | 15,750 | 15,853 |

*S. Value.*—Sixteen carbon atoms.

| | $C_{16}H_{34}$ | | Palmitic acid. |
|---|---|---|---|
| Pressure, 7·15 .. .. .. | 2,549 | — | 10,375 |

*F. Value.*—Eight carbon atoms.

| | Octane. | Octyl alcohol. | Caprylic acid. |
|---|---|---|---|
| Pressure, 96 .. .. .. | 57·5 | 44 | 27·7 |

When the lubricant is composed of two chemical substances which do not react with one another chemically.

| | |
|---|---|
| N.R. .. .. .. | No obvious relation to adsorption. |
| T.R. .. .. .. | Simply related to adsorption. |

The most striking difference, however, lies in the relation to $h$. Both T.R. and N.R. increase as $h$ decreases, but the former increases with no upper limit, or, rather, with an upper limit fixed only by the capacity of the system to bear the load, whilst the latter increases to a maximum. The curve for N.R. (*see* values A and B in fig. 7) is concave to the axes, whilst that for T.R. (value F) is convex to the axes.

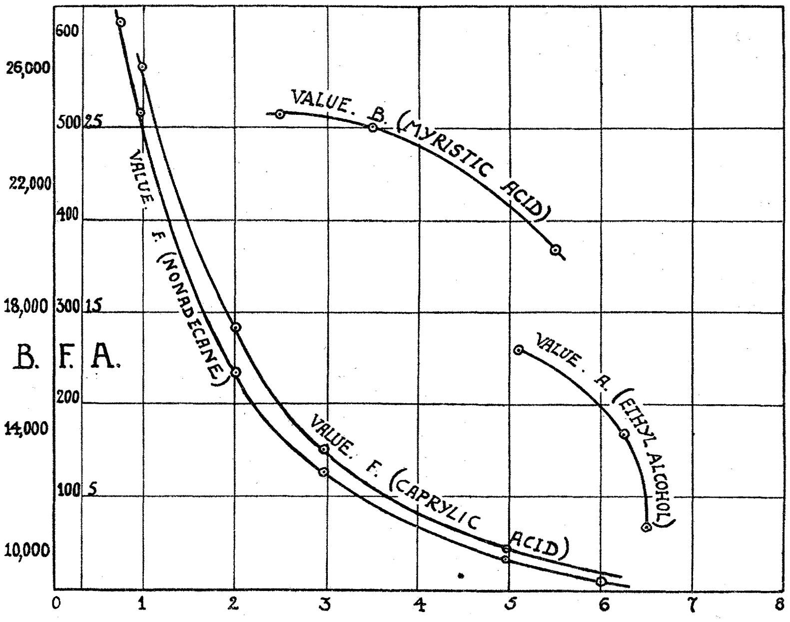

FIG. 7.—Ordinates in grammes per cm.². Abscissa in μ.

*Section* 3.—*The Leslie Pressure.*—Two explanations of the Leslie pressure are possible, the simpler based upon direct Laplacian attraction, the more difficult based upon diachysis.

Consider a fluid and a solid the interface being plane, and let the solid attract the fluid by a force which decreases with increase in the distance between two attracting particles and becomes insensible when this distance is $a$. $a$ is a length large compared to molecular dimensions. According to the classical theory of capillarity the total normal attraction of the solid for the fluid reckoned to a surface distant $z$ from the interface is $2\pi \int_z^a \psi(z)\,dz$. Call this integral Lz.

Across any surface in the interior of the fluid removed from the influence of the solid, the cohesive attraction $C_0$ will be in equilibrium with an intrinsic pressure $I_0$. At any surface parallel to the interface but within the capillary layer

$$(C - C_0)_z = (I - I_0)_z = L_z.$$

$L_z$ is the excess of cohesive attraction reckoned along the normal to the interface, it is a quantity which vanishes when $z = a$ and is maximal when $z = 0$. The Leslie pressure, as defined by LESLIE himself, is the value when $z = 0$, namely, $2\pi \int_0^a \psi(z)\, dz$.

The balancing intrinsic pressure he takes for granted. In the treatment of short range forces customary at his time, it was merged in the assumptions of incompressibility and contact. C and I, however, should be dealt with separately since they are not functions of the same thing. C is a function of molecular attraction and orientation, I of motion of translation of molecules; if temperature be indicated by $\theta$, C has the form $\int_z^a \psi(z)\, dz$, and I the form $\phi(\theta)$.

In the case of a solid cylinder immersed in fluid the tangential components of the attraction have to be reckoned with over the curved surface. These can be equated to a surface of tension in the usual way, and if R be the radius of the cylinder and T the tension, $T = \int_0^a z\psi(z)\, dz$ then, if T′ is the tension due to the attraction of the fluid for itself, there will be an excess of pressure on the curved surface over the plane ends of $(T - T')/R$. This excess must be balanced somewhere and the balance is found in the curvature of the surface of tension round the edges of the cylinder.

Let the plane ends of two cylinders of equal radius, of the same material, and immersed in a fluid, approach one another and let $h$ denote the distance between them. Experiment proves that external normal force is needed to drive the ends of the cylinders together, and that if P be this force per unit area there is a value of $h$ corresponding to each value of P at which the least value of the excess of pressure between the ends of the cylinder over the pressure in the surrounding fluid is equal to P. What is the origin of this excess ?

Put shortly the answer is to be found in the overlapping of the attraction fields of the solids, so that a portion of the lubricant is attracted by both solids. Therefore, when $h = 2a$, P vanishes, and this would then be the limit for boundary lubrication. The limit $2a$ is fixed by the curve, fig. 1, at $6 \cdot 5\ \mu$.

At the periphery of the disc of lubricant the attraction of the solids for the fluid can be resolved in the plane and along the radii of the disc into an inwardly directed pressure $p$ which must vary in the plane midway between the solid faces between the limits $p = 0$ when $h = 2a$, and $p = L + \frac{(T - T')}{R}$ when $h = 0$.

