XVI. *On the Relation between the Thickness and the Surface Tension of Liquid Films.*

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[Plate 33.]

Introduction.

Laplace's theory of capillarity is based upon the assumption that the forces in play between the neighbouring molecules of a liquid are insensible at sensible distances. Each molecule is thus frequently considered as the centre of a sphere which bounds the "insensible" region within which the molecular forces exerted by the central molecule on others are appreciable. The radius of this sphere is called "the radius of molecular action." It is evident from its definition that it is not a determinate physical constant. The point at which a force ceases to be "sensible" depends upon the delicacy of the methods which are employed to detect its effects, and thus also upon the nature of the particular effect which is studied. Many physicists have, however, rightly considered that an approximate measurement of the distance at which the mutual actions of neighbouring molecules become negligible was well worth obtaining. They have, therefore, by different methods sought indications of the magnitude of this distance, and, if successful, have added their result to the other recorded measurements of the radius of molecular action. The nomenclature thus adopted is somewhat vague, but we are not aware that any general misconception exists as to the indefinite character of the magnitude, to which, nevertheless, a definite name is given.

The theory that molecular forces are only sensible at very small distances leads us to regard a liquid as bounded by a very thin external layer, the properties of which are different from those of the mass in the interior. To this the name of the *surface layer* may be given. The definition of its thickness is subject to the same difficulties as the definition of the magnitude of the radius of molecular action. The two, however defined, are closely related and are generally assumed to be equal.

Plateau, arguing that the surface tension would decrease if the thickness of a soap film became less than twice that of the surface layer, first investigated the question as to whether the pressure exerted on the enclosed air depended on the thickness of the bubble. His method,* as is well known, consisted in forming a bubble at the end of a tube which was bent so as to serve as a water-manometer for the measurement of the internal pressure. He concluded that the radius of molecular action was less than 59×10^{-6} mm., because no regular change was observed in the case of a bubble which thinned till it displayed a colour which, according to NEWTON's scale, indicated twice that thickness, viz., the pale yellow of the first order.

LÜDTGE † formed a soap film at the end of a tube, and, when it had become thin, closed the other end by a new film. Some air was then forced in, the films assumed the form of spherical segments, and their curvatures were compared. He concluded that the thicker film had the less surface tension, and that almost immediately after its formation the thickness of a film was less than twice the radius of molecular action.

These experiments were carefully repeated by VAN DER MENSBRUGGHE, ‡ who kept one of the films moderately thick by dropping liquid upon it, so that it displayed the red and green of the higher orders. He describes the other film as showing bright colours, especially towards the top. He could not detect any change in the curvature of the films, and concluded that the tensions were the same, though the thicknesses were different. Later, VAN DER MENSBRUGGHE's views appear to have undergone some modification. He based an explanation of a number of curious phenomena on the principle, enunciated by Sir WILLIAM THOMSON, that if a soap film is extended it is cooled. He thought, therefore, that "les expériences de LÜDTGE s'expliquent de la manière la plus nette pourvu que les augmentations de tension admises par le physicien allemand dans certaines parties d'une lame soient attribuées au développement de surfaces fraîches sur les deux faces de cette lame, et à la diminution de température qui en résulte."§

If VAN DER MENSBRUGGHE's later views are correct it is evident that his earlier test of LÜDTGE's observations is open to objection, as, if a film be kept thick by dropping liquid upon it, new surfaces must necessarily be produced. Indeed, he seems to think that much less potent causes might produce results which can be easily detected.

We describe one of his experiments, to give an example of his method of applying Sir WILLIAM THOMSON's law ‖ :—

A circular hole about 4 cm. in diameter was bored in an iron plate furnished with a handle. The edge of the hole was bevelled, and it was made the common basis of two bubbles forming spherical segments which enclosed a lens-shaped space. If the plate were placed horizontally, if the weights of the films were negligible, and if

* PLATEAU, 'Statique des Liquides,' 1873, vol. 1, p. 210.

† 'Poggendorff, Annalen,' vol. 139, 1870, p. 620.

‡ 'Bruxelles, Acad. Sci. Bull.,' vol. 30, 1870, p. 322.

§ 'Bruxelles, Acad. Sci. Mém.,' vol. 43, 1882 (No. 4, p. 18).

‖ *Loc. cit.*, p. 19.

their surface tensions were identical, the curvature of each would be the same. VAN DER MENSBRUGGHE, however, considers that a zone of liquid in the upper bubble would in descending increase its surface, while in the lower bubble the surface of the descending mass would diminish. Hence the upper bubble would become cooled, while the temperature of the lower one would be raised, and this would be indicated by a difference of curvature, due to the fact that the surface tensions were not the same. Observation showed that such a difference of curvature existed. In one experiment the sagittæ of the spherical segments differed by 1·15 mm., which diminished after 45^{m} to 0·1 mm. When the system had apparently reached a permanent state the plate was reversed, the upper and lower bubbles exchanged places, and the fact that the measurements were to within the error of experiment the same as before was taken as evidence that the phenomenon observed was not due to any inequality produced directly by the weight of the films.

The investigations of these observers have not left the question of the relation between the surface tension and the thickness of a liquid film in a satisfactory state.

We have already pointed out* that the experiment of PLATEAU, who observed a bubble formed of *liquide glycérique* which lasted for three days, and was enclosed in a vessel containing sticks of caustic potash to dry the air, offers no guarantee that the composition of the liquid remained unaltered. As we have found that under circumstances much less favourable to change† a soap film lost in thirty-eight minutes 23 out of the 57·7 volumes of water contained in every 100 volumes of solution, it is practically certain that the constitution of PLATEAU'S bubble could not have been constant.

LÜDTGE and VAN DER MENSBRUGGHE were on their guard against this difficulty, and, though they experimented with *liquide glycérique* without any of the elaborate precautions which we have since shown to be necessary if the percentage of water is to remain unaltered, they checked these observations with others made with solutions of Quillaja and of Marseilles soap. Neither, however, appears to have put his conclusions to a certain and satisfactory test. If it be true that the surface tension of a film varies with its thickness it would be a matter of the highest interest to determine the law of change. No such attempt was made by LÜDTGE, who remarked only that the method did not admit of great accuracy, and that one of his experiments indicated a change of tension in the ratio of 2·8 to 2·84 in five minutes. VAN DER MENSBRUGGHE, on the other hand, though he has no doubt suggested a *vera causa* which may completely explain some of the phenomena he describes, made no attempt to determine whether the lowering of temperature to which he ascribes them could be produced by such increments of the surface as could reasonably be supposed to take place. For this purpose the change of tension must be measured, and though he gives the data for the calculation he does not make it. The reason for this probably was

* 'Phil. Trans.,' vol. 172 (Part 2, 1881), p. 448.

† *Loc. cit.*, p. 486.

that he was evidently aware that other causes might affect the result, and that the differences of surface tension given by different experiments varied considerably.

Thus, if we attempt to compare the surface tensions of two spherical films by measuring their sagittæ, the question of the real magnitude of their circular bases becomes important. The fact that a film adheres to its solid support by means of a ring of comparatively thick liquid makes it uncertain whether the dimensions of the film can be directly inferred from those of the solid.

In one of VAN DER MENSBRUGGHE'S experiments the films were formed on a ring 4 cm. in diameter, and their sagittæ were 16·55 and 17·70 mm. respectively. If, therefore, the bases of both segments had the same diameter as the ring, the radii of the spheres, of which they were parts, were 2·036 and 2·015 cm. This might indicate that the surface tensions differed by about 1 per cent. The inequality can also be accounted for by supposing that the films had the same surface tension, but that, owing to some little difference in the size of the thick liquid rings which united them to the solid, the radii of their bases differed by 0·18 mm. This calculation, at all events, proves that small errors of this kind might produce differences of the same order as those ascribed to changes in surface tension.

The experiments of previous observers were all made with comparatively thick films. We have had considerable experience in producing films which display the black of the first order. Their thickness, the measurement of which we have described in a previous communication,* is about one-tenth of that ascribed by PLATEAU to the bubble on which he based his conclusion. It was quite possible that the two surface layers might be separate in his experiment and yet give evidence of mingling in a film ten times thinner.

[† A preliminary objection may be taken to the observations of PLATEAU and LÜDTGE, as it may be urged that, if the tension of a film alters as it becomes thinner, it must break when it has become thin enough for the tensions of the thicker and thinner parts to differ by an appreciable amount. We have elsewhere‡ expressed an opinion that the possibility of the existence of a film in such a state depends on the relative magnitudes of its viscosity, and of the difference of tension in question. As the matter has an important bearing on the subject of this paper, it may be well to discuss it a little more fully.

There can of course be no doubt but that a difference of surface tension in two parts of the same film must produce motion. Is it therefore *a priori* certain that, if large enough to be measured, it must either produce rupture or motion so violent as to prevent the measurements being made?

In considering this question, it must be observed that no calculations had been made previous to our own as to what difference of surface tension is measurable by

* 'Phil. Trans.,' vol. 174 (Part 2, 1883), p. 645.

† The paragraphs within these brackets were added Nov. 10, 1886.

‡ 'Phil. Trans.,' vol. 172 (Part 2, 1881), p. 489.

the various methods which had been employed. Theoretically, these methods can be made infinitely sensitive, and practically, slight variations in the adjustment of the apparatus alter very considerably the value of the experiment as a means of detecting small changes in the tension. VAN DER MENSBRUGGHE had indeed proved that LÜDTGE's experiment is infinitely sensitive when the two films are hemispheres. As we have already stated, he had not, as far as we are aware, calculated the value of the difference of surface tension in play in any particular observation. We have in the following pages discussed the theory of the methods of experiment, instituted a comparison between them, and, in the case of the arrangement which we ourselves adopted, have investigated the various sources of error to which it is subject. For such a purpose calculation alone would not suffice. The practical limit to the sensitiveness is fixed by the impossibility of eliminating small perturbations, and could therefore only be found by trial.

While, therefore, on the one hand, it seemed that experiment alone could decide what could be done by experiment, on the other hand, it was theoretically probable that, if the thickness of a black film was less than twice that of the surface layer, its viscosity might be great. The surface layer of a liquid must consist of elementary layers, the properties of which are different. The mean viscosity of the surface layer being, in the case of soap solution, greater than that of the liquid, the viscosity of some of the elementary layers must be, to an unknown extent, greater than this mean. Thus it is probable that, when the thickness of a film becomes less than twice the radius of molecular action, its viscosity increases. It would not be safe to extend to a black film conclusions drawn from experiments which prove that the liquid of which a moderately thick film is composed moves readily under the influence of a small difference of surface tension.

If, therefore, the general opinion that it was possible that a change in the tension of thin films might be detected by experiment was erroneous, it was not possible to confute it by *a priori* reasoning. It had the support of high authority. Professor CLERK MAXWELL, in his article on "Capillary Action," says, "measurements of the tensions of a film, when drawn out to different degrees of thickness, may possibly lead to an estimate of the range of the molecular forces, or at least of the depth within a liquid mass at which its properties become sensibly uniform. We shall, therefore, indicate a method of investigating the tension of such films," &c.

On the whole, then, though all *a priori* considerations pointed to the conclusion that, if any difference of surface tension existed between the black and coloured parts of a film, it must be small, it appeared to us that the question as to whether it existed could only be settled beyond the possibility of dispute by experiment. We have, therefore, assumed in this paper that such a difference is possible. We have also supposed that the relation between the difference of surface tension and the other properties of the film is such that the only considerable movement to which it gives rise is a change of curvature. Having by experiments, conducted on these favourable assumptions, decided whether or no evidence of a difference of surface tension exceeding a given amount is forthcoming, we are then at liberty to reconsider the probable constitution of the film in view of the facts which experiment has elicited.]

In studying the properties of the black portion of a soap film, it is also important to remember that it has a well-defined boundary which indicates an apparent discontinuity in the thickness. It may be urged that if the thickness is less than that of two surface layers there must also be an apparent discontinuity in the surface tension at the edge of the black. If this were so, a free globular bubble, consisting of two parts, a coloured portion and a black "polar cap," could not be spherical, but must consist of two spherical segments which meet at a finite angle. This condition is not consistent with equilibrium, and therefore the black and coloured portions of the film must have the same tension.

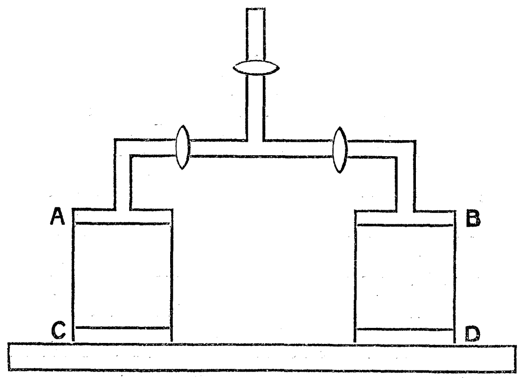
We think this argument deserves consideration, but we have not thought that it is so conclusive as to obviate the necessity of experiment to determine the facts. In the first place we are not aware that any evidence is on record that a perfectly free spherical bubble can have a black "cap." If the bubble is attached to a tube or other solid support the argument no longer applies, as that part which is in contact with the solid is not constrained to meet the axis of revolution, and may therefore be an unduloid or nodoid which can meet the spherical segment without any discontinuity. In order, therefore, that the argument might have the necessary basis of ascertained fact it would be requisite that bubbles should be formed without any solid supports, and should under these conditions be observed to reach a state in which they were partly black and partly coloured. Spherical bubbles when supported do not ordinarily exhibit more than a very small circular patch of black, and it would probably be very difficult to produce free spherical bubbles which should thin with sufficient rapidity for the purpose in view.

Even supposing that such a result had been obtained, anything like accurate measurement to ascertain the spherical form of the bubble would under the required conditions be difficult or impossible. Unless these measurements were made the experiment would be open to the objection that the bubble might not be truly spherical, and that the same conditions which cause the sudden change in thickness at the edge of the black might also explain a very rapid change in curvature.

It did not therefore seem wise to rely with implicit confidence on *a priori* reasoning as to a region in the film which is the seat of phenomena which are confessedly imperfectly understood. If experiment is necessary, observations on free spherical bubbles did not seem likely to be easy or conclusive. We therefore determined to adopt a modification of LÜDTGE's method, and to balance against each other two films of different degrees of tenuity.

It was essential that our method of experiment should be such as would enable us readily to produce black films. We have found that this end is most easily obtained with cylinders. In most of our experiments, therefore, one of the films has been cylindrical. The other, though of the same mean curvature, has been of various forms as convenience suggested.

The general idea of the apparatus is represented in the accompanying diagram. Bubbles are blown on the inverted cups A and B, until they adhere to the rings C and D. They can be cut off from or put into communication with each other or with the external air by means of stopcocks. By withdrawing or forcing in air they can be made to assume any required form.



This arrangement, like LÜDTGE'S, possesses the great advantage that the indications sought for are not complicated by changes in the temperature or in the pressure of the atmosphere. These may cause the diameter of the films to increase or contract, but will affect them equally. A difference in surface tension would be indicated by a difference in their magnitudes.

The two simplest surfaces which can be formed with such an apparatus are the cylinder and the sphere. The fact that if they change their shape they become unduloids or nodoids has, of course, made the mathematical theory of the experiment more complicated. The justification of the particular method adopted is, however, to be found in the fact that liquid cylinders offer such much greater facilities for obtaining a completely black film than any other geometrical form, that every other consideration has been made to give way to this, which, for reasons to be detailed hereafter, we conceive to be of prime importance.

In the following pages we shall deduce from the assumption that films of different thicknesses have different surface tensions the conclusions to which it leads, and shall then submit to the test of experiment the question as to whether these conclusions are in accord with the observed facts.

On the Sensitiveness of the Methods of measuring Changes in the Surface Tension of a Film.

All the methods which we have described measure the change in the surface tension of the film indirectly by a change in length. In PLATEAU'S experiment the movement of the liquid in the manometer, in the others the alterations in the sagittæ or diameters of the films, furnish the required indication. Let an increment dT in the surface tension T produce an alteration dL in this length. The fraction TdL/dT may then be conveniently taken as a measure of the *sensitiveness* of the experiment. The quantities dL and dT may be finite or infinitely small. In the latter case the expression gives the *limiting sensitiveness* for an infinitely small variation in T.

If the increment dL observed in any experiment is divided by the sensitiveness, the quotient is the fraction of itself by which the tension has altered. The relative values of different methods of measuring dT is best obtained by comparing the sensitivenesses for equal values of dT/T.

It is easy to see that, as has been stated, experiments can be arranged in which the sensitiveness is infinite, *i.e.*, in which the equilibrium is unstable, so that an infinitely small change in T would produce a finite change in L. Two bubbles, each greater than a hemisphere, and the interiors of which were connected, would form such an arrangement. Great sensitiveness may be obtained by approaching the conditions of instability as nearly as may be practically convenient.

In the following calculations we have treated the air as incompressible by the small forces due to slight changes in the surface tensions of the films by which it is enclosed. In LÜDTGE's experiment, if the volume of the tube is large compared with that of the spherical segments, it might be necessary to allow for variations in the density of the air. If the apparatus be properly designed, the necessity for this complication is avoided. The surface tension of water is about 81 dynes per linear cm. A water bubble 1 cm. in radius would therefore exert upon the enclosed air a pressure of 324 dynes per sq. cm. The changes of surface tension to be studied are but small fractions of the whole, and as the atmospheric pressure is 10^6 dynes per sq. cm. it may safely be said that they could not alter the volume of the enclosed air by more than a few millionths of the total space occupied.

