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MEASUREMENT OF SURFACE TENSION

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ABSTRACT

This paper (*a*) presents a brief survey of the more important of the methods which have been employed in the measurement of surface tension, (*b*) calls attention to some of the more important facts which must be kept in mind by one wishing to succeed in such measurements, (*c*) indicates certain errors which are frequently made and shows how they may be avoided, and (*d*) gives the working equations that are applicable to the methods considered. A bibliography of more than 100 selected papers is appended. In each instance the purpose for which the reference was selected is indicated.

CONTENTS

I. INTRODUCTION

Every set of measurements connecting the curvature of a liquid surface at a given point with the difference in the hydrostatic pressure on the two sides of the surface at that point; every set of observations connecting the velocity of propagation of a deformation over the surface of a liquid with the nature of the deformation, the size of the liquid mass, the undeformed shape of the surface, the density of the liquid, and the forces that enter into the phenomenon; and every set of observations connecting the frequency of oscillation of a liquid mass with its size, undisturbed form, and the forces that enter into the problem, may be used to determine the value of the surface tension of the surface concerned. The number of methods is almost unlimited; and in point of fact the number that are more or less workable in practice, and even the number which have been actually used, is great, and the latter is being increased continually.

Such a wealth of available methods is ideal for the detection and the elimination of constant experimental errors, but it is also fruitful of great discordance when due attention is not paid to such errors. In the past, surface-tension measurements have frequently been marked by excessive care to secure a high reproducibility, accompanied by scant attention to the possible presence of constant errors and to the real significance of the quantity which is reproduced. There is a great need for a careful study of the various methods in order to determine (*a*) the proper interpretation of the quantity which is determined by each, (*b*) the magnitude of the errors which are introduced by known small departures from the ideal conditions upon which the interpretation rests, and (*c*) the limits within which each of the several methods are trustworthy. Ferguson (21)[1] has started upon such a program. His work will be followed with much interest. Unfortunately, the mathematical discussions in some of his earlier papers have been marred by errors (66, 78, 79); it is hoped that all such errors will be corrected as the work progresses.

The object of the present paper is much less ambitious. Its aim is to present a brief survey of the more important of the methods which have been employed, to call attention to some of the more important facts which must be kept in mind by one wishing to succeed in such measurements, to indicate certain errors which are frequently made and to show how they may be avoided, and to give the working equations that are applicable to the methods which are here considered. The derivations of the equations and directions for the construction and use of the necessary apparatus will have to be sought in other places, to the more important of which references will be given. The list of references does not pretend to be complete but is intended merely to direct the reader to one or more of the sources from which the required information can be obtained most satisfactorily.

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[1] The figures given in parentheses here and throughout the text relate to the reference numbers in the bibliography given at the end of this paper.

II. GENERAL REMARKS

1. SURFACE TENSION

The term "surface tension" conveys a fictitious, though very valuable, picture of the phenomenon under consideration. In the body of a liquid the molecular attractions acting upon an element of the liquid are, on the whole, completely balanced; the element is pulled as strongly in one direction as in another. As the surface is approached this balance is destroyed. Near the surface the element is pulled more strongly toward the liquid than toward the other medium from which the surface separates the liquid, or else the reverse is true. This lack of balance in the molecular forces acting upon the elements of the liquid is what gives rise to the property that we call surface tension. The lack of balance, and consequently the surface tension, depends upon the properties of both of the media of which the surface is the common boundary. Surface tension is not a property of one medium, but is the joint property of two media. When one speaks of the surface tension of a particular liquid, what is meant, or at least what should be meant, is the surface tension of the liquid in contact with its own pure vapor at the same temperature. Actually the surface tension of the interface separating a liquid from a gas or vapor depends but little upon the nature of the latter, provided that it does not react chemically with the liquid, and that certain exceptional conditions are excluded.

When we enlarge a clean liquid surface we do not stretch it in any proper sense of this term; we merely bring into being an additional area of the same kind of surface as we had before. When we speak of a surface tending to contract under the action of its surface tension we do not mean that the particles in the surface tend to crowd nearer together while remaining in the surface, but that they tend to withdraw from the surface into the interior of the liquid. As we are concerned with a condition of stable equilibrium it is obvious that they can not so withdraw unless provision is made for a corresponding decrease in the area of the surface.

The range through which the forces are unbalanced is negligibly small as compared with the smallest difference in length which we can experimentally measure under the conditions with which we are here concerned. All the equations employed in the reduction of surface-tension measurements are based upon the assumption that the transition layer in which the forces are unbalanced is of negligible thickness. Should conditions ever arise in which this assumption is not justified, then either we must completely reconsider the equations, taking into account the variation in the forces as we pass through the surface layer, or we must change the scale of our operations in such a manner that the thickness of the transition layer becomes negligible in comparison with the smallest length which we can measure upon the revised scale. Indeed, unless our scale is so coarse that the transition layer is negligibly thin, the concept of a "surface" tension loses its significance.

2. NEGLIGIBLE QUANTITIES

Although frequently forgotten, it should be remembered that the terms "negligible" and "small" are purely relative. To say that something is negligible or small, without indicating either directly or by implication anything with which it is thus compared, is to talk nonsense. It can be negligible or small only in comparison with something else of the same kind. It is especially necessary to keep this clearly in mind when considering the equations applicable to surface-tension phenomena. With few exceptions the working equations are approximate only and are validly applicable only under the condition that certain lengths are negligible with reference to certain other lengths involved in the phenomenon. It makes no difference how small the first length is, the equation is not applicable unless the comparison length is so great that the first is negligible in comparison with it. By this we mean that in any sum or difference of the two lengths the first may be neglected without changing the value of the sum or difference by an amount that is experimentally significant. It does not mean that when the first length occurs as the numerator of a fraction of which the second is the denominator that this fraction can always be ignored; that depends upon the connection in which the fraction occurs. Will the value of the sum or other function in which it enters be changed by a significant amount if this fraction is made zero? If so, then the fraction is not negligible with reference to the other terms that enter into the function.