$\frac{T - T'}{R}$ may probably be neglected, as can be seen, by giving T the impossibly high value of the surface tension of mercury and comparing the calculated value with the observed pressure needed to force the face of a cylinder on to a plate.

At the midway plane on the disc $\frac{1}{2}h$ distant from each face the excess attraction, when $h$ is less than $2a$ but greater than $a$, is $4\pi \int_{h/2}^{a} \psi(z)\, dz$. Call this C′ then $C' = 0$ when $h = 2a$. The condition of equilibrium at that plane is

$$P + [C' + C_0] = p + [I' + I_0]$$

or, since $C_0 = I_0$

$$P = [I' - C'] + p.$$

It might seem unnecessary to specify $C_0$ and $I_0$, since they cancel out, but it must be remembered that terms in C and terms in I are not the same functions of $z$.

When $h < a$ we have

$$C' = 4\pi \left[ \int_{h/2}^{a} \psi(z)\, dz - \int_{h}^{a} \psi(z)\, dz \right].$$

As $h$ approaches zero C′ tends to vanish whilst $p$ tends to become equal to $2\pi \int_{0}^{a} \psi(z)\, dz$, therefore as $h$ becomes smaller $p$ becomes continuously greater than C′.

The real difficulty is met when an attempt is made to allow for the direct attraction of one solid for the other. Call the range of this attraction $w$. Is $w$ of the same order as $a$?

If we put $w = a$ then when $h < a$ there is a direct attraction between the solids which gives rise to a pressure at the midway surface of, say $X = 2\pi \int_{h}^{a} \phi(z)\, dz$, which increases as $h$ decreases.

If X has a sensible value at the midway face, then $P = (I'' - C' - X) + p$.

When $h = 0$ the attraction X should be equal to the complete cohesion between the solids. Actually $h$ cannot be reduced to zero, at any rate by merely wringing the faces together until they seize. Metallic contact, it is true, takes place, but only at those few points where the surfaces appear torn when the solids are again separated. Elsewhere the lubricant persists, and the fact that seized faces are forced apart by lubricants with a sensible vapour pressure shows that $\phi(z)$ falls off very rapidly with distance.

The alternative explanation is not so easily stated. Consider first the case of a liquid and let $a$ now be the distance at which the attraction of the solid ceases sensibly to orient the molecules of the liquid so that at any distance greater than $a$ from a plane solid face the arrangement of the molecules is random. There, owing to the random disposition and motion of translation of the molecules the intrinsic pressure $I_0$ may be taken to act in all directions. It is a true hydrostatic pressure.

Within the plate of lubricant between the plane ends of the cylinders, however, the molecules are oriented and fixed in position by the attraction fields of the solids, with the result that the hydrostatic pressure is less than $I_0$ so far as $I_0$ is due to motion of translation of the molecules. It may be taken to vanish when the lubricant is reduced to two primary films, because in these films the molecules are as completely fixed in position as they are in a solid. As $h$ increases, however, and the directing influence of the solid faces at $h/2$ decreases, the motion of translation of the molecules increases and with it the hydrostatic pressure.

The result is that, whilst there is in the surrounding fluid a hydrostatic pressure $= I_0$, there is at the surface $h/2$ a pressure I which is equal to 0 when $h$ is equal to the depth of two primary films and is $= I_0$ when $h = 2a$. The Leslie pressure then is

$$P = I_0 - I$$

and if L be the load ÷ area

$$L = P.$$

The Leslie pressure on this view is strictly an osmotic pressure like that which causes a gel to swell, and the different molecular species concerned, though they may be the same chemically, differ in their degrees of freedom, according as they are within the range of influence of the solids or beyond it.

On both views, so long as the joint is sunk in a pool of the same fluid as that which forms the lubricant, the adhesion (value A) will be the difference between the tensile strength Q and the Leslie pressure, or

$$A = Q - P,$$

but when the lubricant is enclosed in a skin and the pool removed, P vanishes and $A = Q$.

P vanishes also when the lubricant is frozen, therefore

$$B = Q$$

In these equations the terms on the right must be reckoned at the moment of break.

The Leslie pressure in clean air offers no difficulty on the hypothesis of Laplacian attraction, and formidable difficulties on the hypothesis of polarisation. It is not easy to picture structure in a permanent gas but it must be present in a gas near to the surface of a solid, for we are at liberty to suppose that molecules of gas like molecules of liquid will be oriented and suffer constraint in their movement of translation, whilst they are within the range of attraction of a solid face. Let us take the extreme case and suppose that this range is only of the order of dimensions of a molecule. There will then be a layer of highly polarised molecules, the equivalent of a monomolecular layer. From this, owing to the heat motions, abnormal molecules will escape and the depth of the layer of gas whose properties are modified by the attraction field of the solid will depend upon the rate at which these recover normality. Within this zone of influence the specification of the gas in mass does not hold, because some of the molecules have an abnormal energy content and the movements of translation are not at random. Within the body of the gas, molecules have their direction of movement changed and their energy content altered by collisions, but the statistical distribution of these variations in space and time is a random one. When two solid faces approach one another, the whole of the enclosed gas will be abnormal when the gap is twice the range of influence.

There is also an electrical effect to be reckoned with. In HELMHOLTZ's theory of contact potential the charges lie in parallel surfaces. In the modern view of the contact potential between a solid and fluid, the electric charge of the latter is not referred to a surface but to a layer of ionised molecules of finite depth. The molecules of fluid in contact with the solid face may be supposed to form a layer of electrically-charged molecules, but owing to the heat movements some of these are detached and the depth of the charged layer will be determined by the normal component of their free path in the charged state. Call this depth $v$, then when two plane surfaces of similar solids approach one another there will be resistance to further approach when the distance between them becomes less than $2v$, the repulsive pressure being due to repulsion between charges of the same sign.