In experiments in which the equilibrium is stable the change of form produced by the change in surface tension is generally such as to reduce the change of pressure which would otherwise be produced. The contraction or expansion of the enclosed air would also affect both films, and its effects would be the same as those of a small change in temperature.

Limiting Sensitiveness of PLATEAU'S *Experiment.*

Let V be the volume of the bubble, r_1 the radius of the manometer tube, and l the distance through which the liquid is depressed. Let r_2 be the radius of the tube from which the bubble hangs, R the radius, and nr_2 the sagitta of the bubble. Then

$$R = r_2(1+n^2)/2n, \quad V = \pi r_2^3 n(n^2+3)/6.$$

Also, if $v = \pi r_1^2 l$, we must have

$$V + v = \text{a constant} \quad \ldots \ldots \ldots \quad (1)$$

If p be the pressure due to the film, T the tension, and σ the density of the liquid in the manometer,

$$p=4\mathrm{T}/\mathrm{R}=2\sigma gl.$$

Hence

$$\mathrm{R}=\frac{2\mathrm{T}}{\sigma gl}=\frac{r_2(1+n^2)}{2n}. \qquad (2)$$

From these equations we get

$$2\mathrm{T}dl/d\mathrm{T}=\frac{2nr_2^3(1+n^2)^2}{\frac{\sigma g}{4\mathrm{T}}r_2^4(1+n^2)^3-2r_1^2(n^2-1)}.$$

This expression gives the sensitiveness, since the total movement (down and up) of the liquid in the manometer is $2dl$.

In PLATEAU'S experiment T = 60 dynes (about) per linear cm., $r_1=0{\cdot}5$ cm., $r_2=0{\cdot}25$ cm., $\sigma=1$.

Substituting these values in the denominator, and equating to zero, we get

$$(1+n^2)^3-31{\cdot}315(n^2-1)=0.$$

This equation in n^2 has one negative and two positive roots. The latter are

$$n^2=1{\cdot}497 \quad\text{and}\quad n^2=2{\cdot}912,$$

which give

$$n=1{\cdot}224 \quad\text{and}\quad n=1{\cdot}707.$$

When n has these values the sensitiveness is infinite. The meaning of this result is as follows. If a bubble be blown at the end of a tube connected with a manometer the bubble will increase, and the liquid in the manometer will become more depressed until the film is a hemisphere. Thereafter the pressure will diminish, and though V will increase v will become less. If the radius of the manometer tube is such that the decrement dv is greater than the increment $d\mathrm{V}$, an increase in the size of the bubble would necessarily be attended with a decrease in the total volume of enclosed air. Under these conditions the equilibrium would be unstable, and the system would transform itself into a form in which the volume of the bubble was such that $d\mathrm{V}+dv$ was positive. If the bubble were originally on the borders of instability a small change in T would produce a finite change in the position of the liquid in the manometer, and thus the sensitiveness would be infinite. In the case of the apparatus used by PLATEAU the whole phenomenon must have occurred within narrow limits and would easily escape attention.

The following table explains itself, and illustrates the fact that as the sagitta increases $\mathrm{V}+v$ has successively a maximum and a minimum value.

TABLE I.

R	n	$2\mathrm{T}dl/d\mathrm{T}$	l	V/π	v/π	$(\mathrm{V}+v)/\pi$
cm.			cm.			
2	$8+\sqrt{63}$	0·12	0·06116	10·6660	0·01529	10·6813
1	$4+\sqrt{15}$	0·25	0·12232	1·3323	0·03058	1·3629
0·5	$2+\sqrt{3}$	0·56	0·24464	0·16452	0·06116	0·22568
0·286	1·707	$+\infty-$	0·42771	0·02629	0·10693	0·13322
0·271	1·500		0·45128	0·02051	0·11282	0·13333
0·256	1·224	$-\infty+$	0·47783	0·01433	0·11946	0·13379
0·250	1·000	0·98	0·48930	0·01042	0·12232	0·13274
0·5	$2-\sqrt{3}$	0·02	0·24464	0·00799	0·06116	0·06916
∞	0	0	0	0	0	0

The importance of this table for our present purpose depends, however, chiefly on the figures in the first three rows. The radii are chosen to correspond with those of bubbles which PLATEAU used. As he does not mention the radius of the bubble on which he based his estimate of the superior limit of the radius of molecular attraction, it is impossible to estimate exactly the sensitiveness of his experiment. Probably it did not exceed 0·56.

Limiting Sensitiveness of LÜDTGE'S *Experiment.*

The expression for this quantity has been calculated by VAN DER MENSBRUGGHE.* Let the radius of the tube at the extremities of which the films are formed be r, and let the sagittæ of the two spherical segments be nr and $n'r$ respectively. Then from equation (2)

$$p=\frac{8\mathrm{T}n}{r(1+n^2)}=\frac{8\mathrm{T}'n'}{r(1+n'^2)}.$$

If the tensions alter, the change in the pressure exerted on the internal air must be the same for both films, so that

$$\frac{nd\mathrm{T}}{1+n^2}+\frac{\mathrm{T}(1-n^2)}{(1+n^2)^2}dn=\frac{n'd\mathrm{T}'}{1+n'^2}+\frac{\mathrm{T}'(1-n'^2)}{(1+n'^2)^2}dn'.$$

If both films had at first the same surface tension, $\mathrm{T}=\mathrm{T}'$ and $n=n'$. Also, since the total volume is constant, $dn=-dn'$. Hence

$$2\mathrm{T}rdn/(d\mathrm{T}-d\mathrm{T}')=-nr(1+n^2)/(1-n^2).$$

In the following table we have taken $r=1$, so that the sensitiveness for a tube of any given radius is obtained by multiplying the figures in the second column by the radius expressed in centimetres.

* 'Bruxelles, Acad. Sci. Bull.,' vol. 30, 1870, pp. 322–332.

If one of the films be maintained in a constant state the increment of T for that film is zero.

TABLE II. ($n=1$.)

n	$2\mathrm{T}dn/d\mathrm{T}$
0	0
0·25	0·2833
0·50	0·8333
0·75	2·6786
1·00	∞

If $n>1$ the arrangement is unstable.

VAN DER MENSBRUGGHE'S experiments described above are, from the mathematical point of view, particular cases of LÜDTGE'S method, and do not require separate discussion.

On the Limiting Sensitiveness of the Experiments described in this Paper.

In most of the experiments hereafter described we have balanced two cylinders against each other. Such figures deform into unduloids, the equations to which could be expressed by the approximate relation

$$y=a+c\sin\frac{x}{a}.$$

We have also balanced spheres against spheres, and a sphere against a cylinder, and it therefore seemed better to deduce general expressions from which the sensitiveness could in each case be calculated.

BEER* has shown that, if the axis of x be the axis of revolution, the equation to the curve which generates a surface of revolution of constant curvature is

$$dx=\pm\frac{y^2\pm\alpha\beta}{\sqrt{(\alpha^2-y^2)(y^2-\beta^2)}}dy. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

In this expression α and β are both taken as positive quantities, and the curve is an unduloid or nodoid according as the positive or negative sign is taken before the product $\alpha\beta$. We shall omit the alternative sign and, taking α positive and always numerically $>\beta$, shall assume that β may be either positive or negative. We shall also assume that normally the origin lies on a maximum ordinate. In that case dx/dy is negative for positive values of y which correspond to values of x less than that for which the first minimum value of y occurs if β is positive, and less than that for which $y^2+\alpha\beta=0$ if β is negative. In most of the cases with which we have had to deal

* 'Tractatus de theoriâ mathematicâ phænomenorum in liquidis actioni gravitatis detractis observatorum,' Bonn, 1857. See also PLATEAU, 'Statique des Liquides,' vol. 1, p. 139.

there has only been one maximum or minimum value of y in the part of the curves under consideration.

Again, when $y^2 < -\alpha\beta$, which can only be the case when β is negative, the curve is convex towards the axis of revolution, and the pressure is exerted outwards. This is also a case we have not practically realized, so that it will be convenient to take the square root as affected with the negative sign.

If then, with BEER, we assume

$$y^2 = \beta^2 \sin^2 \phi + \alpha^2 \cos^2 \phi \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

$$k^2 = (\alpha^2 - \beta^2)/\alpha^2 \quad \text{and} \quad \Delta = \sqrt{1 - k^2 \sin^2 \phi},$$

we get from the differential equation

$$x = \alpha \mathrm{E} + \beta \mathrm{F},$$

where F and E are elliptic integrals of the first and second kinds respectively.

As the lower limit of the integrals is zero, the origin is assumed to lie on a maximum ordinate, for $y = \pm\alpha$ when $\phi = 0$.

When it is convenient to transfer the origin to a minimum ordinate, ϕ is $> \pi/2$ for positive values of x; and, taking this as the upper limit, we may write

$$x = \alpha(\mathrm{E} - \mathrm{E}_1) + \beta(\mathrm{F} - \mathrm{F}_1),$$

where F_1 and E_1 are the complete integrals taken between the limits $\pi/2$ and 0.

Again, if V is the volume included between the plane through the origin perpendicular to the axis of x and any other parallel plane,

$$\mathrm{V}/\pi = \left(\frac{2}{3}\alpha^3 + \beta\alpha^2 + \frac{2}{3}\alpha\beta^2\right)\mathrm{E} - \frac{1}{3}\alpha\beta^2\mathrm{F} + \frac{1}{6}\alpha(\alpha^2 - \beta^2)\,\Delta \sin 2\phi \quad . \quad . \quad . \quad . \quad . \quad (5)$$

This expression has been given by BEER. If the origin lies on a minimum ordinate we must, as before, write $\mathrm{E} - \mathrm{E}_1$ and $\mathrm{F} - \mathrm{F}_1$ for E and F respectively, remembering that ϕ is $> \pi/2$.

Let us suppose that two rings of radius Y are arranged with their planes perpendicular to the straight line on which their centres lie, the distance between them being 2X.

Let the rings be joined by a liquid film, the maximum or minimum ordinate of which lies half-way between them. It is convenient to speak of this as the *principal ordinate.* Let ϕ_1 be the value of ϕ which corresponds to Y, and Δ_1 the value of Δ when $\phi = \phi_1$.

If then the form of the film be altered, but so that it remains a surface of revolution of constant curvature, the quantities α, β, and ϕ_1 must vary subject to the conditions that X and Y are constant.

Hence, differentiating the expressions for X and Y given above, we have

$$d\alpha\left\{\mathrm{E}-\frac{\beta^2}{\alpha^2}\int\frac{\sin^2\phi}{\Delta}d\phi+\frac{\beta^3}{\alpha^3}\int\frac{\sin^2\phi}{\Delta^3}d\phi\right\}+d\beta\left\{\mathrm{F}+\frac{\beta}{\alpha}\int\frac{\sin^2\phi}{\Delta}d\phi-\frac{\beta^2}{\alpha^2}\int\frac{\sin^2\phi}{\Delta^3}d\phi\right\}$$

$$+d\phi_1\left\{\alpha\Delta_1+\frac{\beta}{\Delta_1}\right\}=0, \quad \ldots \quad (6)$$

and

$$\beta\sin^2\phi_1 d\beta+\alpha\cos^2\phi_1 d\alpha-(\alpha^2-\beta^2)\sin\phi_1\cos\phi_1 d\phi_1=0. \quad \ldots \quad (7)$$

The limits of the integrals are ϕ_1 and 0, or ϕ_1 and $\pi/2$, according as the origin lies on a maximum or minimum ordinate. In the latter case $\mathrm{E}-\mathrm{E}_1$ and $\mathrm{F}-\mathrm{F}_1$ must be written for E and F.

But

$$\int\frac{\sin^2\phi}{\Delta^3}d\phi=\frac{1}{k^2}\int\frac{1-(1-k^2\sin^2\phi)}{\Delta^3}d\phi=\frac{1}{k^2}\int\frac{d\phi}{\Delta^3}-\frac{\mathrm{F}}{k^2},$$

$$\int\frac{\sin^2\phi}{\Delta}d\phi=\frac{\mathrm{F}-\mathrm{E}}{k^2}, \text{ and } \int\frac{d\phi}{\Delta^3}=\frac{\alpha^2}{\beta^2}\left\{\mathrm{E}-\frac{k^2\sin\phi_1\cos\phi_1}{\Delta_1}\right\}.$$

Hence, substituting from these expressions, and eliminating $d\phi_1$ between (6) and (7),

$$d\alpha\{\beta^2\mathrm{F}-\alpha^2\mathrm{E}-\alpha^2\Delta_1\cot\phi_1\}+\alpha^2 d\beta(\mathrm{E}-\mathrm{F}-\Delta_1\tan\phi_1)=0 \quad \ldots \quad (8)$$

Again, differentiating the expression for V given in equation (5), we get in the general case, when $d\alpha$, $d\beta$, and $d\phi_1$ are independent,

$$\begin{aligned}
d\mathrm{V}/\pi=d\alpha\Big\{&(2\alpha^2+2\alpha\beta+\tfrac{2}{3}\beta^2)\mathrm{E}-\tfrac{1}{3}\beta^2\mathrm{F}\\
&+\tfrac{1}{6}(3\alpha^2-\beta^2)\Delta_1\sin 2\phi_1-\frac{\beta^2}{\alpha^2}\Big(\tfrac{2}{3}\alpha^2+\alpha\beta+\tfrac{2}{3}\beta^2\Big)\int\frac{\sin^2\phi}{\Delta}d\phi\\
&-\frac{1}{3}\frac{\beta^4}{\alpha^2}\int\frac{\sin^2\phi}{\Delta^3}d\phi-\frac{1}{6}\frac{\beta^2(\alpha^2-\beta^2)}{\alpha^2\Delta_1}\sin^2\phi_1\sin 2\phi_1\Big\}\\
+d\beta\Big\{&(\alpha^2+\tfrac{4}{3}\alpha\beta)\mathrm{E}-\tfrac{2}{3}\alpha\beta\mathrm{F}-\frac{\alpha\beta}{3}\Delta_1\sin 2\phi_1\\
&+\Big(\tfrac{2}{3}\alpha^2+\alpha\beta+\tfrac{2}{3}\beta^2\Big)\frac{\beta}{\alpha}\int\frac{\sin^2\phi}{\Delta}d\phi+\frac{1}{3}\frac{\beta^3}{\alpha}\int\frac{\sin^2\phi}{\Delta^3}d\phi\\
&+\frac{1}{6}\frac{\beta(\alpha^2-\beta^2)}{\alpha\Delta_1}\sin^2\phi_1\sin 2\phi_1\Big\}\\
+d\phi_1\Big\{&\Big(\tfrac{2}{3}\alpha^3+\alpha^2\beta+\tfrac{2}{3}\alpha\beta^2\Big)\Delta_1-\frac{1}{3}\frac{\alpha\beta^2}{\Delta_1}\\
&+\tfrac{1}{6}\alpha(\alpha^2-\beta^2)\Big(2\Delta_1\cos 2\phi_1-\frac{\alpha^2-\beta^2}{\alpha^2}\frac{\sin^2 2\phi_1}{2\Delta_1}\Big)\Big\}.
\end{aligned}$$

Whence, substituting as above for the integrals, we get

$$dV/\pi = d\alpha\left[\frac{\alpha}{\alpha-\beta}\{(2\alpha^2-\beta^2)E-F\beta^2\}+\alpha^2\Delta_1\sin\phi_1\cos\phi_1\right]$$
$$+d\beta\left[\frac{\alpha}{\alpha-\beta}\{(\alpha^2-2\beta^2)E+F\beta^2\}-\alpha\beta\Delta_1\sin\phi_1\cos\phi_1\right]$$
$$+d\phi_1\Delta_1\alpha^2(\alpha+\beta)\left(1-\frac{\alpha-\beta}{\alpha}\sin^2\phi_1\right).$$

If Y is constant this becomes from (7)

$$dV/\pi=\frac{\alpha}{\alpha-\beta}[d\alpha\{(2\alpha^2-\beta^2)E-F\beta^2+\Delta_1\alpha^2\cot\phi_1\}$$
$$+d\beta\{(\alpha^2-2\beta^2)E+F\beta^2+\Delta_1\beta^2\tan\phi_1\}], \quad . \quad . \quad . \quad . \quad . \quad (9)$$

and, if both X and Y are constant, we get from (8)

$$dV/\pi=d\alpha\times\frac{\alpha+\beta}{\alpha}\{(2E\alpha^2-F\beta^2+\Delta_1\alpha^2\cot\phi_1)(2E-F-\Delta_1\tan\phi_1)$$
$$-E^2\alpha^2\}\div(E-F-\Delta_1\tan\phi_1)$$
$$=-d\beta\times\alpha(\alpha+\beta)\{(2E\alpha^2-F\beta^2+\Delta_1\alpha^2\cot\phi_1)(2E-F-\Delta_1\tan\phi_1)$$
$$-E^2\alpha^2\}\div(F\beta^2-E\alpha^2-\alpha^2\Delta_1\cot\phi_1). \quad . \quad . \quad . \quad . \quad . \quad (10)$$

These equations applied to the problem under discussion enable us in the first place to determine what arrangements of two films in communication will be stable.