WATSON and MENON found the air gap always conducted when plate and cylinder were clean (XV, 197). It must, therefore, have contained charged particles under the conditions of the experiments, and I was able to show by direct experiment that a free film of starch paste or saponin and water is composed of a central plate of liquid at an electrical potential different from that of the adsorbed films enclosing it. The central plate was positive and both films negative. This disposition, as I then pointed out (XIV, 608), would give the repulsion required to account for the stability of such free films.

In one way or another, therefore, the molecules in a thin layer of gas enclosed between two attracting surfaces must differ in the specification of their energy content from the molecules in the body of the gas and, like those in an enclosed layer of liquid, they form a different osmotic species, but the difficulties in the way of this hypothesis are serious :— An air gap of 0·004 to 0·007 mm. seems inconsistent with the rate of relaxation of strain in a gas. An even more formidable difficulty lies in the fact that the gap is unchanged when the air is displaced by liquid (XI, 224), for two different causes are unlikely to produce precisely the same effect. Finally, electric repulsion of the kind indicated above seems inconsistent with the fact that the gap is the same, namely, 0·004 mm. for carefully-trued cylinders and plates of materials so dissimilar electrically as steel and glass.

The position may be summarised as follows :—

Any theory of the Leslie pressure must account for four curious facts :—

(1) The distance $h$ at which the cylinder floats above the plate is independent of the nature of the lubricant and of the solids, provided the surfaces are clean.

(2) The distance is the same in clean air as it is when the air is displaced by a liquid and remains the same until the pressure of the air is reduced to 2 mm. of mercury.

(3) The distance in clean air was decreased by contaminating the solid faces.

(4) The difficulty with which a cylinder can be forced down on to a plate and the relative ease with which it can be wrung down.

Of these the two first are perhaps accounted for by the fact that on either hypothesis the pressure P is the difference between two quantities, both of which may be functions of the nature of the lubricant and of the solids. P may then be a pure function of the geometry of the system over an extremely wide range of conditions.

The effect of the contaminant seems to point to the conclusion that the attraction of the solid is not a shadowless force as Laplace assumed, but a force which, like chemical affinity, can be saturated. The effect may, however, be due simply to the contaminant making the surface irregular.

The relative efficacy of wringing is no doubt due to purely mechanical action. In wringing a cylinder down on to a plate the surfaces are not kept parallel, the resistance encountered is therefore at no time equal to the pressure P (at the least distance between the surfaces) × area. By tilting the cylinder the resistance can, in fact, be made vanishingly small. When any part of the cylinder has been forced down it rises under capillary pressure relatively slowly, as the table (X), p. 67, shows. There is, therefore a kind of ratchet and pawl action.

Experiment shows that once the cylinder has been wrung down, it stays there if the surfaces are contaminated by liquid, save when the joint is surrounded by a fluid freely miscible with the liquid lubricant. It will therefore not rise in air, but clean faces wrung down, even to seizing, float apart in clean air. This, of course, does not mean that the pressure P in clean air is greater than metallic cohesion, for the injury to the polished faces show that seizing has taken place at only a few points, so we have, if A be the area of the plane end of the cylinder and $a$ the total area of seizing,

$$PA > Ka,$$

where K is the cohesive attraction per unit area of metal for metal and $A/a$ is a large quantity.

Since P is the pressure with which fluid lubricant is drawn between the faces from a pool, and is independent of the nature of the lubricant, it is not at first obvious why some liquids will displace air. It will be sufficient perhaps simply to point out that this displacement is due to the tension of the air-liquid interface.

The position may be summarised by saying that relatively long range Laplacian attraction cannot be rejected until the air gap is satisfactorily accounted for, in spite of the proof given in the next section that such attraction will not provide the properties of solid joints.

*Section* 4.—*Mean Value Rule.*—This rule holds both for the tangential and normal reaction. It can be stated as follows.

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Let $X_{ss}$ denote a value when both solids are, for example, of steel, $X_{cc}$ when both are of copper, and $X_{sc}$ when one is steel and the other copper, then

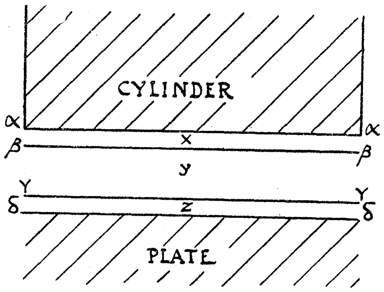
$$X_{ss} + X_{cc} = 2X_{sc}.$$

The rule seems to govern all the mechanical relations of the boundary state, it holds for all values, even for the A value, and does not appear to be an approximation. The better the craftsmanship the more closely does it fit experiment. Take for example the value B, the adhesion of a solid joint (VII, 220), we have as the mean for acids :—

$$B_{ss} = 14546 \quad B_{cc} = 12917 : \text{mean } 13731$$
$$\text{and } B_{sc} = 13740.$$

The mean value rule is a property of those significant surfaces which are also surfaces of least traction or least adhesion, that is, of surfaces of slip or surfaces of break. It will be convenient in this section to call these surfaces mean value surfaces.

In only three instances is the position of the mean value surface known with certainty, namely, for values F, B and S.



*Value F.*—When a spherical slider is used, the mean value surface is at $\frac{1}{2}h$ and separates the two adsorbed layers $x$ and $z$ in the diagram. The disposition of the parts is symmetrical about this surface, and the rule offers no difficulties.

*Values B and S* are respectively the strength in tension and the strength in shear of a solid joint. The former also is the normal reaction of the mean value surface, as we have seen earlier. Only a few measurements have been made of value S (XI, 288), attention will therefore be confined to value B.

The solid joint was formed by running fluid lubricant between the faces, allowing the lubricant to come into equilibrium with the attraction fields of the solids, and then lowering the temperature until the lubricant froze (XI, 209). All the measurements, which will be referred to, were made with load 5·6 grammes, loading (load divided by area) 7·15 grammes, and distance between cylinder and plate $h = 0{\cdot}007$ mm. for clean surfaces and ± 0·005 mm. for contaminated surfaces. When the joint was broken, the surface of break was seen under the microscope to lie between an adsorbed layer of insensible thickness, $x$ or $z$ in the diagram, and a median crystal plate $y$. The presence of an invisible adsorbed layer was detected by the fact that after the joint was broken the friction was that of a fully lubricated surface (XI, 214). The significant surfaces of a solid joint then are placed as shown in the diagram at $\beta$ and $\gamma$. When cylinder and plate were both of steel or both of copper, the break took place at both $\beta$ and $\gamma$. When one of the two was of copper and the other of steel, it was, at the significant surface nearer to the copper, the solid which gave lower adhesion (value B steel-steel = 14546, copper-copper = 12917).

The significant surfaces β and γ are placed where the attraction fields of the solids are no longer able to overcome the forces which drive the molecules into the crystal lattice. Following H. A. Wilson (' Proc. Camb. Phil. Soc.,' vol. 10, p. 25, 989) we may say that these surfaces are where the pressure driving atoms into the crystal lattice is equal to the pressure forcing the atoms towards the metal face. The position of those surfaces will therefore depend upon the attraction field, but there is a quantum effect because each surface can move outwards from the metal face only by the full depth of a layer of molecules of the lubricant. The surfaces β and γ are the surfaces of natural cleavage spoken of earlier.

So far the ground is firm, but the position of the mean value surface or surfaces cannot be fixed by direct observation when the lubricant is fluid and the distance H greater than two primary layers. Both the number of the surfaces and their position is indeterminate unless the law of variation along the normal to the surfaces α and δ of the influence of the solids be known. Nothing can be inferred from the position of the surfaces β and γ in solid joints, for let us suppose that the surface in a fluid joint is singular and at $h/2$ the pressure of crystallisation might split this surface into two surfaces of identical properties placed where the pressure of crystallisation failed to disturb the orientation.

The experiments with solid joints which we need consider in this section fall into two classes, those in which the lubricant was composed throughout of a single pure chemical substance, and those in which the clean surfaces of either cylinder or plate, or both, were first coated with an invisible film of one pure substance before the joint was completed by running in a second pure substance. Two substances were employed, the paraffin eicosane and myristic acid, the metals being steel and copper.

The clean face of either cylinder or plate, or of both, was contaminated by lightly touching it with clean* linen which had been lightly rubbed on either the solid paraffin or the solid acid. The joint was then formed with the alternative substance, allowed to come into equilibrium and frozen. (For details, *see* XI, 217.)

The method of contamination seems haphazard, the results were surprisingly consistent. Probably the face ceased to pick up the contaminant when a strongly adsorbed monomolecular layer had been formed.

Of the two substances when used alone the acid formed the stronger joint.

| | Acid. | Paraffin. |
|---|---|---|
| | grs. | grs. |
| Steel–Steel .. .. .. .. .. | 13,260 | 8,644 |
| Copper–Copper .. .. .. .. .. | 11,580 | 5,955 |
| Steel–Copper .. .. .. .. .. | 12,437 | 7,281 |

---

* "Clean"—that is, extracted with benzene and alcohol until rubbing clean faces with the linen did not lower friction.

If the likely assumption be made that the adsorbed layer was composed wholly of contaminant the disposition can be indicated by making use of the diagram—

$$\mathrm{X}\overset{\alpha}{|}\,x\,\overset{\beta}{|}\;\;y\;\;\overset{\gamma}{|}\,z\,\overset{\delta}{|}\,\mathrm{Z},$$

in which X and Z are the metals, $x$ and $z$ the adsorbed layers, $y$ the crystal plate, $\alpha$ and $\delta$ the surfaces separating metal and lubricant, and $\beta$ and $\gamma$ the significant surfaces.

This diagram is reproduced in the left hand column of the table, the surface of break, that is, the mean value surface, being indicated by a thick rule. E and M indicate respectively eicosane and myristic acid. Value B is adhesion per square centimetre. S and C are steel and copper.

When the break occurs at both $\beta$ and $\gamma$ surfaces (*see* for details XI), the identity

$$B_\beta = B_\gamma$$

must hold.

When the break occurs at only one of the surfaces, say the $\gamma$ surface, then, if the adhesion of the opposite surface is $E\beta$, we have

$$E_\beta > B_\gamma.$$

TABLE II.—Load, 5·6 grs. Pressure = Load ÷ area, 7·15 grs.

Uncontaminated.

When the surfaces were uncontaminated $h = 0{\cdot}007$ mm.

| | | grs./cm.$^2$ |
|---|---|---|
| 1. | S │ M ┃ M ┃ M │ S value B | 13,260 |
| 2. | C │ M ┃ M ┃ M │ C | 11,580 |
| 3. | S │ M │ M ┃ M │ C | 12,437 |
| 4. | S │ E ┃ E ┃ E │ S | 8,644 |
| 5. | C │ E ┃ E ┃ E │ C | 5,955 |
| 6. | S │ E │ E ┃ E │ C | 7,281 |

Contaminated.

When the surfaces were contaminated $h =$ about 0·006 mm. (XI, 227).

Lubricant, myristic acid; contaminant, eicosane.

| | | grs./cm.$^2$ |
|---|---|---|
| 7. | S │ E ┃ M ┃ E │ S | 9,249 |
| 8. | C │ E ┃ M ┃ E │ C | 6,115 |
| 9. | S │ E ┃ M │ M │ S | 10,590 |
| 10. | C │ E ┃ M │ M │ C | 5,702 |
| 11. | S │ E │ M ┃ E │ C | 7,578 |
| 12. | S │ E ┃ M │ M │ C | 8,845 |
| 13. | C │ E ┃ M │ M │ S | 7,511 |

Lubricant, eicosane: contaminant, myristic acid.

| | | grs./cm.$^2$ |
|---|---|---|
| 14. | S │ M ┃ E ┃ M │ S | 10,540 |
| 15. | S │ M │ E ┃ E │ S | 9,745 |
| 16. | S │ M │ E ┃ M │ C | 9,017 |
| 17. | S │ M │ E ┃ E │ C | 8,085 |
| 18. | C │ M │ E ┃ E │ S | 8,736 |

That the experiments with contaminants have a quantitative value is shown by the two groups which ought to give the mean value relation. They are numbers 7, 8 and 11 which give $9249 + 6115 = 2\,(7578)$ or $15364 = 15156$, and numbers 9, 10, 12 and 13, which give 10590 and $5702 = 8845 + 7511$ or $16292 = 16356$.