MAXWELL * has shown that a slight bulge in a cylinder will increase or decrease the pressure according as the cylinder is shorter or longer than half the circumference of the rings to which it is attached. Hence two cylinders of equal length and radius will be unstable if their lengths exceed the limit thus laid down. For, if one cylinder expands and the other contracts a little, the pressure in the first will fall off, and that in the second will increase. Hence, the tendency will be to depart still further from the position of equilibrium. We found (as was to be expected) that it was impossible to keep the cylinders steady if we approached too near to the limit of stability. The theoretical limit is X=1·57Y, but in practice X should not be >1·25Y. Hence, in general, the length of the cylinders has been one-and-a-quarter diameters.

It is easy to apply the formulæ to the case of any two similar surfaces of constant curvature.

The unduloid and nodoid are the roulettes of the foci of an ellipse and hyperbola respectively. LINDELÖF has shown that the sum of the principal curvatures at any point in the surfaces of revolution described by these curves about their axes is the

* 'Encyclop. Brit.,' Art. "Capillary Action."

same as the curvature of the circle the diameter of which is the major axis of the generating ellipse in the one case, and the transverse axis of the hyperbola in the other.

Now, since α and β are the maximum and minimum ordinates, it is evident that in the ordinary notation

$$\alpha = a(1+e), \quad \beta = a(1-e).$$

Hence

$$\frac{1}{R}+\frac{1}{R'}=\frac{1}{a}=\frac{2}{\alpha+\beta}.$$

If then α and β alter, the increment in the curvature is

$$-2(d\alpha+d\beta)/(\alpha+\beta)^2.$$

If the variations take place subject to the conditions that X and Y are constant, and if (8) be written in the form

$$\mathrm{M}d\alpha+\alpha^2\mathrm{N}d\beta=0,$$

we have

$$\frac{(\alpha+\beta)^2}{2}d\left(\frac{1}{R}+\frac{1}{R'}\right)=-\frac{\alpha^2\mathrm{N}-\mathrm{M}}{\alpha^2\mathrm{N}}d\alpha=\frac{\alpha^2\mathrm{N}-\mathrm{M}}{\mathrm{M}}d\beta. \quad \quad (11)$$

In the case of a spherical film

$$\beta=0,\ k^2=1,\ \Delta_1=\cos\phi_1,\ \mathrm{E}=\sin\phi_1,\ \mathrm{F}=\log_e\tan\left(\frac{\pi}{4}+\frac{\phi_1}{2}\right).$$

Hence

$$\mathrm{M}=-\alpha^2/\sin\phi_1,\ \mathrm{N}=-\log_e\tan\left(\frac{\pi}{4}+\frac{\phi_1}{2}\right),$$

and from (11)

$$d\left(\frac{1}{R}+\frac{1}{R'}\right)=\frac{2}{\alpha^2}\,\frac{\operatorname{cosec}\phi_1-\log_e\tan\left(\frac{\pi}{4}+\frac{\phi_1}{2}\right)}{\log_e\tan\left(\frac{\pi}{4}+\frac{\phi_1}{2}\right)}.d\alpha.$$

The denominator of this expression is positive, and possible for positive values of $\phi_1<\pi/2$. The numerator may be shown by trial to be positive for values of $\phi_1<56°\ 28'$. When this value is reached it becomes zero and changes sign.

Now in the case of a sphere

$$\mathrm{X}=\alpha\sin\phi_1;\ \text{ and, since } \alpha^2=\mathrm{X}^2+\mathrm{Y}^2,\ \ \mathrm{Y}=\mathrm{X}\cot\phi_1.$$

Therefore, if $\phi_1=56°\ 28'$,

$$2\mathrm{X}=3{\cdot}0179\mathrm{Y}=0{\cdot}4803\times2\pi\mathrm{Y},$$

and

$$\alpha=1{\cdot}8102\mathrm{Y}.$$

Thus a slight increase in the principal ordinate of a spherical film converts it into a nodoid the mean curvature of which is greater or less than that of the sphere according as the distance between the rings is less or greater than the circumference of a ring $\times 0{\cdot}4803$.

If this distance between the rings is exceeded, an arrangement consisting of two spherical films, the interiors of which are in communication, will be unstable.

We have next to investigate the sensitiveness of our experiment.

If two films, which are in communication, are in equilibrium, the pressure exerted on the internal air must be the same. Hence

$$p=\frac{4\text{T}}{\alpha+\beta}=\frac{4\text{T}'}{\alpha'+\beta'}\,.$$

If the equilibrium is maintained after a change in any or all of these quantities,

$$\frac{d\text{T}}{\alpha+\beta}-\frac{\text{T}(d\alpha+d\beta)}{(\alpha+\beta)^2}=\frac{d\text{T}'}{\alpha'+\beta'}-\frac{\text{T}'(d\alpha'+d\beta')}{(\alpha'+\beta')^2}\,. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (12)$$

The six quantities $d\alpha$, $d\beta$, $d\phi_1$, and $d\alpha'$, $d\beta'$, $d\phi_1'$ can be determined from the six conditions that the values of X and Y shall in each case remain unaltered, that the changes of volume shall be equal in magnitude and opposite in sign, and that the change of pressure shall be the same for each film.

If the two films are similar the condition $d\text{V}=-d\text{V}'$ leads in general to the result $d\alpha=-d\alpha'$ and $d\beta=-d\beta'$.

In the case of two cylinders an expansion of the one is accompanied by a contraction of the other. If both were initially similar in all respects it is easy to show that $d\alpha=-d\beta'$, where the latter symbol refers to the film which has undergone a contraction.

For, since the lengths of the cylinders were the same, and in the case of the cylinder

$$\alpha=\beta=\text{Y} \quad \text{and} \quad \text{E}=\text{F}=\phi,$$

we have

$$\text{X}=\alpha\text{E}+\beta\text{F}=2\text{Y}\phi_1=2\text{Y}\left(\phi_1'-\frac{\pi}{2}\right), \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (13)$$

and from (10), since $d\text{V}=-d\text{V}'$,

$$d\alpha\{\phi_1(\cot\phi_1-\tan\phi_1)-1\}/\tan\phi_1=d\beta'\left\{\left(\phi_1'-\frac{\pi}{2}\right)(\cot\phi_1'-\tan\phi_1')-1\right\}/\cot\phi_1',$$

which, by (13), gives $d\alpha=-d\beta'$, and in like manner $d\alpha'=-d\beta$.

Hence, from (12), if we put $d\text{T}'=0$,

$$2(d\alpha+d\beta)\text{T}=(\alpha+\beta)d\text{T}=2\text{Y}d\text{T},$$

and from (8)

$$\frac{d\alpha}{\tan\phi_1}=\frac{d\beta}{-\cot\phi_1}=\frac{d\alpha+d\beta}{-2\cot 2\phi_1},$$

so that

$$4d\alpha\mathrm{T}/d\mathrm{T}=-4\mathrm{Y}\sin^2\phi_1/\cos 2\phi_1.$$

This expression gives the limiting sensitiveness, since the total alteration in the lengths of the two diameters is $2(d\alpha-d\beta')=4d\alpha$.

If the films were initially spheres and the arrangements were in all respects the same for both we have $d\alpha=-d\alpha'$, $d\beta=-d\beta'$. Also, substituting the proper values of E and F, given above in equation (8),

$$\frac{d\alpha}{\log_e\tan\left(\frac{\pi}{4}+\frac{\phi_1}{2}\right)}=-\frac{d\beta}{\operatorname{cosec}\phi_1}=\frac{d\alpha+d\beta}{\log_e\tan\left(\frac{\pi}{4}+\frac{\phi_1}{2}\right)-\operatorname{cosec}\phi_1},$$

whence, and from (12), if we put $d\mathrm{T}'=0$,

$$4d\alpha\mathrm{T}/d\mathrm{T}=\frac{2\alpha\log_e\tan\left(\frac{\pi}{4}+\frac{\phi_1}{2}\right)}{\log_e\tan\left(\frac{\pi}{4}+\frac{\phi_1}{2}\right)-\operatorname{cosec}\phi_1}.$$

By the aid of these expressions we have calculated the following table. The radius of the rings is taken as the unit of length. The value of X is therefore numerically equal to the distance between the rings in terms of their diameters. The values of ϕ_1 have been so chosen as to give approximately equal values of X in the parts of the table which refer to the cylinders and spheres respectively.

TABLE III.

Two cylinders (Y=1).				Two spheres (Y=1).			
ϕ_1 expressed in		$X=2\phi_1$.	$4d\alpha T/dT$.	ϕ_1 expressed in degrees.	$X=\tan\phi_1$.	$\alpha=\sec\phi_1$.	$4d\alpha T/dT$.
Circular measure.	Degrees.						
1/8	7°·16	0·25	0·064	14° 0′	0·249	1·0306	0·13
1/4	14·32	0·50	0·279	27 0	0·509	1·1223	0·64
3/8	21·49	0·75	0·734	37 0	0·754	1·2521	1·80
1/2	28·65	1·00	1·700	45 0	1·000	1·4142	4·68
5/8	35·81	1·25	4·343	51 21	1·250	1·6011	14·24
$\pi/4$	45·00	$\pi/2$	∞	56 28	$0{\cdot}961\times\pi/2$	1·8102	∞

If a sphere and cylinder are in communication, the radius of the sphere must be twice that of the cylinder if the films are to be in equilibrium when they have the same surface tension. The following results apply to a case in which the radii of the rings which support the sphere are 1·6 times greater than that of those to which the cylinder is attached. The symbols with dashes affixed refer to the sphere.

$$Y=1, \quad X=1\cdot 25, \quad \phi_1=0\cdot 625=35^\circ\ 48',$$
$$\alpha=\beta=1, \quad E=F=\phi_1, \quad \Delta_1=1,$$
$$Y'=1\cdot 6, \quad X'=1\cdot 25, \quad \alpha'=2, \quad \beta'=0,$$
$$\text{Sec}\ \phi_1'=\alpha'/Y'=1\cdot 25, \quad \therefore\ \phi_1'=36^\circ\ 52',$$
$$E=\sin\phi_1'=0\cdot 59995, \quad F=\log_e\tan\left(\frac{\pi}{4}+\frac{\phi_1'}{2}\right)=0\cdot 69307,$$
$$\Delta_1'=\cos\phi_1'.$$

Since $dV=-dV'$, we get from equation (10)

$$d\alpha\{1-\phi_1(\cot\phi_1-\tan\phi_1)\}/\tan\phi_1$$
$$=2d\alpha'\left\{1-(\sin\phi_1'+\text{cosec}\,\phi_1')\log_e\tan\left(\frac{\pi}{4}+\frac{\phi_1'}{2}\right)\right\}/\log_e\tan\left(\frac{\pi}{4}+\frac{\phi_1'}{2}\right),$$

or

$$d\alpha=-2\cdot 0343 d\alpha'.$$

In like manner, from equation (8)

$$d\alpha+d\beta=-0\cdot 9223 d\alpha,$$
$$d\alpha'+d\beta'=-1\cdot 405 d\alpha'.$$

If, as before, $dT'=0$, we get from (12)

$$dT=\frac{T}{\alpha+\beta}\times 3\cdot 2812 d\alpha'=-\frac{T}{\alpha+\beta}\times 1\cdot 6129 d\alpha,$$

or, since $\alpha+\beta=2$,

$$2(d\alpha-d\alpha')T/dT=-3\cdot 699, \quad \ldots \quad (14)$$

which gives the sensitiveness in this case.

The general result of this investigation is to prove that our apparatus was capable of being used so as to be far more sensitive than PLATEAU'S, and probably than LÜDTGE'S, as used by him. The latter does not mention the diameter of the tube he employed; but if we assume that PLATEAU'S bubble had a radius of 0·5 cm. (which seems to have been the smallest he used), and that LÜDTGE'S tube had a radius of 1 cm., and that the sagittæ of the spherical segments were half the radius, we find from Tables I. and II. that the limiting sensitiveness of the experiments was 0·56 in the one case and 0·83 in the other. MENSBRUGGHE purposely used segments which differed but little from hemispheres, and may therefore have attained very great sensitiveness. The highest value to be deduced from the experiments he describes is 11·5.

We used two sets of rings the diameters of which were 2·08 and 3·25 cm. respectively. When the two cylinders were employed the sensitivenesses (see Table III.) were

$$4·34 \times 1·04 = 4·51 \text{ and } 4·34 \times 1·62 = 7·03,$$

the distance between the rings being in each case 1·25 times the diameter.

In like manner when two spheres were used the values were 14·81 with the small rings and 23·06 with the large ones. Such high sensitiveness was found in practice inconvenient, and this arrangement was not often employed.

We have for simplicity calculated the sensitiveness of the sphere and cylinder on the assumption that the ratio of the diameter of the rings used was 1·6. It was really 3·25/2·08 = 1·56. We may, however, without serious error, assume the value 3·7 to be correct.

If, then, we credit PLATEAU and VAN DER MENSBRUGGHE with the most favourable arrangements described by them, and make the above probable assumptions for LÜDTGE, we get the following Table of sensitiveness :—

PLATEAU	0·56	MENSBRUGGHE	11·5
LÜDTGE	0·83 (?)	R. & R. Two spheres—	
R. & R. Sphere and cylinder	3·7	Small rings	14·81
„ Two cylinders—		Large rings	23·06
Small rings . .	4·51		
Large rings . .	7·03		

These numbers express the relative merits of the different experiments regarded as null methods. They are inversely proportional to the differences of surface tension which could in each case exist without detection. It is, however, proper to point out that the more sensitive methods are also more liable to accidental disturbances of various kinds, and do not therefore present so great an advantage as the theory would indicate.

This remark does not apply to a method which we employed, and by which the sensitiveness is doubled, viz., keeping each film thick in turn. By this means the indications of a difference of surface tension were twice as great as they would otherwise have been, and the figures given above may be multiplied by two.

Description of the Apparatus.

The film box was rectangular in shape, 20 cm. long, 10 cm. broad, and 17 cm. high. It was made entirely of thick plate glass, with the exception of the cover, which was of ebonite and about half an inch thick. The cover fitted accurately into its place, and to it were attached the thermometers, hygrometer, supports for the film, &c., so that all the apparatus connected with the films could be removed from the box by lifting the cover.

The supports for the films are shown at A, B, A′, B′ (Plate 33, fig. 2). A and A′ are cylindrical platinum cups, 20·8 mm. in diameter, with carefully turned edges. They are screwed to brass tubes C and C′, the upper portions of which carry rackwork and are moved up and down the larger tubes D, D′, by the pinions seen at E, E′. The supports for the pinions, as well as the tubes in which the racks slide, are attached to brass discs F, F′ (figs. 1 and 2), the lower faces of which are ground plane, and rest, when they are in their places, in good contact with the top of the ebonite cover. The holes in the cover, closed by these discs, are large enough to allow the upper cups to pass freely through, so that the latter may be introduced and adjusted to their proper positions after the cover has been put in its place.

The cylindrical rings B, B′, are the lower supports of the films. They are about 5 mm. deep, of the same diameter as the upper cups, and are screwed to platinum wires bent at right angles and soldered to brass rods H, H′.

These rods pass through tubes K, K′, fixed to the ebonite cover. By the ebonite buttons *a*, *a*′, the platinum rings can be turned on one side in such a way as to allow the upper cups to be brought into contact with the soap solution, with which the floor of the box is covered to a depth of 2·5 mm.

Both the upper and lower supports for the films can be unscrewed, and others of different size or material substituted for them. We have used (as already stated) platinum rings of 20·8 mm. and 32·5 mm. in diameter respectively, and occasionally glass rings 32·5 mm. in diameter.

In order to maintain one or other of the two films thick, or to thicken them after they had become thin, two different methods were adopted. For carrying out the first method, strips of linen were cut about 16 mm. broad, and long enough to pass one and a half times round one of the upper cups. Each strip was folded so as to have half its original width, and was wrapped round the cup in such a way that its edge projected above it, and formed a cavity into which liquid could be poured. It was secured in its place by cotton thread. Liquid was supplied to the cavity formed in this way by the bent glass tubes L, L′, which were open at the top, and were drawn out to conical terminations below. They were supported by corks placed in holes cut in the cover, and could be turned round or moved up and down, so as to bring their points just over the cavity formed by the linen wrappers. By pouring a little of the soap solution down the tube, the linen could be made to supply liquid at a greater or less rate to the film to prevent its thinning. It is convenient to describe this operation, to which we shall have frequently to refer, as *flooding* the film. As it was important that the total quantity of liquid on the floor of the box should not increase, as this would have involved a slow change in the forms of the films, the liquid used in flooding was always taken from the box itself. Two holes R, R′ (fig. 1), were provided at the back of the cover for the insertion of a small pipette, and liquid was drawn up to a fixed mark on the tube so as to supply on each occasion the same amount of liquid to the film. By this means also we ensured, as far as possible, that the temperature of the liquid used in flooding should be the same as that of the film itself.

The second method which was used to prevent or retard thinning consisted in passing an electric current up the film. The binding screws for attaching the leads are seen at *b*, *b′*, *c*, *c′* (fig. 2). The electromotive force generally used was about 45 volts, and a reflecting galvanometer in the circuit indicated the strength of the current. An account of the effect of an electric current in retarding or accelerating the thinning of a liquid film has been already published by us.*

The wires M, M′, pass through perforations in two discs of sheet india-rubber, and can be moved in any direction. If the pointed ends are wetted with the solution, they may be used to detach and carry away small bubbles which sometimes cling to the supports, and which might, if allowed to remain, cause irregular thinning.