These observations seem to be inexplicable by direct Laplacian attraction, for in number 9 let $S_1S_2$ be the pressure due to the mutual attraction of steel for steel, whose plane surfaces are $h$ apart: $S_1M_y$ the pressure at the surface of break $\beta$ due to the mutual attraction between the steel nearer to the surface of break and the median plate of myristic acid, $S_2E_1$ the pressure at the surface of break due to the mutual attraction between the steel further from the surface of break and the adsorbed layer $x$ of eicosane nearer to the surface of break, then, using this notation throughout, we have from numbers 7 and 9—

$$S_1S_2 + S_1\,(M_y + E_2) + S_2E_1 + E_1\,(M_y + E_2) = 9249 \text{ grs.}$$

$$S_1S_2 + S_1\,(M_y + M_2) + S_2E_1 + E_1\,(M_y + M_2) = 10590 \text{ grs.}$$

therefore

$$S_1\,(M_2 - E_2) + E_1\,(M_2 - E_2) = 1341 \text{ grs.}$$

But the first of these terms is the difference between the attraction of steel for two monomolecular layers distant 0·006 mm. and the second the difference between the attraction between monomolecular layers separated from each other by nearly the same distance. All these quantities may be regarded as negligible and certainly not competent to give the substantial difference, 1341, actually found.

If further proof of the short range of cohesive forces be needed, it can be found in the remarkable effect of an insensible film of oxide present on the copper. Such a film, so thin as to leave the polished face visibly unchanged, raises the adhesion of copper above that of steel (XVII). The values are as follows :—

| | Lubricant, palmitic acid. |
|---|---|
| Steel on steel .. .. .. .. .. | 15,860 grs. per square cm. |
| Copper on copper .. .. .. .. | 14,200 ,, ,, ,, |
| Passive copper on passive copper .. .. | 21,000 ,, ,, ,, |

It is not possible to suppose that the range of cohesive attraction is of one order in the metal and of quite a different order in the lubricant. Therefore, if the range be of the order 0·005 mm., in the latter the pressure at the mean value surface must be due to the total attraction of a disc of metal many thousands of molecules in thickness. It is not credible that the cohesive attraction of a layer of oxide, probably one molecule in thickness, should be of the same order as that of such a disc of metal, but it is credible that the cohesive attraction of a highly polarised film of oxide should be of the same order or greater than that of a film of metal of the same thickness.

Since Laplacian attraction in any simple form is inadmissible the properties of the mean value surface will be considered solely from the point of view of diachysis—that is of polarisation which is transmitted from molecule to molecule with a decrement.

It will be noticed that wherever myristic acid replaces eicosane whether in one or other or both adsorbed layers ($x$ and $z$) or in the crystal plate ($y$) it increases the adhesion. In other words, displacement of less polarisable molecules by more polarisable molecules increases adhesion. The inference that adhesion is a function of the polarisation of the mean value surface is obvious.

The polarisation of the mean value surface is not, however, determined solely by the constitution of the molecules which lie immediately on either side of it, but is contributed to by all parts of the system. This can be inferred from the mean value rule, and the inference is directly confirmed by experiments with contaminants. Compare, for example, numbers 7 and 9. The $\beta$ surface is in both cases a surface of break and the effect of substituting the acid for the paraffin in the *opposite* adsorbed layer is to raise the value of adhesion from 9249 to 10590.

The crystal plate $y$ therefore conducts,* and it conducts with a decrement for no matter what may be the composition of the layers $x$, $y$, $z$, adhesion is always increased when $h$ is decreased by increasing the load, and the microscope shows that the effect of such increase in the load is merely to bring the $\beta$ and $\gamma$ surfaces closer together (for curve connecting $h$ with adhesion, *see* XI, 226).

The B value depends, however, not only on the thickness of the crystal plate, but also on its composition. Compare for example, number 7 with number 14 and number 11 with number 16. Taking the first pair the polarisation of both $\beta$ and $\gamma$ surfaces is between eicosane and myristic acid, but the crystal plate is of acid in the one and of eicosane in the other. The proof is admittedly not rigid because the paraffin is next to the steel in number 7, and the acid next to it in number 14.

The form of the equation is now clear and may be exhibited by taking any one of the equations, say, number 9, as an example. Let $(\sigma_{em})_1$ represent the polarisation produced by the nearer steel, at the mean value surface $\beta$ which lies between eicosane and myristic acid; $(\sigma_{mm})_2$ that due to the opposite steel at the opposite surface $\gamma$ and $y_m$ the decrement due to conduction from surface $\gamma$ to the mean value surface $\beta$, then

$$(\sigma_{em})_1 + [(\sigma_{mm})_2 - y_m] = 10{,}590.$$

---

* To speak of the crystal plate "conducting" is to use a word of too active significance, but none other suggests itself. There is, of course, no conduction in the sense in which heat or electricity is conducted but a state of strain impressed by the attraction fields on the crystals when they form. When a gel of gelatine and water is frozen, it is strained by the expansion of the ice phase and becomes doubly refractive. The state of strain persists after thawing and is relaxed only near the melting point of the gel. The strain extends throughout the gel and may, with propriety, be said to be "conducted" from each centre of crystallisation (XVI). It is in this sense that the word is applied to the crystal plate, "conduction" is one aspect of the complex play of forces during crystallisation.

It will be noticed that the polarisation is put numerically equal to the adhesion. This assumption will not affect the argument and it enables the results to be stated in a simple way. It amounts to an affirmation that the excess tensile strength of a substance as lubricant over that of a rod of the lubricant (*see* p. 1) varies directly with the polarisation of the former, the unknown constant being omitted from the equations.