A glass partition N, about 3 inches broad, is attached to the cover of the box, and extends to within half an inch of the liquid at the bottom. It was designed to prevent the spray caused by the bursting of one of the films from injuring the other.

Two thermometers T, T′, were fitted by corks into holes in the lid near the back of the box, one at each side, and a hair hygrometer P served to indicate any change which might occur in the hygrometric state of the air.

To ensure constancy of temperature, the film box was enclosed in a glass tank filled with water, the dimensions of which were such that there were 3 inches of water on every side of the box except at the top and bottom.

The experiments described below were all made under such conditions that the variations of temperature and hygrometric state were within the limits which previous experiment had proved to be necessary to maintain the films in a constant state. We have not therefore thought it necessary to give the thermometer and hygrometer readings.

The lengths of the films were measured by a cathetometer placed at a distance of 11 feet from the box. Their diameters were measured by a small telescope moving along an optical bench of Prof. CLIFTON'S pattern. The position of the telescope could be read by a vernier to one or two hundredths of a millimetre. The optical bench rested on a solid stone table, and was about 8 feet from the film box. Usually a narrow strip of millboard was placed behind each film, and the edge of the film was thus viewed by reflected light. When the film was thick enough to show colours, the readings

* 'Phys. Soc. Proc.,' vol. 6, p. 357.

could be made with considerable precision. The difficulty was greater when it became black, but even in this case the accuracy attainable was greater than might have been expected considering the small amount of light reflected.

The liquid used was, unless the contrary is stated, made with Potash Soap (Brit. Pharm.). Its composition has been described by us in the paper on the influence of the electric current on the rate of thinning of films previously referred to. Its refractive index was 1·3366 for the sodium line D.

As nothing in this paper depends on the very accurate measurement of the thickness of the films, we estimated it approximately by noting the colour near the edge, so that the light was nearly at grazing incidence. The thickness corresponding to any colour may therefore be taken as one and a half times greater than if the incidence had been normal. The error made in this assumption is probably not more than 2 per cent. Inasmuch also as we had to deal with much thinner films than those used in our experiments on the electrical conductivity of the films, the difficulty of estimating the colour accurately was much greater.

The thickness of the film indicated by a certain colour is thus $1{\cdot}5/1{\cdot}3366 = 9/8$, very nearly, of that of a plate of air showing the same colour by means of light falling upon it at normal incidence.

In the following Table, Column I. contains the name of the colour, Column II. the symbol of the middle of the colour on the system previously adopted by us. In these symbols the letter is the first letter of the name of the colour, the first figure in the brackets indicates the order. The colour is divided into ten parts, numbered 0, 1, 2, &c., in the order of increasing thickness, and the second number indicates the part of the colour displayed. In the third column are the thicknesses expressed in millionths of a millimetre, corresponding to the colours when displayed in a thin plate of air at normal incidence. In the first order these numbers are (with the exception of the red and black) taken from NEWTON's table. They are probably only very roughly accurate. The other orders are taken from our own table.* They are only approximate below the blue of the second order. Above that colour they are probably correct to 1 per cent. In the fourth column are the same numbers as in Column III., each increased by one-eighth. They give the thickness of the film corresponding to a given colour when mentioned in the present paper.

* 'Phil. Trans.,' vol. 172 (Part 2, 1881), p. 456.

TABLE IV.

I.	II.	III.	IV.
First order—			
Black	*b*	. .	12
Grey	G (1, 5)	(?)	(?)
White.	W (1, 5)	131	147
Yellow	Y (1, 5)	178	200
Orange	O (1, 5)	200	225
Red	R (1, 5)	284	320
Second order—			
Violet.	V (2, 5)	305	343
Blue	B (2, 5)	353	397
Green.	G (2, 5)	409	460
Yellow	Y (2, 5)	454	511
Orange	O (2, 5)	491	552
Red	R (2, 5)	522	587
Third order—			
Purple	P (3, 5)	559	629
Blue	B (3, 5)	603	678
Green.	G (3, 5)	656	738
Yellow	Y (3, 5)	710	799
Red	R (3, 5)	765	861
Bluish-red . . .	BR (3, 5)	815	917
Fourth order—			
Green.	G (4, 5)	893	1005
Yellow-green . .	YG (4, 5)	964	1085
Red	R (4, 5)	1052	1184
Fifth order—			
Green.	G (5, 5)	1188	1337
Red	R (5, 5)	1335	1502
Sixth order—			
Green.	G (6, 5)	1479	1664
Red	R (6, 5)	1627	1830
Seventh order—			
Green.	G (7, 5)	1787	2010
Red	R (7, 5)	1936	2178

In describing the experiments it is convenient to have a symbol which enables us to express the colour shortly. The two films are distinguished as the right and left respectively, and C_r and C_l are used to indicate their colours.

Thus, if the film was uniform in tint, C_r=G (2, 5) means—the colour of the right film was the middle of the green of the second order.

If two colours are indicated between brackets they are those of the top and bottom of the film respectively. Thus

$$C_l=\{B\ (2,\ 5),\ G\ (3,\ 5)\}$$

may be read—the colour of the left film varied between the middle of the blue of the second order at the top and the middle of the green of the third order at the bottom.

If the film displayed any black, the length in millimetres is written first; thus

$$C_r=\{5b,\ W\ (1,\ 5),\ O\ (1,\ 0)\}$$

means—the right film displayed five millimetres of black at the top, and the tint of the remainder varied between the middle of the white of the first order, which was in contact with the black, and the beginning of the orange of the first order at the bottom.

Results of Preliminary Experiments.

The first experiments which we performed were designed to test the observations of LÜDTGE and VAN DER MENSBRUGGHE as to the difference of tension between two films, of which one had been formed more recently than the other.

The symbols ρ and λ indicate the principal diameters of the right and left films respectively, and $\delta=\rho-\lambda$.

The diameter of the rings is 2Y, the distance between them 2X.

All lengths are given in millimetres except when otherwise stated. In calculations in which the sensitiveness is used they must be expressed in centimetres.

The following experiment was made as a test of the rapidity with which the films would return to their position of equilibrium when disturbed. This gave an idea of the readiness with which the arrangement would respond to a change of tension.

Experiment I.

$$2Y=20{\cdot}8, \quad 2X=2{\cdot}5Y=26{\cdot}0.$$

Two films were made, flooded, and put into communication. Five minutes and eight minutes afterwards the diameters were measured. The time elapsed since the formation of the films is indicated by *t*. The results were as follows :—

t	C_r	C_l	ρ	λ	δ
m.					
5	Colourless		20·90	20·83	0·07
8	G (4, 5)	R (4, 5)	20·94	20·89	0·05

The two films were now separated, and the right hand one was blown out a little. The diameters were then measured.

t	C_r	C_l	ρ	λ	δ
m.					
11	G (3, 5)	G (3, 5)	22·18	20·91	1·27
13	,,	,,	22·20	20·88	1·32

At 17^{m} the stop-cock was opened, so that the interiors of the films were again in communication, and the following observations taken. The colour of both films was still the green of the third order.

t	ρ	λ	δ
m.			
19	21·58	21·43	0·15
21	21·74	21·52	0·22

The result of this experiment was satisfactory. The mean difference of the diameters, having been increased from 0·06 mm. to 1·30 mm., was reduced to 0·18 mm. two minutes after communication between the films was re-established. There appears to have been a slight alteration of the zero reading, but the new position of equilibrium was rapidly taken up. When the large rings were used the movements of the films were slower, but, as all the principal experiments described in this paper were made with the small rings, the above observation is the only one which need be given in full to illustrate the point.

Experiment II.

The following is a typical example of a large number of experiments which proved that in general the thicker film behaved as though it had the greater surface tension. The left film was flooded at intervals of ten minutes, while the right was allowed to thin. The diameters were measured every ten minutes. When the first traces of black appeared in the right film it was flooded, and the left was allowed to thin till traces of black appeared. The interval between the two extreme measurements, which are alone given below, was $1^h\ 20^m$. During this time the temperature of the film box was steady at 19°·2 C.

The glass rings were used. 2Y=32·5, 2X=2·5Y.

C_r	C_l	$\delta=\rho-\lambda$
{R (2, 3), R (2, 9)}	Colourless	3·18
Colourless	{R (2, 1), P (2, 5)}	−2·25

We have already remarked that the alternate flooding of the two films doubles the sensitiveness of the apparatus as a means of detecting small changes in surface tension. If, therefore, the values given on p. 645 may be applied to such considerable differences of the diameters, we have

$$d\mathrm{T}/\mathrm{T}=0{\cdot}543/2\times 7{\cdot}03\equiv 3{\cdot}8 \text{ per cent.}$$

This calculation is given chiefly as an illustration of the sensitiveness of our method. A number of possible objections have to be considered before it can be accepted as a trustworthy determination of an actual difference of surface tension between the films.

In the first place, we may state that we were most scrupulously careful about the cleanliness of the apparatus. It was always taken to pieces as soon as the experiments were over, and the glass box, rings, tubes, linen bands, &c., were all washed in distilled water. The bands were left to soak all night, and when required were wrung out and dried with blotting paper. The films were always flooded before an experiment began, so that the cups and bands were well washed down with the solution. We found also that successive films, when thus treated, behaved in a much more uniform way than if the flooding was omitted. We have at times replaced the metal rings by the glass ones, and been most careful that the liquid should touch nothing but glass and linen, but the phenomenon above described was as marked as before. Lastly, if one of the films was thickened by the electric current it contracted just as it would do if thickened by flooding. The fact that the thicker film displayed the greater surface tension cannot, therefore, be due to any peculiarity of the apparatus or mode of thickening adopted.

Experiment III.

As a crucial test as to whether the weight of the thicker film had anything to do with the phenomenon, we placed the larger rings on the upper and the smaller rings on the lower supports. We thus obtained two unduloidal films, which may be described as approximately cones with the smaller ends below. It is evident that if one of these films were heavier than the other the pressure exerted on the enclosed air would thereby be diminished, and the heavier film would bulge. Experiment proved that, on the contrary, it contracted, thus indicating that the pressure was increased.

Experiment IV.

The question as to whether the phenomenon was due to the fact that in the thicker film the liquid is falling more or less rapidly was answered by closing the cock until the down-rush was practically over. When communication between the films was restored the thicker one contracted as usual.

The fact that the film contracted if it was slowly thickened from below by the electric current pointed to the same conclusion.

Experiment V.

It was, in the next place, important to determine whether the gradual disappearance of the liquid rings by which the thinning film is attached to the solid supports could produce changes in the value of Y which would account wholly or partially for the phenomenon observed.

If an unduloid differs but little from a cylinder of radius Y, we may write for its maximum and minimum ordinates $Y+d\alpha$ and $Y+d\beta$. Any other ordinate may be expressed by $Y+dy$.

Hence, if we neglect the squares of small quantities,

$$k^2=(\alpha^2-\beta^2)/\alpha^2=2(d\alpha-d\beta)/Y \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (15)$$

If x be the difference of the abscissæ of two points for which ϕ_1 and ϕ_2 are the values of ϕ, then, to the same approximation,

$$x=\alpha\int_{\phi_2}^{\phi_1}\Delta\, d\phi+\beta\int_{\phi_2}^{\phi_1}\frac{d\phi}{\Delta}=2\alpha\left(1-\frac{k^2}{4}\right)(\phi_1-\phi_2)=2Y\left\{1+\frac{d\alpha+d\beta}{2Y}\right\}(\phi_1-\phi_2). \quad . \quad (16)$$

Let

$$x/2Y=\xi.$$

Then

$$\phi_1-\phi_2=\xi\left\{1-\frac{d\alpha+d\beta}{2Y}\right\}.$$

Now from equation (4)

$$(Y+dy_1)^2=(Y+d\alpha)^2\cos^2\phi_1+(Y+d\beta)^2\sin^2\phi_1,$$

or, neglecting the squares of small quantities,

$$dy_1=\frac{d\alpha+d\beta}{2}+\frac{d\alpha-d\beta}{2}\cos 2\phi_1 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (17)$$

If now we take three points on the unduloid, such that the distances between consecutive points measured parallel to the axis are equal, then to the first approximation

$$\phi_1-\phi_2=\phi_2-\phi_3=\xi.$$

But, from two equations similar to (17),

$$dy_1+dy_3=d\alpha+d\beta+(d\alpha-d\beta)\cos 2\phi_2\cos 2\xi.$$

Also

$$dy_2=\frac{d\alpha+d\beta}{2}+\frac{d\alpha-d\beta}{2}\cos 2\phi_2.$$

Multiplying the last equation by $2\cos 2\xi$, and subtracting,

$$d\alpha+d\beta=\frac{dy_1+dy_3-2dy_2\cos 2\xi}{2\sin^2\xi}.$$

Since $d\alpha$ and $d\beta$ are independent, we may suppose the unduloid to have been derived from any convenient cylinder, and the calculations are simplified if we select that the radius of which $(\bar{Y})$ is the mean of the three quantities $Y+dy_1$, &c.

In this case,

$$dy_1+dy_2+dy_3=0,$$

and

$$d\alpha+d\beta=-dy_2\frac{1+2\cos 2\xi}{2\sin^2\xi}.$$

This formula affords a means of deciding whether any slipping of the liquid ring takes place. We have carried out the above calculations to the second degree of approximation, but, as the numerical work is troublesome and the correction introduced is small, we here neglect the squares of small quantities.

A vertical millimetre scale was placed by the film box, and the reading on this was determined, which corresponded to the middle of the distance between the cups to which the films were attached. The diameters were then measured not only in this horizontal, but also in planes 1 cm. above and below it.

The values of $\overline{\mathrm{Y}}$, dy_1, dy_2, and dy_3 were thus found, and $d\alpha+d\beta$ was determined without any assumption as to the nature of the attachments of the films to the cups.

Since the pressures exerted by the films on the internal air were the same, we have

$$\frac{\mathrm{T}+d\mathrm{T}}{2\overline{\mathrm{Y}}+d\alpha+d\beta}=\frac{\mathrm{T}}{2\overline{\mathrm{Y}}'+d\alpha'+d\beta'} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (18)$$

whence $d\mathrm{T}/\mathrm{T}$ is found.

It can also be calculated from the measurements of the principal ordinates and from the sensitiveness. If the results of the two methods agree the assumption made in the earlier part of this paper that the generating curve of the film passes through the edges of the upper and lower cups is justified.

In making an experiment with a thick film as the standard of comparison, it is necessary that the same amount of liquid should always be used in flooding, and that the measurements should always be made at the same interval after that operation. In the experiment now to be described the flooding took place between each pair of readings near the top, middle, and bottom of the films. One minute elapsed between the flooding and the beginning of the measurements, and three minutes between consecutive floodings. The readings were taken in the order: top, bottom, middle, bottom, top, &c., so that the measurement of the principal diameter corresponded to the mean of the two for the top and bottom, from which it was in point of time equidistant. Any error due to slow changes in the position of equilibrium was thus as far as possible obviated.

The following results were obtained when the left film was colourless, and when $\mathrm{C}_r=\{1b,\ \mathrm{Y}(2,9)\}$:—

	Right.	Left.
Diameter	23·05	18·80
$2\overline{Y}$	22·213	19·643
$2dy_2$	+0·837	−0·843
ξ	25° 48′	29° 10′

Using equation (18), we find that the surface tension of one film exceeded that of the other by 8·8 per cent.

Also, since $\delta = 0\cdot425$ cm. and the limiting sensitiveness for the two cylinders is 4·51,

$$dT/T = 0\cdot425/4\cdot51 = 0\cdot094.$$

So that by this formula the difference of surface tension is given as 9·4 per cent.

Considering that both equation (18) and the limiting sensitiveness are here applied to films which differ considerably from cylinders, these results are in satisfactory agreement and prove that the greater part of the difference of form of the two films cannot be ascribed to any slipping of the liquid attachments to the solid supports.

To show that this point needed careful investigation, we may remark that it seemed *prima facie* probable that the bulging film might be forced out and the contracting film drawn in a little so that they were virtually attached to rings a little larger and a little smaller than those actually employed. If this had affected the radii only to the extent of 0·1 mm. the effect on the calculated difference of surface tension would have been very great. Thus, assuming the principal diameters to have remained unaltered, but the others to have been increased in the right and diminished in the left film by 0·2 mm., the values of $2\overline{Y}$ in the above table would have been 22·346 and 19·510. The difference of surface tension given by these numbers is 3·8 per cent., while that calculated from the sensitiveness remains, as before, 9·4 per cent. It is evident, therefore, that it was only by careful measurement that we could assure ourselves that the source of error we are now investigating was not affecting our results to a very serious amount.

We have made a considerable number of similar experiments which prove that the method of measuring three ordinates generally gives results from 0·5 per cent. to 1 per cent. lower than those obtained from the sensitiveness. The following Table is a sample of our results when the films had settled down to a constant state. It shows the numbers obtained by a series of consecutive measurements on the same film. The value of dT is given in percentages. The left film was flooded at three minute intervals.

TABLE V.