When the disposition is symmetrical as it is in the uncontaminated numbers 1, 2, 4 and 5, the crystal plate may be taken to conduct equally in either direction. Therefore, taking number 1 as an example, it becomes

$$2\sigma_{mm} - y_m = 13{,}260.$$

Conduction is not the same in both directions, however, when the disposition is not symmetrical. In numbers 3 and 6, for example, since the surface of break is at $\gamma$, the adhesion of that surface must be less than that of surface $\beta$. Therefore

$$\sigma_{mm} + [\kappa_{mm} - (y_m)_{cs}] > \kappa_{mm} + [\sigma_{mm} - (y_m)_{sc}]$$

and

$$\sigma_{ee} + [\kappa_{ee} - (y_e)_{cs}] > \kappa_{ee} + [\sigma_{ee} - (y_e)_{sc}]$$

or

$$(y_m)_{sc} > (y_m)_{cs} \quad \text{and} \quad (y_e)_{sc} > (y_e)_{cs},$$

where the order of the subscript letters *s* and *c* denotes the direction of conduction. The crystal plate, therefore, conducts better from the stronger field of the steel to the weaker field of the copper than it does in the reverse direction.

When eicosane is applied to the steel in a steel-copper pair the break is transferred to the side of the stronger metal. This was unexpected, it follows, however, from the unequal conduction in the crystal plate. Numbers 12 and 18 give

$$\kappa_{mm} + [\sigma_{em} - (y_m)_{sc}] > \sigma_{em} + [\kappa_{mm} - (y_m)_{cs}]$$

$$\kappa_{me} + [\sigma_{ee} - (y_e)_{sc}] > \sigma_{ee} + [\kappa_{me} - (y_e)_{cs}]$$

$$\text{or} \quad y_{cs} > y_{sc}.$$

From numbers 7, 8 and 11, the relation $(y_m)_{ss} + (y_m)_{cc} = 2\,(y_m)_{sc}$ can be derived, and from numbers 9, 10, 12 and 13 $(y_m)_{ss} + (y_m)_{cc} = y_{m_{sc}} + y_{m_{cs}}$.

The simplest interpretation of this is that the crystal plate conducts with a decrement which is a function only of its thickness and of its chemical composition. The mean value rule for the normal reaction of solid joints would then have the form

$$[2\,\phi\,(\mathrm{X}) - y] + [2\,\psi\,(z) - y] = 2\,[\phi\,(\mathrm{X}) + \psi\,(\mathrm{Z}) - y]$$

$\phi\,(\mathrm{X})$ and $\psi\,(\mathrm{Z})$ are respectively the polarisation produced by the metal X or Z at the nearer significant surface.

The fundamental assumption of diachysis will now be obvious, namely, that the direct influence of the attraction field of a solid embraces only the adsorption layer in contact with it and its contribution to the properties of the significant surface of the opposite side is made by strain conducted through the crystal plate $y$. Therefore, at the limit when the loading is great enough to bring the $\beta$ and $\gamma$ surfaces together, at $h/2$ the mean value rule takes the simple form $2x + 2z = 2(x + z)$, where $x$ and $z$ are respectively the polarisation of the mean value surface due to the metals X or Z. It might be expected that the mean value rule would be upset when the intensity of the effect of the surfaces upon the lubricant was widely different. That may prove to be the case. All that can be affirmed at present is the validity of the rule for pairs of solids chosen from examples as diverse as are hard and soft steel, bronze, copper, bismuth and glass.

*Section* 5.—*The effect of the chemical constitution of the lubricant.*—The relation of the tangential and normal reactions to the chemical constitution of the lubricant and solids can be expressed in simple empirical linear equations of the form

$$T = x - y\,M.$$
$$N = x' + y'\,M.$$

In this section one example only will be considered, namely, the tangential reaction when the lubricant consists of a single pure chemical substance and is reduced to two primary films by the use of a spherical slider or by a heavily loaded plane slider. The equation will be taken in the form $\mu = b - a\,M$, in which $\mu$ is the coefficient of friction (F ÷ load).

$a$ is a parameter wholly independent of the nature of the solids. It fixes the slope of the curve and is a pure function of the configuration of the molecule of the lubricant. For normal acids, alcohols and paraffins the expression $a$M can be written in the form $c\,(n - 2)$ where $n$ is the number of carbon atoms in the chain. In this form, it shows the remarkable fact that each such carbon atom produces the same effect up to a chain of thirty atoms which was the longest chain tested. The configuration of the substances used is :—

| | |
|---|---|
| Paraffins .. .. .. | $CH_3 - CH_2 - \ldots\ldots\ldots - CH_2 - CH_3$. |
| Alcohols .. .. .. | $CH_3 - CH_2 - \ldots\ldots\ldots - CH_2 - COH$. |
| Acids .. .. .. | $CH_3 - CH_2 - \ldots\ldots\ldots - CH_2 - COOH$. |

The carbinols are alcohols in which the hydroxyl group has been shifted to the third position.

Carbinols . . . $CH_3 - CH_2 - \ldots - CH_2 - CHOH - CH_2 - CH_3$.

The end groups then are $CH_3$ and $C_2H_5 . CHOH$ and this large group, as the curve fig. 8 shows, increases the effect of the two nearest carbon atoms so that the steady state is reached only at the fourth carbon atom and the expression becomes $c\,(n - 6)$.

Since the parameter $c$ is dependent only on the end groups, it must express the effect of the internal polarisation of the molecule upon the tangential reaction, and we may add upon the normal reaction also.

Miss DOUBLEDAY rightly draws attention to the relation of friction to the optical properties of the carbinols (VI). The first eight points on her curves refer to dextro-rotary, the last six to lævorotary forms. The change in the rotation has no effect upon the form of the curve. On the other hand, the one *dl* — form available, namely, *dl* ethyl-*n*-hexylcarbinol, gave a value well off the curve. The specimen of dodecylcarbinol probably was slightly impure.

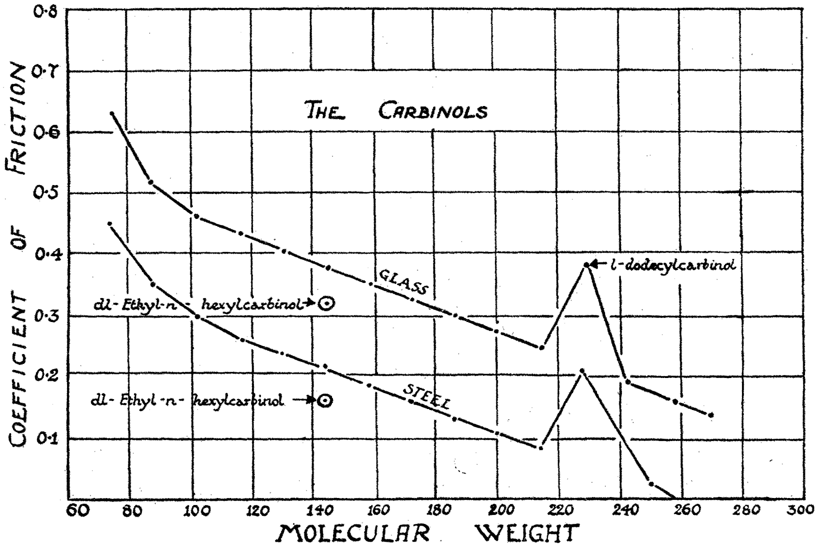


FIG. 8.

The parameter *b* is the value when M = 0, it is a function of the nature of the solids and the configuration of the end groups of the molecules of lubricant. One way of evaluating the latter is to put the former equal to the coefficient of friction of the clean solid. Call this $b_0$ and let $b = b_0 - d$ : $d$ is now found to be constant for the same end groups. The equation becomes

$$\mu = (b_0 - d) - c\,(n - 2)\,;\ \text{ or } c\,(n - 6) \text{ for carbinols.}$$

TABLE III.

| Lubricant. | A. | B. | C. | D. | E. | Glass. |
|---|---|---|---|---|---|---|
| $b_0$ | 0·88 | 0·83 | 0·93 | 0·79 | 0·94 | 0·95 |
| $n$-Paraffins $c = 0·0207$ . . . $d$ | 0·21 | 0·20 | 0·20 | 0·20 | 0·20 | 0·19 |
| $n$-Alcohols $c = 0·0237$ . . . . $d$ | 0·28 | 0·27 | 0·28 | 0·27 | 0·28 | 0·29 |
| $n$-Acids $c = 0·0602$ . . . . $d$ | + 0·01 | — 0·02 | + 0·01 | — 0·02 | + 0·02 | — 0·01 |
| Carbinols $c = 0·027$ . . . . $d$ | — | 0·51 | — | — | — | — |

A. 50-ton steel. B. Medium carbon steel. C. Nickel chrome steel. D. Mild carbon steel. E. Phosphor bronze.

The values for acids do not agree with those in Table 10 of IX, 26. The latter, I regret to say, are wrong owing to an error in arithmetic made in calculating $c$, which appears as $a$ in the table just referred to when $c\,(n - 2) = a\,\mathrm{M}$.

The paraffins being symmetrical give the value of $c$, that is the decrement due to each carbon atom, when it is undisturbed by a difference between the end groups : we have therefore

| | |
|---|---|
| Paraffins | $c = 0{\cdot}021$ |
| Alcohols | $c = 0{\cdot}021 + 0{\cdot}003$ |
| Carbinols | $c = 0{\cdot}021 + 0{\cdot}006$ |
| Acids | $c = 0{\cdot}021 + 0{\cdot}039$ |

The figures in the left hand column give the effect of lengthening the chain by one carbon atom, and those in the right hand column reflect the change in the internal polarisation of the molecule due to the substitution of one $-\mathrm{CH_3}$ group by $-\mathrm{COH}$, $-\mathrm{C_2H_5\,CH\,(OH)}$, or $-\mathrm{COOH}$.

The parameter $d$ may be taken to refer not to the internal polarisation of the molecule but to the influence of the end group upon the field of the solids. The fact that $d = 0$ for acids might be taken to mean that the molecules are attached to the metal by the $\mathrm{CH_3}$ group because the metal is electro-positive and the COOH group also positive owing to its replaceable hydrogen, but this suggestion is not applicable to glass.

Why should the effect of a carbon atom in the chain be independent of the length of the chain ? There is at least one parallel case. The heat of crystallisation of long chain compounds is proportional to the length of the chain (XXI) but the relation is unusual. So far as I am aware the effect of a change in an end group commonly decreases as the chain lengthens. For example, when a hydrogen of the $-\mathrm{CH_3}$ group of an $n-$ acid is replaced by a negative atom, such as Cl—

$$\begin{array}{l}\mathrm{CH_3} \quad - \mathrm{CH_2} \,\ldots\ldots\ldots\, .\mathrm{CH_2} - \mathrm{COOH}\\ \mathrm{CH_2Cl} - \mathrm{CH_2} \,\ldots\ldots\ldots\, .\mathrm{CH_2} - \mathrm{COOH}\end{array}$$

the work needed to detach the hydrogen atom of the $-\mathrm{COOH}$ is lessened but the effect diminishes as the chain is lengthened. It is not possible to assume that $c$ is the sum of two terms contributed by the two boundary solids,

$$c = c_x' + c_x''$$

and that the sum is the same for any pair of solids because it is the same also for two dissimilar solids—or $c = c_x' + c_z''$. $c$ appears always to be entirely independent of the solids.

Perhaps the most difficult problem of the boundary state is presented by the fact that $c$ is positive for the normal reaction and negative for the tangential reaction. The external force which calls forth the tangential reaction may be taken to be applied as a traction on the surfaces $\alpha$ and $\delta$, and an increase in the length of molecules whose long axis was normal to those surfaces would increase the moment of the force at the surface of slip $h/2$. But the S value relates to a traction and $c$ is positive for this value.