C_r	δ	dT found by measurement of	
		(1) Three ordinates.	(2) One ordinate.
		Per cent.	Per cent.
{2·5*b*, G (3, 5)}	2·35	4·1	5·2
{3*b*, Y (2, 6)}.	2·69	5·5	6·0
{8*b*, B (2, 5)}.	2·42	4·5	5·4
{10*b*, O (1, 9), B (2, 5)} . .	2·53	5·3	5·6
{18*b*, O (1, 9), B (2, 5)} . .	2·37	4·3	5·3

When both films are flooded, and are therefore presumably in the same state, there is, notwithstanding, in general a more or less marked difference between their diameters. To this we generally refer as the zero error.

The following results were obtained under these conditions with six different films:—

TABLE VI.

δ	dT found by measurement of	
	(1) Three ordinates.	(2) One ordinate.
	Per cent.	Per cent.
0·76	0·7	1·7
0·36	1·0	0·8
0·19	0·8	0·4
0·12	1·1	0·3
0·43	−0·4	1·0
0·01	0·0	0·0
Mean . .	0·53	0·70

These results do not show such a constant difference between the two methods as is exhibited in the previous table, and it is, therefore, probable that when the bulging and contraction of the films becomes considerable there is a little slipping.

Taking, however, the lowest figures, these experiments are, we think, fatal to VAN DER MENSBRUGGHE'S explanation. He explains similar phenomena by means of the general principle: "Si la couche superficielle d'un liquide augmente, ou qu'elle devienne le siége d'une énergie potentielle qu'elle ne possédait pas d'abord, il y a refroidissement, et la tension est plus grande que primitivement, &c."*

From this point of view the surface of the liquid of which the thick film is formed is continually being renewed, it is therefore cooled, and the result is due to the increase of surface tension which follows.

* 'Bruxelles, Acad. Sci. Mém.,' vol. 43 (No. 4, p. 7).

It is, however, impossible to account for the smallest of the differences of surface tension shown in Table V. in this way.

If a gramme of water were drawn out into a film of 100 sq. cm. the cooling effect would be 1/4803 degree C.* But the thickness of the thinnest soap films has been proved by us to be about 10^{-6} cm. Hence, in thinning to this degree of tenuity, the film would be cooled only a little more than 2° C. But since, if t is the temperature Centigrade,

$$\frac{dT}{dt} = -\frac{T}{550},$$

the increase of surface tension due to the cooling would be only about 0·4 per cent.

Now a colourless film, which has been recently flooded, is certainly 250 times thicker than a black one, so that if the heat were distributed uniformly throughout the whole mass of the film the increase of surface tension would be only 0·0016 per cent.

The enormous discrepancy between this number and that actually given by our experiments (9 per cent. in Experiment III.) cannot be explained away by the small corrections which would no doubt have to be made if data were used which apply accurately to the soap solution instead of those derived from water. One of these corrections would indeed strengthen the argument, for, as the surface tension of the solution is less than that of water, the cooling effect of the stretching would be decreased.

Calculations based on VAN DER MENSBRUGGHE'S experiments indicate differences of surface tension as great as those on which our argument depends. We have, however, proved that the various possible sources of error discussed above, and which have not been previously investigated, do not seriously affect the result. We may add that, although we have only cited a few experiments, we have performed many. Thus when we balanced a sphere against a sphere the sensitiveness was so great that the films broke before the limit to the movement was approached. The change of form was so great that the limiting sensitiveness could not be considered to apply even approximately.

It is not, however, easy to decide what is the particular cause, if it can be referred to one cause only, to which the change in the surface tension of one of the films is due.

Experiment VI.

We tried the effect of increasing largely the quantity of carbonic acid and of oxygen in the air within and without the films, and to this end passed gentle currents of these gases through the film box, and formed the films by means of them instead of air.

As was to be expected, the liquid became turbid under the action of the carbonic

* Baynes' 'Thermodynamics,' p. 156.

acid, and if fresh liquid which had not been exposed to the action of the gas was used to flood the thick film it bulged instead of contracting.

Oxygen, on the other hand, appeared to increase the phenomenon ordinarily observed, or, at all events, to accelerate it.

Thus, when the film box was filled with air, the difference of the diameters increased by 2·07 mm. in 24^m, when the left film was flooded at 3 minute intervals, the right film being allowed to thin.

The films were then blown with purified oxygen, and a current was passed through the box.

In two successive experiments which were then made under the same conditions as before, except that oxygen was used, the change in the diameter was 2·96 mm. and 2·80 mm. in 9 minutes.

These experiments cannot be considered conclusive, but they indicate that the phenomenon under discussion is affected by the nature of the gas with which the films are in contact. To have put the matter to a thoroughly satisfactory test would have required a complete remodelling of our apparatus. We did not carry the inquiry further, partly on this account, and partly because we had collected evidence which proved that the greater tension of the thicker film was not due merely to its thickness. The cause of the difference was therefore outside the immediate scope of our investigation.

One reason for this conclusion is that the results obtained with the same liquid are very irregular. In three consecutive experiments, performed on the same day, in each of which the thin film displayed the colours of the third order, the values of δ were 3·37, 2·50, and 1·73. On the previous day, when a longer interval elapsed between the floodings, two consecutive experiments gave for similar thicknesses $\delta = 1·05$ and 1·56. Again, different solutions behaved very differently. The above results were obtained with a solution of potash soap which had been recently made. An exactly similar solution a year old gave $\delta = 0·48$ when displaying the green of the third order.

In the next place, so much of the change takes place before the thinner film is thin enough to display any colours that if it is really due to the thinness of the film the radius of molecular attraction must be at least$=10^{-3}$ mm. Many of our experiments have shown that between one half and one quarter of the total change takes place while the thin film is still colourless.

On the whole, then, we are inclined to the view that this phenomenon is merely a striking instance of the difficulty which many observers have found in preserving a liquid surface pure. OBERBECK found that the superficial viscosity of water exposed for 24 hours to the air became immeasurably large, but regained its former value when the surface was cleansed by a clean strip of platinum. He concludes, "Wir müssen daher schliessen, entweder, dass der freien Wasseroberfläche ein recht bedeutender Oberflächenwiderstand zukommt, oder dass eine reine Wasseroberfläche in

Berührung mit Luft überhaupt nicht existirt."* It seems probable that a liquid drawn out into a film would be especially liable to such changes, and that the constant renewal of the surface of the thick film would tend to maintain its purity, and therewith its surface tension.

Adopting, then, the conclusion that the rapid fall in the surface tension of a newly formed film is due, not to its thinning, but to a disturbing cause, it remains to be seen whether this can be reduced or eliminated so as to permit a comparison of films of very different thicknesses. We have found that this is possible, but, though the methods which we have adopted are such as would naturally suggest themselves, the determination of the best conditions of experiment has cost a large expenditure of time and trouble.

In the first place, we have employed the method of measuring the principal ordinates only, and using the sensitiveness to calculate the difference of tension (if any) between the films. In what follows these differences will be very small, and we have shown that, in this case, both methods lead to very similar mean results. The method of measuring three ordinates is also too laborious to be used if another will serve equally well. It necessitates continual measurements being made, and, though very useful for the elucidation of the particular point to which it was directed, is very troublesome and fatiguing, as twenty-three readings are necessary to obtain a single comparison. Again, we were not satisfied with the flooded film as a standard with which to compare that which was allowed to thin. The difference of the surface tensions, and, therefore, of the forms of the films, was too great for accuracy. It was thought possible that the comparatively small disturbance produced by retarding the thinning by the electric current might make a film, up which a current was either constantly or at intervals passed, a better standard than one which was flooded between consecutive measurements.

The following experiment, which was made to see if a film could be kept thick and in an approximately constant state by short intermittent applications of the current, will perhaps serve to show the difficulty of eliminating the disturbing cause by any such means.

Experiment VII.

Two cylinders were formed, flooded, and put into communication.

Five minutes afterwards $\delta = -0{\cdot}20$ mm. Both films were colourless for the most part, but displayed thin rings of colour at the top.

The current was then sent up the right cylinder for 10^s. The coloured rings disappeared.

At 9^m from the beginning of the experiment, and about 3^m after the passage of the current, the right film was colourless.

* 'WIEDEMANN, Annalen,' vol. 11, 1880, p. 650.

C_l=G (6, 5) with rings of higher orders at the top.

$\delta=-0{\cdot}38.$

At 14^m, C_l=G (5, 5); the right was colourless, and both had rings at the top.

$\delta=-0{\cdot}27.$

Now, remembering that $\delta=\rho-\lambda$, and that a negative value of δ therefore means that the left film had the larger diameter, this experiment indicates that the passage of the current for 10^s only produced a difference in the diameter of the rings which 3^m afterwards amounted to 0·18 mm., and 8^m afterwards to 0·07 mm., and that the film disturbed by the current had the greater surface tension.

At 15^m the current was sent up the right film for 12^s. The coloured rings disappeared.

At 19^m the right film was faintly coloured, and

$$C_l=\{0{\cdot}5b,\ \text{YG}\ (4,5)\},$$
$$\delta=-0{\cdot}28.$$

The disturbance produced by the current was less than before, which is accounted for by the fact that the film, though colourless, was really thinner than when it was previously applied, and thus, the resistance in circuit being greater, the current was weaker. That the film was thinner is proved by the fact that, whereas after the first application of the current the right film remained for the most part colourless for eight minutes, on the second occasion it showed faint colours after four minutes. This observation shows that in a film which is not very thick the current may be passed for a few seconds without leaving any trace of its action three minutes afterwards, but unfortunately it also proves that such treatment is not sufficient to prevent the film from thinning.

At 20^m the current was sent up the right film for 20^s, and the following measurements were made:—

At 24^m—

$$C_r=\text{R}\ (5,\ 0),\quad C_l=\{1{\cdot}5b,\ \text{G}\ (4,\ 0)\}.$$
$$\delta=-0{\cdot}90.$$

At 29^m—

$$C_r=\text{G}\ (5,\ 7),\quad C_l=\{3{\cdot}0b,\ \text{Y}\ (3,\ 9)\}.$$
$$\delta=-0{\cdot}44.$$

In this case the longer passage of the current caused a considerable disturbance, the effects of which were very marked 9^m afterwards. The experiment was continued in the same way, the measurement showing that a current which produced an appreciable retardation in the thinning also produced an appreciable difference in the diameters.

Seventy-one minutes after the beginning the state of things was as follows:—

$$C_r=\{1{\cdot}0b,\ \text{B}\ (3,\ 5)\},\quad C_l=\{11{\cdot}0b,\ \text{Y}\ (2,\ 7)\}.$$
$$\delta=-0{\cdot}77.$$

The films were then cut off from communication, and the current was passed up the right film for 90^s: the black disappeared and the lower part became colourless. The stop-cock was opened again eight minutes after the passage of the current, and a measurement taken when it had been open two minutes.

$$C_r = \{B\ (3,\ 0),\ \text{colourless}\},\quad C_l = \{14{\cdot}0b,\ R\ (2,\ 0)\}.$$
$$\delta = -1{\cdot}18.$$

Shortly afterwards the thin film broke.

The foregoing observations proved that the disturbance produced by thickening one of the films died out some minutes after the disturbing cause was removed. If, then, the surface tension assumed its final value while a film was still moderately thick it might be possible, by balancing films of very different thicknesses, to obtain some evidence as to whether any further difference of tension due only to the difference in thickness could be detected. We, therefore, gave one of the films a start by thickening the others some time after their first formation, and then compared them when another considerable interval of time had elapsed.

This method is attended with several difficulties. In the first place, the operation takes a long time, during which slow changes in the zero error take place. Thus, if the two films are first compared when both have been recently flooded, and afterwards when one is black and the other coloured, a slight difference in the position of equilibrium may be observed, due to changes in the liquid rings, &c. On some occasions, when one of the films has been entirely black, the lower liquid ring has disappeared. This phenomenon is accompanied by a slight shift in the position of equilibrium. Again, if the start is too short the films are too similar to make the comparison of much use; if it is too long the thin film is apt to break before the thick one is ready for observation. These difficulties are increased by the fact that it is not safe to leave the films in communication while one of them is being thickened. A black film is almost certain to break if subject to a disturbance which may alter its diameter by one or two millimetres. It is, therefore, necessary to separate the films while the thickening takes place, and not to put them again into communication until after the interval which experience has proved to be sufficient to prevent any great change in diameter. We have attempted as far as possible to overcome these difficulties, and have carried out our observations in two different ways.

First Method of Experiment.

The fact that the method of measuring three ordinates confirmed that based upon the measurement of the principal diameters only, in indicating a small difference of surface tension between the films, even when both had been recently flooded, proves either that such differences really exist or that some slight outstanding cause of error affects both methods equally. In either case it seemed best to argue in each experiment, not from the theoretical position of equilibrium, but from that assumed by two films which were as similar as we could make them.

Two cylindrical films were therefore flooded and put into communication. Their diameters were measured several times, and the difference, if constant, gave the zero reading. After an interval, which depended on the rate of thinning, the films were separated, and one was thickened by means of the current, generally until the colours of the third order reached the top. If no black appeared on the thicker film communication was re-established after 17^m, and the diameters were measured about 3^m afterwards. If the black began to appear at the top of the thick film before 17^m after thickening, the stop-cock was opened sooner. By this means we generally succeeded in comparing two films, one of which was nearly all black, while the other displayed a little black and the colours of the first or second orders. If the position of equilibrium was the same as when both films were thick the experiment gave no evidence of any difference of surface tension between a black film and one many times thicker than itself. If it was not the same the apparent difference of surface tension was calculated from the sensitiveness.

Both films were then allowed to thin, and, assuming that that which was already black remained in a constant state, we were able to observe whether any change of diameter took place as the coloured film became black. If it did it furnished us with another measurement of the difference of surface tension under investigation. It is evident that the mean of two such measures obtained from the same films would probably be free from error caused by any slight change in the position of equilibrium due to causes other than the increasing tenuity of the films. Accidental errors would of course disappear on the mean of a number of experiments.

This method is, however, open to an objection which requires discussion. We were seeking for evidence of a difference of surface tension (if any such existed) between a black and a coloured film. Most of the films observed were, however, partly black and partly coloured. If any difference of tension existed between their different parts the films would not be cylinders or simple unduloids, but the black and coloured portions would be of different curvatures. Measurements based on the sensitiveness would not therefore be trustworthy if, upon the comparatively simple changes of form assumed in the calculation of that quantity, other and more complex variations were superposed. We have therefore investigated the form of a film consisting of two parts of different surface tensions, assuming that it does not differ much from a cylinder.

If the surface tensions are T and $T+dT$, the generating curve of the film may be regarded as consisting of two parts, PR and RQ, which produce unduloidal surfaces of different curvatures.

The conditions which these curves must satisfy are as follows :—

(1.) If X_1 and X_2 are the differences of the abscissæ of R and P, and Q and R, respectively, then X_1 and X_2 may be considered as constants which are given by the conditions of the problem.

(2.) The values of the ordinates which correspond to P and Q must both be Y.

(3.) The ordinate of $R(=y)$ must be the same for both curves.

(4.) The tangent at R must be the same for both curves.

(5.) The sum of the volumes of the two unduloids contained between the rings may be taken as given.

(6.) The pressures exerted by the two parts of the film on the enclosed air must be the same.

These eight conditions may be used to determine the eight unknowns, viz., $d\alpha_1$, $d\beta_1$, $d\alpha_2$, $d\beta_2$, ϕ_1 and ϕ_2, the values of ϕ which correspond to P and Q, and ψ_1 and ψ_2, the values of ψ which correspond to R, considered as belonging in the first case to PR, and in the second to RQ.

The discontinuity at R is dependent on the fact that in the cylinder the value of ϕ which corresponds to any given point is indeterminate. We shall carry out the calculation to the first order of small quantities only.

Using the same notation as before, we have, as in equations (15) and (16),

$$k_1^2=\frac{2(d\alpha_1-d\beta_1)}{Y}, \qquad k_2^2=\frac{2(d\alpha_2-d\beta_2)}{Y}, \quad \ldots \ldots \quad (19)$$

$$\left.\begin{aligned} \psi_1-\phi_1&=\xi_1\left\{1-\frac{d\alpha_1+d\beta_1}{2Y}\right\} \\ \phi_2-\psi_2&=\xi_2\left\{1-\frac{d\alpha_2+d\beta_2}{2Y}\right\} \end{aligned}\right\} . \quad \ldots \ldots \quad (20)$$

In like manner we get from (5)

$$V_1/\pi=2\alpha_1^3(1-\tfrac{3}{4}k_1^2)(\psi_1-\phi_1)+\frac{\alpha_1^3k_1^2}{2}(\sin 2\psi_1-\sin 2\phi_1),$$

whence, substituting from (19) and (20),

$$V_1/\pi=2Y^3\xi_1\left(1+\frac{d\alpha_1+d\beta_1}{Y}\right)+Y^2(d\alpha_1-d\beta_1)(\sin 2\psi_1-\sin 2\phi_1).$$

But $2\pi Y^3\xi_1=\pi Y^2X_1$, so that, if dV be the difference between the sum of the volumes of the figures generated by PR and RQ and the volume of the cylinder,

$$\begin{aligned} dV/\pi Y^2=&2\xi_1(d\alpha_1+d\beta_1)+(d\alpha_1-d\beta_1)(\sin 2\psi_1-\sin 2\phi_1) \\ &+2\xi_2(d\alpha_2+d\beta_2)+(d\alpha_2-d\beta_2)(\sin 2\phi_2-\sin 2\psi_2). \quad \ldots \quad (21) \end{aligned}$$

Again, since

$$Y^2=\beta_1^2\sin^2\phi_1+\alpha_1^2\cos^2\phi_1,$$

$$\left.\begin{array}{c} d\beta_1\sin^2\phi_1+d\alpha_1\cos^2\phi_1=0 \\ \text{and similarly} \\ d\beta_2\sin^2\phi_2+d\alpha_2\cos^2\phi_2=0 \end{array}\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (22)$$

Equating the two expressions for the square of the common ordinate at R, we get

$$d\beta_1\sin^2\psi_1+d\alpha_1\cos^2\psi_1=d\beta_2\sin^2\psi_2+d\alpha_2\cos^2\psi_2. \quad . \quad . \quad . \quad . \quad . \quad (23)$$

Since, by BEER's equation,

$$\frac{dy}{dx}=-\frac{\sqrt{(\alpha^2-y^2)(y^2-\beta^2)}}{y^2+\alpha\beta},$$

we have, by equating the expressions obtained by substituting the values of y in terms of α_1, β_1, and ψ_1, and α_2, β_2, and ψ_2,

$$(d\alpha_1-d\beta_1)\sin 2\psi_1=(d\alpha_2-d\beta_2)\sin 2\psi_2. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (24)$$

Substituting from (20) in (23) and (24),

$$d\beta_1\sin^2(\phi_1+\xi_1)+d\alpha_1\cos^2(\phi_1+\xi_1)=d\beta_2\sin^2(\phi_2-\xi_2)+d\alpha_2\cos^2(\phi_2-\xi_2),$$

and

$$(d\alpha_1-d\beta_1)\sin 2(\phi_1+\xi_1)=(d\alpha_2-d\beta_2)\sin 2(\phi_2-\xi_1).$$

Again, substituting in these equations from (22),

$$\frac{d\alpha_1}{d\alpha_2}=\frac{\sin^2\phi_2\cos^2(\phi_2-\xi_2)-\cos^2\phi_2\sin^2(\phi_2-\xi_2)}{\sin^2\phi_1\cos^2(\phi_1+\xi_1)-\cos^2\phi_1\sin^2(\phi_1+\xi_1)}\times\frac{\sin^2\phi_1}{\sin^2\phi_2}, \quad . \quad . \quad . \quad . \quad (25)$$

and also

$$=\frac{\sin 2(\phi_2-\xi_2)}{\sin 2(\phi_1+\xi_1)}\times\frac{\sin^2\phi_1}{\sin^2\phi_2},$$

therefore

$$\frac{\sin(2\phi_2-\xi_2)\sin\xi_2}{-\sin(2\phi_1+\xi_1)\sin\xi_1}=\frac{\sin 2(\phi_2-\xi_2)}{\sin 2(\phi_1+\xi_1)}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (26)$$

Also from (21) and (24)

$$dV/\pi Y^2=2\xi_1(d\alpha_1+d\beta_1)+2\xi_2(d\alpha_2+d\beta_2)-(d\alpha_1-d\beta_1)\sin 2\phi_1+(d\alpha_2-d\beta_2)\sin 2\phi_2$$

$$=\frac{d\alpha_2}{\sin^2\phi_2}(\sin 2\phi_2-2\xi_2\cos 2\phi_2)-\frac{d\alpha_1}{\sin^2\phi_1}(\sin 2\phi_1+2\xi_1\cos 2\phi_1). \quad . \quad . \quad . \quad . \quad (27)$$

Now, if we are dealing with one film only which is not connected with another, and if it would assume the cylindrical form when of uniform surface tension, $d\mathrm{V}=0$. In this case we get from equations (26) and (27)

$$\frac{\tan 2\phi_2 \sin 2\xi_2-1+\cos 2\xi_2}{-\tan 2\phi_1 \sin 2\xi_1-1+\cos 2\xi_1}=\frac{\tan 2\phi_2 \cos 2\xi_2-\sin 2\xi_2}{\tan 2\phi_1 \cos 2\xi_1+\sin 2\xi_1}=\frac{\tan 2\phi_2-2\xi_2}{\tan 2\phi_1+2\xi_1},$$

and, solving these equations, we get

$$\left.\begin{aligned} \tan 2\phi_1 &= \frac{\xi_1 \sin^2 \xi_2-\xi_2 \sin \xi_1 \sin(\xi_1+2\xi_2)+\sin \xi_1 \sin \xi_2 \sin(\xi_1+\xi_2)}{\sin(\xi_1+\xi_2)\{\xi_2 \cos(\xi_1+\xi_2)-\sin \xi_2 \cos \xi_1\}} \\ \tan 2\phi_2 &= -\frac{\xi_2 \sin^2 \xi_1-\xi_1 \sin \xi_2 \sin(\xi_2+2\xi_1)+\sin \xi_1 \sin \xi_2 \sin(\xi_1+\xi_2)}{\sin(\xi_1+\xi_2)\{\xi_1 \cos(\xi_1+\xi_2)-\sin \xi_1 \cos \xi_2\}} \end{aligned}\right\} \quad \ldots \quad (28)$$

If dp is the difference between the internal pressure and that exerted by a cylindrical film of radius Y,

$$dp=-\frac{\mathrm{T}}{\mathrm{Y}^2}(d\alpha_1+d\beta_1)=\frac{2d\mathrm{T}}{\mathrm{Y}}-\frac{\mathrm{T}}{\mathrm{Y}^2}(d\alpha_2+d\beta_2),$$

or, from (22),

$$dp=\frac{\mathrm{T}}{\mathrm{Y}^2}\frac{\cos 2\phi_1}{\sin^2 \phi_1}d\alpha_1=\frac{2d\mathrm{T}}{\mathrm{Y}}+\frac{\mathrm{T}}{\mathrm{Y}^2}\frac{\cos 2\phi_2}{\sin^2 \phi_2}d\alpha_2. \quad \ldots \ldots \quad (29)$$

The angles ϕ_1 and ϕ_2 can now be found from (28). By means of (25) and (29) $d\alpha_1$ and $d\alpha_2$ are given in terms of $d\mathrm{T}$, and thus $d\beta_1$ and $d\beta_2$ are known from (22).

We shall suppose that the suffix 2 refers to the black part of the film. The general nature of the changes of form which the film would undergo as ξ_2 increased can easily be deduced from the equations. When $\xi_2=0$, $\tan 2\phi_2=0$, $\tan 2\phi_1=0/0$.

From the first of these conditions we deduce $\phi_2=0$ or $\pi/2$. The first of these values corresponds to the case where $d\mathrm{T}$ is negative, when the black part of the surface would bulge; the second to the case where $d\mathrm{T}$ is positive. Since in each case the tangent to the unduloid is parallel to the axis, an infinitely thin ring, of different surface tension to the rest of the film, would not cause any finite change of form.

Evaluating $\tan 2\phi_1$, we get

$$\tan 2\phi_1=(\sin 2\xi_1-2\xi_1)/2\sin^2 \xi_1,$$

which gives the initial value of ϕ_1.

The distance from the point halfway between the rings of the point at which the initial unduloid would cut the generating line of the cylinder is $\mathrm{Y}(2\phi_1-\xi_1)$, where ϕ_1 and ξ_1 have, of course, their initial values.

If ξ_1' and ξ_2' be such that $\xi_1=\xi_2'$ and $\xi_2=\xi_1'$, it is evident from (28) that $\tan 2\phi_1=-\tan 2\phi_2'$ and $\tan 2\phi_2=-\tan 2\phi_1'$, so that $\phi_1+\phi_2'=\phi_2+\phi_1'=\pi/2$.

But from (29) and (25)

$$\frac{d\alpha_1}{\sin^2\phi_1}\left\{\frac{\cos 2\phi_1 \sin 2(\phi_2-\xi_2)-\cos 2\phi_2 \sin 2(\phi_1+\xi_1)}{\sin 2(\phi_2-\xi_2)}\right\}=\frac{2\text{Y}d\text{T}}{\text{T}},$$

and from the same equations and (22)

$$-\frac{d\beta_2'}{\cos^2\phi_2'}\left\{\frac{\cos 2\phi_1' \sin 2(\phi_2'-\xi_2')-\cos 2\phi_2' \sin 2(\phi_1'+\xi_1')}{\sin 2(\phi_1'+\xi_1')}\right\}=\frac{2\text{Y}d\text{T}}{\text{T}},$$

whence, substituting for ϕ_1', ϕ_2', ξ_1', and ξ_2' in terms of ϕ_1, ϕ_2, ξ_1, and ξ_2, $d\alpha_1=-d\beta'_2$, and in like manner $d\alpha_2=-d\beta_1'$. It follows that the maximum distances of the two parts of the film from the cylinder are the same whether the black covers $1/n$th or $1-1/n$th of the entire film, but that the maximum contraction in the one case is equal to the maximum bulge in the other, and *vice versâ.*

The following Table contains in the first column the fraction of the entire length of the film over which the change in surface tension is supposed to have extended. In the second and third columns are the corresponding values of ϕ_1 and ϕ_2, calculated for the case in which $\text{X}=1\cdot25/\text{Y}$. The next four columns contain quantities from which $d\alpha_1$, &c., can be determined. In the last column is the ratio of the change of pressure caused by a partial change of surface tension to that produced by the extension of the change over the entire film. Throughout $d\text{T}$ is considered positive.

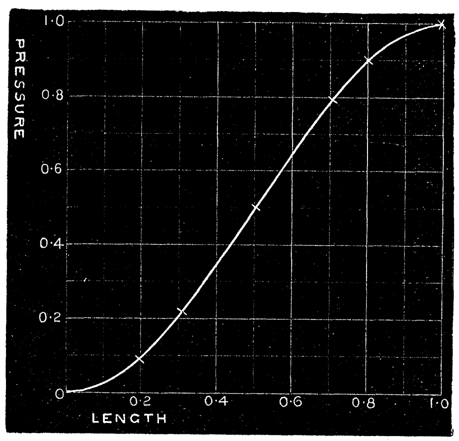
TABLE VII.

$\xi_2/(\xi_1+\xi_2)$	ϕ_1	ϕ_2	$\text{T}d\alpha_1/\text{Y}d\text{T}$	$\text{T}d\beta_1/\text{Y}d\text{T}$	$\text{T}d\alpha_2/\text{Y}d\text{T}$	$\text{T}d\beta_2/\text{Y}d\text{T}$	$\text{Y}dp/d\text{T}$	dp/dp'
0	−23° 16′	90° 0′	0	0	2	0	0	0
0·2	−21 40	100 30	0·037	−0·234	1·867	−0·064	0·197	0·0985
0·3	−20 35	103 40	0·069	−0·489	1·679	−0·099	0·420	0·2100
0·5	−17 54	107 54	0·116	−1·116	1·116	−0·116	1·000	0·5000
0·7	−13 40	110 35	0·099	−1·679	0·489	−0·069	1·580	0·7900
0·8	−10 30	111 40	0·064	−1·867	0·234	−0·037	1·803	0·9015
1·0	0	113 16	0	−2	0	0	2	1·0000

Since, when $d\text{T}$ is positive, $d\beta_1$ and $d\alpha_2$ refer to parts of the two unduloids which do not lie between the rings, it follows from this Table that the greatest divergence of any part of the generating curves from the generating line of the initial cylinder is $0\cdot116\text{Y}d\text{T}/\text{T}$.

If, therefore, as in most of our experiments, Y = 10 mm. (nearly), and if we take $d\text{T}/\text{T}=0\cdot01$, it follows that the greatest change in the diameter of the film caused by the gradual spread of a change of surface tension of 1 per cent. would be only a little greater than 0·02 mm., a quantity which certainly lies within the limits of the error of experiment. If, therefore, a film was half black and half coloured it would differ inappreciably from a cylinder if the difference of surface tension was only 1 per cent. The pressure, however, would have altered by 0·5 per cent., and if the film were now put into communication with another which was coloured throughout an appreciable change in the principal diameters would take place. This is evident from the fact that, if the change in the pressure exerted by the first film had been due to its surface tension having altered throughout by 0·5 per cent., the difference in the principal diameters would have been 0·451/2=0·225 mm. It follows, therefore, that if two films are in communication, and if the surface tension of a part of one differs slightly from that of the remainder, the asymmetry of this film is small compared with the change produced in the principal diameters of the two films. We may, therefore, as a first approximation to the truth, regard the sensitiveness of an experiment in which part only of the film is black as proportional to dp/dp'.

The numbers given in the last column of Table VII. may be plotted in a curve, the abscissæ being the fractions of the whole length of the cylinder covered by the black, and the ordinates the values of dp/dp'.



If in any experiment the length of the black part of the film increased from (say) 0·2 to 0·8 of the whole length of the cylinder, the effective length would be 0·6; and the alteration of pressure is shown by the curve to be from 0·1 to 0·9, *i.e.*, 0·8 of the whole alteration which would be produced if a coloured film became completely black.

If the thicker film displays some black, the effective length of the black in the thinner film is the difference of the lengths in the two films. It will be observed that different changes in the pressure may be produced by the same change in the effective length. Thus dp/dp' is 0·66 or 0·8 according as the length of the black increases from 0 to 0·6, or from 0·2 to 0·8 of the whole length of the cylinder.

We now proceed to describe the experiments. It is necessary to do this in considerable detail, as no two were alike, and the results do not admit of being stated shortly so as to include all facts which might have affected the results.

Experiment VIII.

Three measurements were made when the films were in similar states.

t	C_r	C_l	δ	Mean.
m.				
24	{2·5b, G (2, 2)}	{0·5b, B (3, 0)}	−0·83	
32	{4b, B (2, 3)}	{2b, G (2, 9)}	−0·86	
37	{5b, R (1, 0)}	{3b, B (2, 6)}	−0·84	−0·84

The films were then separated, and the current was sent up the left film till the colours of the third order reached the top. This operation was repeated at 70^m. The current was taken off at 74^m; at 88^m the films were again connected, and the following observations were taken :—

t	C_r	C_l	δ	Mean.
h. m.				
1 30	All black	{1b, G (2, 0)}	−0·52	
35	" "	{2·5b, B (2, 2)}	−0·78	
40	" "	{4b, O (1, 8)}	−0·69	−0·66

In this case the final measurements gave a comparison between two films, of which one was black and the other displayed on the average 2·5 mm. of black only. The difference between the principal diameters was, however, only 0·18 mm. different from what it was when the films were in very similar states, the change being such as to prove that the left film had contracted a little, *i.e.*, that the surface tension of the right film when black was a little less than when it was coloured.

If this were so, however, since 2·5 mm. of the left film were black, the effective difference between the tensions of the two films was 0·98 of what it would have been, had the left film been coloured throughout. The sensitiveness is therefore $4·51 \times 0·98 = 4·42$, and thus

$$dT/T = -0·018/4·42 = -0·0041.$$

Hence according to this experiment the surface tension of a black film is less than that of a coloured one by 0·41 per cent.

Experiment IX.

In this case one of the films which had become partly black in a previous experiment was used. Hence no initial zero was obtained. The thicker film was again thickened by the current 14^m after the films were first put into communication. The circuit was broken at 23^{m}, and the stop-cock was opened at 32^{m}. The following observations were taken :—

t	C_r	C_l	δ	Mean.
m.				
41	All black	{3b, B (3, 0)}	+0·51	
45	,,	{4b, O (2, 0)}	+0·23	
49	,,	{5b, G (2, 5)}	+0·39	+0·38

The value of δ fell as the left film thinned. The last two observations were as follows :—

t	C_r	C_l	δ	Mean.
h. m.				
1 39	All black	{21b, W (1, 5)}	−0·05	
0 44	,,	{23b, W (1, 5)}	−0·16	−0·10

The right film may be presumed to have remained in the same state throughout the experiment. The length of the black part of the left film increased from 4 mm. to 22 mm. The difference of pressure must therefore have increased from 0·05 dp' to 0·95 dp', *i.e.*, by 0·9 of the total difference between a coloured and a black film. During the same time δ changed by 0·48 mm., the movement being such as to indicate an increase in the diameter, *i.e.*, a falling-off in the tension of the film which was becoming black.

Hence

$$dT/T = -0{\cdot}048/4{\cdot}51 \times 0{\cdot}9 \equiv -1{\cdot}18 \text{ per cent.}$$

Experiment X.

The films were made as usual, and the following preliminary observations were taken :—

t	C_r	C_l	δ	Mean.
m.				
5	R (5, 5)	R (5, 0)	−0·34	
7	R (4, 5)	R (4, 5)	−0·42	
12	R (3, 5)	R (3, 5)	−0·38	−0·38

The right film was then thickened by means of the current. The circuit was broken at 17^{m}, the stop-cock opened at 35^{m}. The first reading gave $\delta = -0{\cdot}16$, and the value of δ increased (algebraically). The following observations were taken at the times indicated :—

t	C_r	C_l	δ	Mean.
h. m. 0 54 0 58	{7*b*, B (2, 3)} {8*b*, B (2, 0)}	{23*b*, W (1, 3)} All black	+0·21 +0·11	+0·16
1 31 1 36	{17*b*, G (2, 0)} {20*b*, G (2, 2)}	All black "	+0·21 +0·20	+0·20

The first comparison showed that δ had altered by 0·54 mm., the movement being such as to indicate an increase in the surface tension of the film which displayed the most black. Since the thicker film had 7·5 mm. of black, while the thinner had an average amount of 24·5 mm., the difference of pressure could only have been 0·8 of its full amount. Hence

$$d\mathrm{T}/\mathrm{T}=0{\cdot}054/4{\cdot}51\times0{\cdot}8\equiv1{\cdot}5 \text{ per cent.}$$

During the second part of the experiment the movement of the zero continued in the same direction, which must be interpreted as a falling-off in the surface tension of the right film, which was now becoming black.