The fact that $c$ is positive for the normal reaction may mean that, whilst a surface of slip is plane and lies between the ends of molecules, a surface of break is not plane because the molecules are pulled apart like teeth out of their sockets, one half of the number moving one way and the other half moving the opposite way (*cf.* p. 15).

6. *Conclusions*.*—The upshot of the discussion and especially of the sections on the Leslie pressure and the mean value rule may be set down as follows.

The most promising view of the Boundary State IN LIQUIDS is that it is due to the formation of chains of highly polarised molecules stretching through the lubricant from one enclosing solid to the other.

Each chain has little strength in shear, great strength in tension and in both the strength decreases as the chain lengthens.

The intensity of polarisation at any level in a chain is the sum of two terms of the same sign contributed independently by the attraction fields at the ends. The influence of each field diminishes as the distance from the solid face increases, and the least value of the sum of the two terms is at a mean value surface or surfaces. In the only instance in which the position is known with certainty the mean value surfaces for slip and for break coincide (values B and S), but this is after the joint has been frozen.

The view of the liquid state taken by Poisson, Maxwell and Poynting ['Phil. Mag.' [5], 42, 289, 1896], contemplates a structure which is in the main solid, but the solid part is continually breaking down and renewing itself so that at any instant the liquid is composed of molecules built into a structure and of "free" molecules. The mobility of the liquid is the number of free molecules crossing unit area of a surface per second. In the Boundary State the attraction fields of the enclosing solids may be supposed to increase the rigidity and decrease the rate of decay of the solid portion, but the change is not uniform throughout the lubricant; to take the simplest assumption rigidity is greatest in the adsorbed layers and least at the surface $h/2$.

Osmotic pressure is the difference in hydrostatic pressure if any needed to make the mobility of the fluid on each side of a surface equal. Compare the tangential surface at $h/2$ with a normal surface cutting the centre of the plate of lubricant. With long chain molecules at any rate the mobility at the former surface is almost certainly nil because movement of molecules along the chains may be neglected, whilst at the latter surface mobility will be nil in the adsorbed layers and reach a positive value at the level $h/2$; hence the rigidity of the structure will be greater for normal than for tangential stress.

Put in another way, this amounts to saying that the structure of the lubricant is not subject to decay in the adsorbed layers but the rate of decay is positive and increases from those layers to the surface $h/2$.

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* Added December 15, 1930.

Consider now the cylindrical surface which encloses a slab of lubricant under a cylinder standing in a pool. It is obvious that there will be on the whole less mobility in the space within that surface than there is without, unless something be done to increase the former. Hydrostatic pressure increases the mobility of a liquid (*cf.* POYNTING) and the Leslie pressure is the pressure needed to equalise the mobilities across the enclosing cylindrical surface at the level $h/2$—it is, in short, the osmotic pressure of the lubricant.

The molecular chains may, of course, help to support the loading by their resistance in compression, in which case the expression for the Leslie pressure would include two terms, one representing the rigidity of the structure, the other representing the defect in mobility, the Leslie pressure would then become strictly analogous to the swelling pressure of a gel.

There is, however, a difficulty. The equation of the Leslie pressure in its simplest form is $P_L = p_0 - p$ where $p_0$ is the mobility of the external fluid and $p$ the mobility of the lubricant, the values being reckoned in an elementary cylinder which encloses the surface $h/2 \, . \, p$ by hypothesis depends upon the length $h$ and upon the strength of the polarising fields, that is, the attraction fields of the solids. When $h$ is fixed the Leslie pressure should therefore depend upon the chemical constitution of the enclosing solids, whereas it seems to be a function only of the geometry of the system. It is possible that this difficulty would be solved by an analysis of the form of the curved equipotential surfaces at the circumference of the plate of lubricant.

The existence of a Leslie pressure IN AIR and the presence of a complete air-gap have been accepted throughout the paper for reasons given on p. 2. It must be admitted that the air-gap if it be real raises theoretical difficulties of the most formidable kind. There are three possible explanations :—

(1) The existence of chains of molecules such as are postulated for fluid lubricant.

(2) The existence of an attraction field on the surface of a solid with a range of at least 0·005 mm.

(3) The presence of solid particles which keep the surfaces apart.

Let us briefly summarise the difficulties of each.

(i) The difficulty here is one of degree and is sufficiently dealt with in the text, p. 23.

(ii) To fit the facts the relatively long range force of attraction cannot be the shadowless force contemplated in the Young-Laplace theory. It must be capable of saturation so that its range in close packed states of matter is reduced to molecular or even atomic limits.

(iii) Solid particles if they are present would need to be perfectly elastic and have always the same dimensions. These conditions might be fulfilled if the particles instead of being casual fragments of matter caught up by

> the solid faces, were formed by the condensation from the air of ultra-microscopic particles on to areas of the solid face where the attraction field was more intense than elsewhere. The existence of such areas is accepted by physicists and they might be due to minute variations in the structure or form of the surface of the metal. The depth of a particle formed in this way would be a function of the excess of attraction at an active area. On this hypothesis, however, the depth and therefore the value of $h$ should be different for different solids.

The total strength of all the chains of molecules in tension increases as the length of the molecules of which they are built increases, whilst the total strength of all the chains in shear decreases and, when allowance is made for perturbation due to the end groups of atoms, the relation in both instances is always linear. When the length of the molecules is great enough strength in shear vanishes.

The strength in tension must be due to the lateral fields of attraction of the molecules at least as much as to the fields at the ends. The decrease in the strength in shear may be due merely to the increase in the moment of the applied force.

(I.) Hardy and Hardy. ‘Phil. Mag.,’ vol. 6, pp. 38, 32 (1919).
(II.) Hardy. ‘Phil. Mag.,’ vol. 6, pp. 38, 49 (1919).
(III.) Hardy. ‘Phil. Mag.,’ vol. 6, pp. 40, 201 (1920).
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