As the black extended only from 7·5 to 18·5 mm.,

$$d\mathrm{T}/\mathrm{T}=-0{\cdot}004/4{\cdot}51\times0{\cdot}6\equiv-0{\cdot}15 \text{ per cent.}$$

This experiment illustrates the importance of obtaining, if possible, two measurements with the same pair of films. The fact that the change in the magnitudes of the principal diameters went on without reference to the thinning of the films is strong evidence that that change was not caused by the alterations in their relative thicknesses.

Experiment XI.

The same films were used as in Experiment I. The final observations in that experiment gave 0·18 as the initial difference of the diameters. At the end both films were first thickened by the current and then flooded. The value of δ found was 0·44. The mean of the two values is 0·32.

During the greater part of the time that the experiment lasted the current was passing. The circuit was broken at $2^h\ 11^m$ after the films were first made, and the following observation was taken :—

t	C_r	C_l	δ
h. m. 2 16	{17*b*, W (1, 0)}	{0·5*b*, W (1, 5), Y (1, 5)}	0·41

The change in the value of δ from the mean of the two values obtained when the films were in the same state was 0·09 mm.

Hence

$$dT/T = -0{\cdot}009/4{\cdot}51 \times 0{\cdot}72 \equiv -0{\cdot}28 \text{ per cent.}$$

Experiment XII.

The following observations were made to determine the zero :—

t	C_r	C_l	δ	Mean.
m.				
17	Colourless	Colourless	1·16	
22	{1*b*, B (2, 5)}	R (2, 5)	1·12	1·14

The current was then passed up the left film, but in spite of this it continued to become thinner. The circuit was broken at 31^m, the stop-cock was opened at 37^m, and the following observations taken :—

t	C_r	C_l	δ
m.			
39	All black	{5*b*, Y (1, 5), B (2, 5)}	1·12
53	" "	All black	0·92

The first comparison gives

$$dT/T = +0{\cdot}002/4{\cdot}51 \times 0{\cdot}89 \equiv +0{\cdot}05 \text{ per cent.}$$

The second gives

$$dT/T = -0{\cdot}020/4{\cdot}51 \times 0{\cdot}90 \equiv -0{\cdot}49 \text{ per cent.}$$

Experiment XIII.

On this occasion the films were allowed to thin for some time before one of them was thickened. The value of δ changed considerably. Thus at 13^m $\delta = 0{\cdot}09$, at 16^m $\delta = 0{\cdot}42$, at 19^m $\delta = 0{\cdot}60$. The last three readings gave the following results :—

t	C_r	C_l	δ	Mean.
m.				
24	{0·75*b*, Y (3, 5)}	{G (4, 0)}	0·58	
29	{0·75*b*, G (3, 0)}	{G (3, 9)}	0·61	
33	{0·75*b*, R (2, 9)}	{1*b*, R (2, 6)}	0·66	0·62

The current was used to accelerate the thinning of the one film and to retard that of the other. The circuit was broken at 53^{m}, and afterwards the following measurements were made :—

t	C_r	C_l	δ	Mean.
h. m. 1 18 21 24	{6b, O (1, 5)} {8b, Y (1, 5)} {10b, Y (1, 2)}	{22b, W (1, 5)} {25b, W (1, 5)} All black	0·10 0·02 0·10	0·07
59	{24b, Y (1, 5)}	All black	−0·14	−0·14

The effective change in the length of the black in the first comparison was from 8 mm. to 24 mm., the alteration in δ was 0·55 mm. in the direction indicating a falling-off in the surface tension of the black film. Hence

$$dT/T = -0{\cdot}055/4{\cdot}51 \times 0{\cdot}77 \equiv -1{\cdot}59 \text{ per cent.}$$

From the second part of the experiment we get

$$dT/T = 0{\cdot}021/4{\cdot}51 \times 0{\cdot}77 \equiv 0{\cdot}60 \text{ per cent.}$$

Second Method of Experiment.

Our second group of experiments was intended to utilize a fact which we had observed, viz., that a spherical film thins more slowly than a cylinder. A cylinder of the usual dimensions (length$=1{\cdot}25\times$diameter) was formed on one of the smaller pairs of rings. The larger rings were used to form the sphere, and, since the ratio of their diameter to that of the smaller pair was very approximately 1·6, it is evident, if the distance between them was made $=1{\cdot}2\times 2Y$, that a sphere would be formed the radius of which was 2Y, and which would therefore be in equilibrium with the cylinder if the surface tensions were identical. In consequence of the slow thinning of the sphere, a longer interval could generally be allowed after flooding with this arrangement than when two cylinders were employed.

It was found that, even when the films were newly formed, the ratio of the two diameters always differed appreciably from its theoretical value of 2 : 1. This was probably due to slight errors of adjustment and to the effect of the liquid rings. The experiment consisted in testing whether the difference between the diameters was the same when the two films were thick as it was when the cylinder was much thinner than the sphere.

The sensitiveness was 3·7.

The spherical film rarely showed more than one or two millimetres of black, the effect of which may be neglected. When the cylindrical film was only partially black the theoretical sensitiveness can be calculated as in the last group of experiments.

We give, as in the last group, *all* the experiments which were made in which a sufficient difference of thickness was established to make the comparison useful.

Experiment XIV.

The stop-cock was opened five minutes after the films had been made and flooded. No further flooding took place. At 9^m after communication had been established readings were begun.

The colours of the sphere and cylinder are indicated by C_s and C_c, the difference between their diameters by δ.

t	C_s	C_c	δ	Mean.
m.				
9	R (4, 5)	Y (3, 5)	17·60	
12	G (4, 5)	B (3, 7)	17·82	17·71

We now omit a number of readings, the differences given by which were

$$\delta = 17{\cdot}77,\ 17{\cdot}67,\ 17{\cdot}83, \text{ and } 17{\cdot}79.$$

Afterwards the following observations were taken :—

t	C_s	C_c	δ
m.			
21·5	B (3, 0)	{ 5*b*, W (1, 9)}	17·90
24·5	R (2, 5)	{23*b*, (?) }	17·89

The sudden formation of the black was in this experiment accompanied by no change in the value of δ, hence $dT=0$.

Experiment XV.

At the beginning of the experiment the following measurements were made :—

t	C_s	C_c	δ	Mean.
m.				
6	Colourless	Colourless	20·36	
11	”	G (5, 2)	20·36	20·36

The films were then separated. At 27^m the sphere was flooded. The stop-cock was opened at 46^m, and the following values of δ were obtained, beginning at 48^m :—

$$\delta = 19{\cdot}87,\ 20{\cdot}03,\ 20{\cdot}15,\ 20{\cdot}04,\ 20{\cdot}11.$$

The last three readings were as follows :—

t	C_s	C_c	δ	Mean.
h. m.				
1 2	{1*b*, G (3, 9)}	{23*b*, Y (1, 3)}	20·09	
5	{1*b*, G (3, 0)}	{24*b*, Y (1, 3)}	20·12	
9	{1*b*, R (2, 6)}	All black	19·96	20·06

We noticed that in this case, when the black reached the bottom, the liquid ring disappeared, and we are, therefore, inclined to attribute the last reading to some slight change in Y.

The decrease in the value of δ indicates a bulging of the cylinder, *i.e.*, a falling-off in its surface tension.

$$dT/T = -0{\cdot}030/3{\cdot}7 \times 0{\cdot}98 \equiv -0{\cdot}83 \text{ per cent.}$$

Experiment XVI.

The first two readings were as follows :—

t	C_s	C_c	δ	Mean.
m.				
10	Colourless	R (6, 0)	19·85	
15	,,	R (6, 0)	19·78	19·81

The films were separated. At 27^m the sphere was flooded. The stop-cock was opened at 49^m, and the following values of δ were obtained, beginning at 51^m :—

$$\delta = 19{\cdot}51,\ 19{\cdot}54,\ 19{\cdot}40,\ 19{\cdot}46.$$

The last four readings were as follows :—

t	C_s	C_c	δ	Mean.
h. m.				
1 7	{1*b*, BR (3, 5)}	{24*b*, O (1, 5)}	19·55	
12	{1*b*, Y (3, 5)}	All black	19·65	
17	{1·5*b*, G (3, 2)}	,,	19·49	
22	{2*b*, B (3, 7)}	,,	19·55	19·56

In this case the liquid ring did not disappear when the black reached the bottom.

$$dT/T = -0{\cdot}025/3{\cdot}7 \equiv -0{\cdot}68 \text{ per cent.}$$

Experiment XVII.

Two measurements were made, when the sphere was colourless, and the cylinder also, with the exception of about 2 mm. at the top, which showed rings of colour.

t	δ	Mean.
m. 5 8	20·67 20·69	20·68

The films were then separated, and the sphere was flooded. At 40^{m} the stop-cock was again opened, and the following readings, beginning at 44^{m}, gave

$$\delta = 20{\cdot}58,\ 20{\cdot}69,\ 20{\cdot}71,\ 20{\cdot}66,\ 20{\cdot}66.$$

The last two readings were as follows :—

t	C_s	C_c	δ	Mean.
m. 58·5 60·0	{2*b*, Y (2, 0)} {2·5*b*, G (2, 5)}	{17*b*, Y (1, 5), R (1, 5)} {18*b*, Y (1, 5)}	20·76 20·79	20·77

$$d\mathrm{T}/\mathrm{T} = 0{\cdot}009/3{\cdot}7 \times 0{\cdot}76 \equiv 0{\cdot}32 \text{ per cent.}$$

Experiment XVIII.

Three measurements were made when the films were colourless, or very nearly so.

t	δ	Mean.
m. 7 10 12	20·69 20·88 20·78	20·78

The following readings gave $\delta = 20{\cdot}61,\ 20{\cdot}85,\ 20{\cdot}76,\ 20{\cdot}80,\ 20{\cdot}71,\ 20{\cdot}84,\ 20{\cdot}96,\ 20{\cdot}75,\ 20{\cdot}97$.

The last two observations were as follows :—

t	C_s	C_c	δ	Mean.
h. m. 1 11 1 18	{0·75*b*, G (4, 5)} {0·75*b*, BR (3, 8)}	{18*b*, G (2, 5)} {22*b*, W (1, 5)}	21·12 21·18	21·15

$$d\mathrm{T}/\mathrm{T} = 0{\cdot}037/3{\cdot}7 \times 0{\cdot}87 \equiv 1{\cdot}15 \text{ per cent.}$$

Experiment XIX.

When both films were colourless the following observations were made :—

t	δ	Mean.
7 8	19·08 19·25	19·16

Successive readings gave afterwards

$$\delta = 19{\cdot}08,\ 19{\cdot}03,\ 19{\cdot}12,\ 19{\cdot}19,\ 18{\cdot}94,\ 19{\cdot}26, \text{ and } 19{\cdot}14.$$

The last two observations were as follows :—

t	C_s	C_c	δ	Mean.
47 51	{1*b*, G (5, 6)} {1*b*, G (5, 6)}	{23*b*, Y (1, 5)} {25*b*, W (1, 5)}	19·29 19·08	19·18

Hence

$$dT/T = 0{\cdot}002/3{\cdot}7 \times 0{\cdot}98 \equiv 0{\cdot}06 \text{ per cent.}$$

Results of the Experiments.

The above experiments give no indication of a continuous change in the surface tension as the film becomes thinner. The differences observed are irregular and such as would arise from accidental causes.

Thus, in Experiment VII., the black film showed a deficiency of surface tension of 0·41 per cent. when balanced against a film which displayed the blue and green of the second order. In Experiment IX. the surface tension of the black film, also balanced against another, which showed the blue of the second order, was in excess by 1·5 per cent.

In all cases where the same experiment has furnished two results they make dT of opposite signs, thereby indicating that the difference between the two films is not due to the fact that one is thicker than the other.

The results are summed up in the following table :—

TABLE VIII.

No. of Experiment.	Average effective length of black in m.m.	$\frac{dp}{dp'}$	dT/T (in percentages).
VIII.	23·5	0·98	−0·41
IX.	18·0	0·90	−1·18
X.	17·0	0·80	1·50
	11·0	0·60	−0·15
XI.	16·5	0·72	−0·28
XII.	20·0	0·89	0·05
	21·0	0·90	−0·49
XIII.	16·0	0·77	−1·59
	16·0	0·77	0·60
XIV.	18·0	0·0	0·0
XV.	24·0	0·98	−0·83
XVI.	26·0	1·00	−0·68
XVII.	17·5	0·76	0·31
XVIII.	20·0	0·87	1·15
XIX.	24·0	0·98	0·06
Mean	..	..	−0·13

The experiments are not all of the same value. Those in which dp/dp' is most nearly unity are better than those in which it is small. So many other considerations, however, affect the weight of the observation, *e.g.*, the time during which it lasts, &c., &c., that we have made no attempt to discriminate between them.

The range of the above observations is from the green of the fifth order to the black of the first. In Experiment XIX. a film almost entirely black was balanced against another, the colour of which was G(5, 6). This tint corresponds to a thickness of about 1350×10^{-6} mm. The value of dT/T was in this case unusually small.

In all these experiments the black extended over the film quietly and regularly. At times the black is formed with something like a convulsion. Not only does it spread with extraordinary rapidity, but the edge is violently disturbed and large patches rise through the coloured part of the film. Whenever this occurs the film breaks before long, but in four cases we were able to obtain measurements before rupture. We are not able to produce this phenomenon at will, but the few observations we have been able to make on it are in agreement among themselves, and we therefore describe them, as we think they make it necessary to generalise our results with very great caution.

In each case we give the colours and value of δ from observations taken immediately before and after the sudden increase of the black surface. A rapid increase was observed in Experiment XIV., but the general character of the mode of formation was normal. The increase tabulated in the last column is the change in δ taken positive when the thinner film bulged.

Experiment XX.

t	C_r	C_l	δ	Increase.
m.				
21	{5*b*, O (1, 3)}	{7*b*, W (1, 7)}	−0·25	
24	{10*b*, W (1, 7)}	{20*b*, W (1, 5)}	−0·60	+0·35

Experiment XXI.

t	C_r	C_l	δ	Increase.
m.				
16	{2·5*b*, R (1, 0)}	{2*b*, R (1, 0)}	+0·12	
20	All black	{13*b*, Y (1, 0)}	+0·65	+0·53

Experiment XXII.

t	C_r	C_l	δ	Increase.
m.				
20	{15*b*, Y (1, 3)}	{4*b*, B (2, 0)}	−0·27	
24	All black	{5*b*, Y (1, 8)}	+0·48	+0·75

Experiment XXIII.

t	C_r	C_l	δ	Increase.
m.				
22	{3*b*, W (1, 5)}	{0·5*b*, O (1, 5)}	+0·40	
25	{23*b*, O (1, 5)}	{3*b*, W (1, 5)}	+1·01	+0·61

In all these cases there was a sudden increase in the diameter of the film which thinned most rapidly in the peculiar way just described. We do not wish to lay too much stress on experiments which can only be produced by accidental circumstances, but they certainly suggest the inquiry whether one of those circumstances may not be something abnormal in the thickness of the black. If its surface tension were really lower than usual, the rapid formation of the black surface and the convulsions by which it is accompanied would be intelligible.

We therefore think it best to state the general result of our inquiry as follows :—

When the black part of a soap film forms in a normal way, spreading slowly over the surface, no evidence of any change in surface tension dependent on the thickness of the film is furnished by a direct comparison of the tensions of thin and thick films over a range of thickness extending from 1350 *to* 12 *millionths of a millimetre.*

Our observations also justify the statement that—

This conclusion is based upon a method of experiment by which a change of one-half per cent. in the value of the tension must have been detected, had it existed.

The further question remains, can any inference be drawn from these observations as to the magnitude of the radius of molecular action?

On this point we venture to think that, if the magnitude of that length is to be settled merely by reference to the equality of the surface tensions of thick and thin films, we have found evidence in favour of its being less than 6×10^{-6} mm. (half the thickness of an ordinary black film), far stronger than that on which the frequently quoted statement of PLATEAU that it is less than 50×10^{-6} mm. is based.

Our observations have been more numerous and more sensitive than his, and on the other hand we have used films much thinner than those employed by him, or by VAN DER MENSBRUGGHE in his confirmatory observations.

We must admit, however, that we are unwilling to draw any such conclusion until an explanation of the discontinuity in the thickness at the edge of the black is forthcoming, which is not incompatible with it. The regular recurrence of that phenomenon suggests that it must in some way be connected with the extreme tenuity of the film on one side of it. We thought it well that PLATEAU's method should be pushed (as we venture to think we have pushed it) beyond the point where he and VAN DER MENSBRUGGHE left it, but the fact that it has led to a negative result does not diminish the significance of the sharp edge of the black.

As far as we are aware, no suggestion has yet been made as to the cause of the discontinuity. We have necessarily had our attention directed to it, and, though our views are at present little more than speculations, yet it may perhaps conduce to a useful discussion if we suggest a cause which might, we think, furnish a satisfactory solution of the difficulty.

Suggestion as to the Cause of the Discontinuity at the Edge of the Black Part of a Soap Film.

It may be convenient if we collect together the various facts which constitute all that is certainly known as to the behaviour and constitution of a black film.

1.* The black part of a soap film in equilibrium, and not subjected to the action of an external force, is always separated from the rest of the film by a clearly defined boundary.

A gradual transition from the black to the thicker parts of the film is only observed either in a film which thins rapidly and breaks soon (when it is a very transient phenomenon) or when an electric current is passed through the film.

2. The discontinuity in the thickness indicated at the boundary varies very much

* 'Roy. Soc. Proc.,' vol. 26, p. 334.

on different occasions. We have seen black at the top of a film of which the rest was colourless, and therefore probably 250 times thicker than the black part.

3.* The thickness of the black in different films varies between narrow limits only, viz., from 7 to 14 millionths of a millimetre.†

4.* In the same film the thickness of the black remains constant, at all events from a short time after its first formation.

5. No certain difference of surface tension can be detected by direct experiment between a persistent black film and a film more than one hundred times thicker.

6.‡ If an electric current of sufficient intensity is passed through a film which is partly black, the boundary becomes ill-defined, and there is a gradual transition from the thickness of the coloured to that of the black part of the film.

7. When the current is broken the grey colour which has bridged over the gap between the black and the rest of the film disappears, and the definite boundary, indicating a discontinuity in thickness, is re-established. This operation occupies only a few seconds.

The existence of the discontinuity and statements (6) and (7) can best be explained if we suppose that for certain thicknesses intermediate between the black and the white of the first order the film is in a state of instability. It may be maintained in this state by the application of an external force, but spontaneously abandons it as soon as the constraint is removed.

The observations recorded in this paper prove that, under ordinary circumstances, the black and coloured films have the same surface tension to within 0·5 per cent. [The re-establishment of the discontinuity between the black and coloured parts of the films, referred to in statement (7) above, is not instantaneous, but takes place in from ten to fifteen seconds. If, then, the force which produces this result is a difference of surface tension, it must be very small. We are not, therefore, compelled to suppose that the viscosity of the black is great, as would have been necessary, had a measurable difference of surface tension been detected.—Nov. 16, 1886.] On the other hand, there is evidence that a difference of surface tension, so small that it would probably be impossible to measure it, may produce movements in the surface of a moderately thick bubble.

Thus FÉLIX PLATEAU § found that the slight elevation of temperature caused by bringing the finger near a film produced movement, and every one is acquainted with the violent currents seen in a newly-formed bubble.

If this be admitted, the discontinuity at the edge of the black could be explained if we suppose that the surface tension has a critical value in the grey part of the film,

* 'Phil. Trans.,' vol. 174 (Pt. 2, 1883), p. 645.

† In fifteen out of eighteen measurements made on single films the results lay between 10·7 and 13·4 millionths of a millimetre.

‡ 'Phil. Mag.,' vol. 19, 1885, p. 94.

§ 'Statique des Liquides,' vol. 1, p. 294.

which is always missing if the film is in equilibrium (*i.e.*, not thinning very rapidly) and under the action of its own molecular forces only.

In discussing such a theory, it is of primary importance to determine whether a critical value of the surface tension is physically possible.

It is usual to assume that if the thickness of the film is less than that of two surface layers the tension must be less than that of the liquid in mass.

Thus PLATEAU* argues that in such a film the two layers "doivent nécessairement exercer des actions moins fortes, et conséquemment la somme de celles-ci, c'est-à-dire la pression sur l'air intérieur, doit être plus petite que ne l'indique la formule."

Such arguments are based upon the assumption that the force in play between neighbouring molecules is attractive at all distances. The force exerted on a molecule by its neighbours must no doubt be, on the whole, attractive, and if the film is thin enough the surface tension must diminish. It is, however, usual, in dealing with other problems in molecular mechanics, to assume the existence of repulsive forces acting at all events between certain limits as to distance. We need only refer to the well-known instance of some forms of the dynamical theory of gases, and to the fact that the most recent theory of the nature of matter lately put forward by Professor OSBORNE REYNOLDS† leads to the conclusion that the force between two molecules which approach each other is alternately attractive and repulsive.

If such an alternation really takes place the surface tension of a thinning film will alternately increase and diminish. This is clearly pointed out by MAXWELL in his article on "Capillary Action" ('Encycl. Brit.'), in which he says :—"The force between the particle and the liquid is certainly on the whole attractive, but if between any two small values of c [the distance of a particle from the surface] it should be repulsive then for films whose thickness lies between these values the tension will increase as the thickness diminishes, but for all other cases the tension will diminish as the thickness diminishes."

It appears, therefore, that a critical value of the surface tension is not inconsistent with received views as to the nature of the forces in play between the particles of a liquid, and if it existed it would produce phenomena similar to those observed at the edge of a black film. In all cases we have supposed that the surface tension finally diminishes when the film is very thin, and is constant when it is very thick. If it has a critical value between these two states, the two simplest suppositions which we can make are (1) that it has a maximum and a minimum value, (2) that it has a maximum value only.

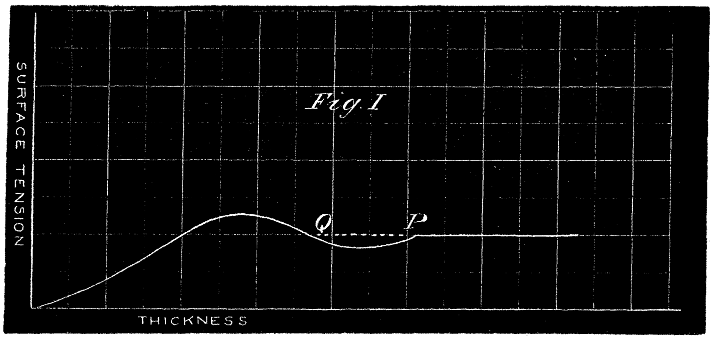
(1.) The first of these, which is the more complex supposition, affords in some respects the better explanation of the behaviour of the black part of the film. Let us suppose that the change in the surface tension as the film becomes thinner is represented by the annexed curve (fig. 1).

* 'Statique des Liquides,' vol. 1, p. 205.

† 'Phil. Mag.,' vol. 20, 1885, p. 479.

When the film became a little thinner than the degree of tenuity represented by P a state of unstable equilibrium would be reached. The thicker parts of the film would tear the thinner parts asunder, but rupture would be prevented by the fact that when the point of minimum surface tension was passed the resistance would increase until, when the thickness corresponding to Q was attained, the tensions of the thin and thick parts of the film would be the same and equilibrium would again be possible. The equilibrium would be stable, because if the film became thinner its surface tension would increase, and it would tend to contract and thus to thicken.

Such a theory would explain the approximately constant thickness of the black, on the ground that it would be impossible for it to exist except at a thickness such that its surface tension was nearly equal to that of the liquid in mass. When the film is very thin its tension would probably alter rapidly with the thickness, and thus the latter would be confined within narrow limits.



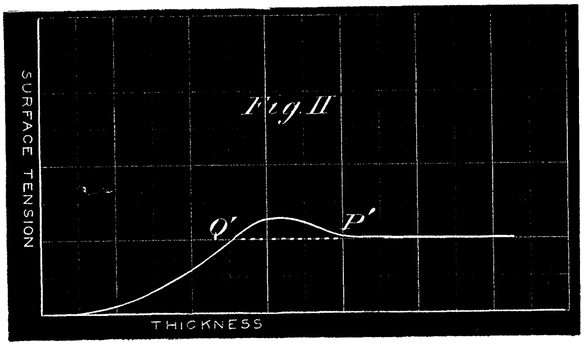
These considerations would not apply to the liquid on the thicker side of the boundary. Its surface tension being independent of the thickness, the magnitude of the latter would be indifferent.

If, as is possible by means of the electric current, the discontinuity was filled up, by liquid being forced into the black space, the equilibrium would be unstable. As soon as the external force was removed the "grey," intermediate in thickness to the black and coloured films, would be absorbed or stretched until it became black.

(2.) If the simpler supposition is made that there is only one alternation of repulsion and attraction to be considered, the law of the change of the surface tension might be represented as in fig. 2.

In this case there would be a preliminary difficulty in explaining the formation of the black, inasmuch as when the point P′ was reached any further decrease in thickness would be resisted by an increase in tension. As a matter of fact, however, the black is generally first formed in small specks, and if, owing to a sudden disturbance, the film were thinned to below the maximum of surface tension, equilibrium would be possible if the thickness were that corresponding to Q′. The parts of the film of thickness intermediate to P′ and Q′ would shrink, and an apparent discontinuity would be established.

This supposition is also less satisfactory than the last, inasmuch as the equilibrium would be unstable. An accidental thinning below Q′ would produce rupture. The fact that this does not occur at once might be explained by supposing that the surface viscosity would play a more important part as the film became thinner.



We need hardly point out that the best way of attempting to test such theories would be to measure the surface tension of a grey film. Unfortunately, however, such a film can only be obtained when the electric current is passing, and the very fact that the grey displays itself is a proof that changes in the surface are going on which may complicate the conclusions to be drawn from the experiment.

We have frequently tried to secure satisfactory observations of this kind, but have not succeeded in obtaining any in which we could with certainty discriminate between the possible effects of the renewal of the surface and a real change in surface tension due to a change in the thickness. Experiments XX. to XXIII. are the only observations we have made in which an apparent change of surface tension could not be accounted for by the change of surface. In these observations, however, the latter cause would have produced a contraction instead of a bulging of the black film, and they cannot therefore be set down as particular cases of the phenomenon studied in the earlier part of the paper.

On one occasion also, when we thickened a black film by passing a current through it till it became grey, no appreciable change of the diameters took place. This is, perhaps, on the whole in favour of the first of the above hypotheses, as the renewal of the surface and the decrease of the "specific" tension would act in opposite directions.

Our observations do not, therefore, throw much light on this intricate question. Experiments which might do so would have to be made with far more complicated apparatus, and with very uncertain prospect of success. Nothing that we have noticed, however, negatives the view that the discontinuity at the edge of the black is connected with a critical value of the surface tension, caused by an alternation from attraction to repulsion in the inter-molecular forces, if the variations in the magnitude of the surface tension for thicknesses $> 12 \times 10^{-6}$ mm. are small. On the other hand, we are not aware of any other suggested explanation. That which we offer is based upon a view of the nature of the inter-molecular forces in a liquid which is frequently neglected, but which was recognised by MAXWELL as tenable. The first hypothesis offers, at all events, a plausible explanation of the discontinuity, of the persistence of the film in spite of the sudden decrease in thickness, and of the constant thickness of the black portion of the film.

POSTSCRIPT.

(Added June 18, 1886.)

Sir WILLIAM THOMSON has informed us in the course of conversation that he suggested a minimum of surface tension as the cause of the sharp edge of the black in a lecture delivered at the Royal Institution on Friday, January 29, 1886. The discourse has not yet been published, but we are, by his kindness, enabled to give the passage in question from a proof:—

"Well-known phenomena of bubbles, and of watery films wetting solids, make it quite certain that the molecular attraction does not become sensible until the distance is much less than 250 micro-millimetres. From the consideration of such phenomena, QUINCKE ('Poggendorff, Annalen,' 1869) came to the conclusion that the molecular attraction does become sensible at distances of about 50 micro-millimetres. His conclusion is strikingly confirmed by the very important discovery of REINOLD and RÜCKER that the black film, always formed before an undisturbed soap bubble breaks, has a uniform or nearly uniform thickness of about 11 or 12 micro-millimètres. The abrupt commencement and the permanent stability of the black film demonstrate a proposition of fundamental importance in the molecular theory. The tension of the film, which is sensibly constant when the thickness exceeds 50 micro-millimetres, diminishes to a minimum, and begins to increase again when the thickness is diminished to 10 micro-millimetrés. It seems not possible to explain this fact by any imaginable law of force between the different portions of the film supposed homogeneous, and we are forced to the conclusion that it depends upon molecular heterogeneousness."

It is, perhaps, unnecessary to say that we were unaware of Sir W. THOMSON'S views till within the last few days, or that we are glad to find that our opinion has the support of so high an authority.

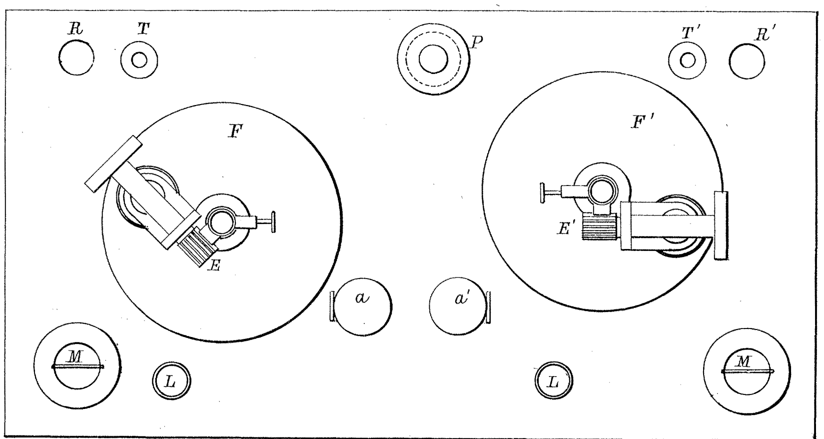


Fig. 2.

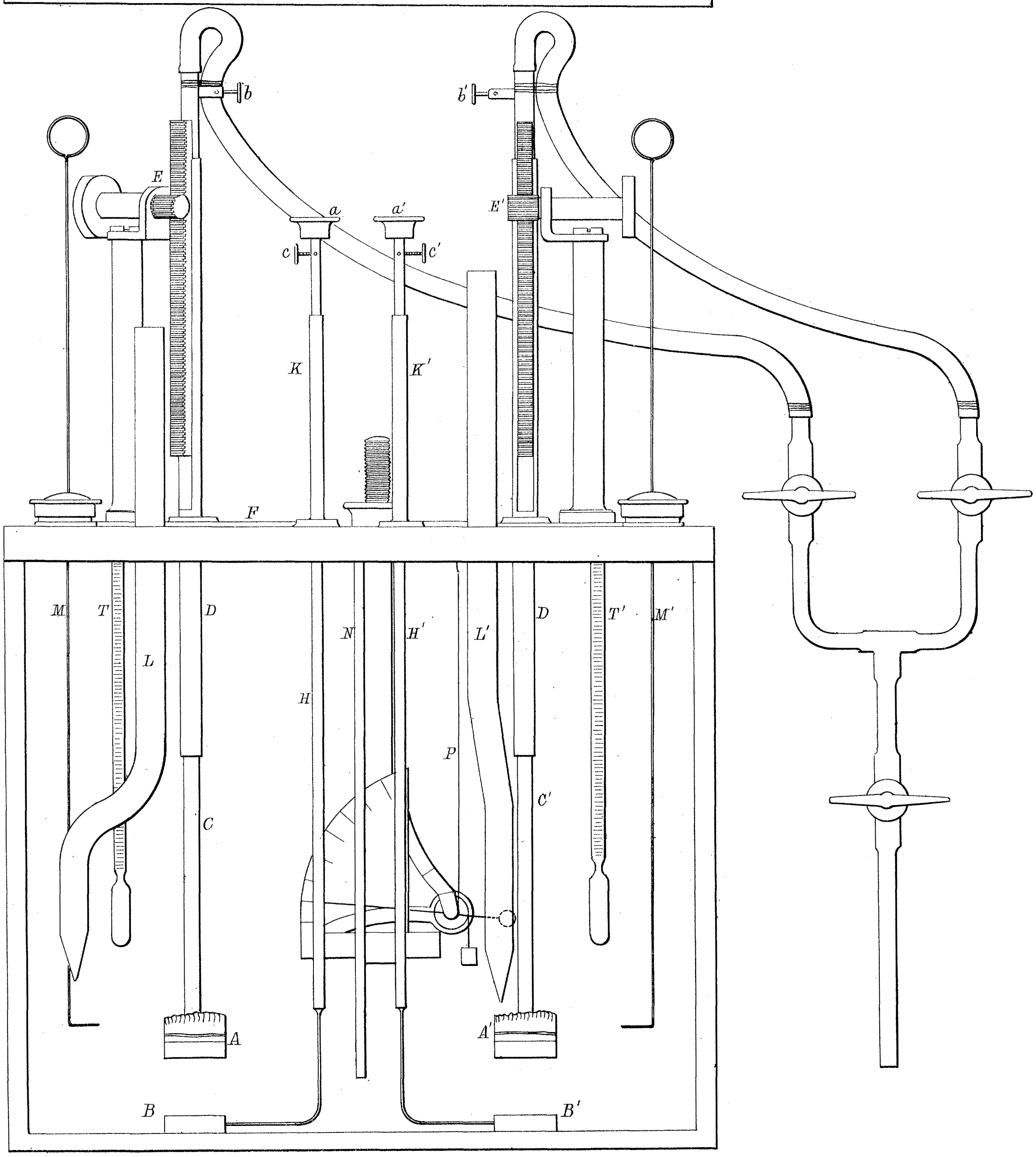


Fig. 1.

Half Size.

West, Newman & Co. lith.