3. PURITY

Although the purity of the materials used is of importance, it should be borne in mind that it is the purity of the surface separating the juxtaposed fluids that must primarily be considered. This is quite a different thing from the chemical purity of the materials in bulk. Exceedingly small amounts of physical contamination may affect the surface most seriously. Whatever tends to lower the surface tension will tend to accumulate in the surface. For this reason, other things being the same, the higher values of the surface tension are worthy of the greater confidence.

For the same reason the concentration of the surface of a solution is, in general, different from that of the solution in bulk. When a fresh surface is formed, diffusion sets in tending to bring about this difference in concentration. Consequently, the properties of a surface bounding a solution should be expected to depend upon the age of the surface. It is merely a question of whether the change takes place slowly enough for us to be able to detect it with the means at our disposal. In some cases it does take place so slowly. Thus, Rayleigh (59) found that the tension of a freshly formed surface separating a soap solution from air differs very little from that of an air-water surface, but decreases markedly within a few seconds. The explanation is to be sought in the progressive accumulation of soap in the superficial layers. More recently du Noüy (50a, 50b) and Johlin (35a) have shown that the surface of many colloidal solutions attain equilibrium very slowly. The tension of the surface may continue to decrease for hours after the surface is first formed, and the final value of the tension may be as much as 50 per cent lower than the initial value. This is explained by the progressive change in the concentration of the surface layer.

In the case of pure fluids no such diffusion phenomena can exist, and it is very probable that the rearrangement of the molecules attendant upon the formation of a fresh surface takes place too rapidly to be detected by any means that has yet been proposed. We might likewise anticipate that the time required for the interface of two pure fluids to become saturated with each would be too short to be detected by any of our usual procedures. This also seems to agree with experience. Nevertheless, it is well to take pains to insure such saturation before making measurements.

When a surface is exposed to the air it gradually becomes contaminated and its properties progressively change. Thus Schmidt (65) observed that the superficial viscosity of mercury increased manyfold in the course of a few hours after it was first exposed to the air. The surface tension is likewise affected by the contamination of the surface—it is reduced. The progressive effect of contamination is of the same sign as that of changing concentration—it is difficult to separate the two effects.

When one of the fluids separated by the surface is a gas, one would anticipate, from the great disparity in the density of a gas and a liquid, that under ordinary conditions the tension of the surface would be very slightly affected by the nature of the overlying gas and would be still less affected by the solution of the gas in the liquid. This appears to be borne out by experiment (100). On the other hand, when a liquid is near its critical point and is in contact with an inert gas under high pressure, it seems possible that the solution of the gas in the liquid might produce a considerable effect.

4. CONTACT ANGLE

In many surface-tension problems it is necessary to know the angle at which the liquid surface meets a given solid wall. But the intersection of two surfaces defines two plane angles; which shall we take as the angle of contact of the liquid with the wall? The acute angle between the tangent to the surface at the point of contact and the tangent to the wall at the same point, each drawn in the plane that is normal to the line of contact, might be taken as defining the angle of contact; but physical considerations reveal that this is not satisfactory. There are two fluids to be considered and two angles are at our disposal. One is to be regarded as the angle of contact of the surface of fluid$_1$ with the wall, and the other as the angle of contact of fluid$_2$ with the wall. Either angle might be chosen as the angle of contact of fluid$_1$, the other being that of fluid$_2$. But the more logical choice appears to be that which is universally accepted; namely, the angle of contact of fluid$_1$ with the wall is the angle of the limiting wedge of fluid$_1$ that is bounded by the fluid$_1$-fluid$_2$ surface and the fluid$_1$-wall surface. It may have any value between 0 and 180°, each included. If the wall has an absolutely sharp edge at the line of contact, the concept of a tangent to the wall at and across the line of contact loses its significance, and consequently the significance of an angle of contact is likewise lost. But if the edge is rounded, no matter how short its radii of curvature, provided that they are long as compared with the range of molecular forces, the concept holds. In practice, an edge is never infinitely sharp. If the surface were free from all other constraints, probably it would adjust itself in such a way that the angle of contact would be always the same for the same surface and wall, temperature and other pertinent conditions being the same. This equilibrium angle of contact is called the "contact angle" of the fluid with the wall under the existing conditions. But all who have worked with mercury manometers know that a liquid surface may be subjected to constraints that appear closely akin to frictional resistance of the kind characteristic of the sliding of solids over solids. Under the action of such constraints the surface can not adjust itself as it otherwise would, and the angle of contact may take any one of a range of values. It is desirable to distinguish between the existing angle of contact and that particular angle of contact which is characteristic of equilibrium in the absence of such constraints as we have considered. For the latter, which is probably a characteristic of the fluids and the wall, we shall reserve the term "contact angle"; the others will be designated as angles of contact.

The existence of constraints is to be expected. An advance of the line of contact is necessarily accompanied by the replacing of an intimate contact of the solid and one fluid by an intimate contact of the solid and the other fluid. If there is any adhesion between the solid and the fluids, the replacement will involve irreversible effects, and constraints of the kind considered will result; and there is always adhesion.

There is, however, one case in which the constraint will be absent. This is when one of the fluids adheres to the solid so strongly that it is not replaced by the second, but the second merely flows over a thin layer of the first which continues to be attached to the solid. We thus have in reality merely one surface—that of the fluid-fluid boundary—the solid merely serving as a support to the thin layer. If the thickness of the adhering layer exceeds the range of the molecular forces, then, except for viscous effects, which merely delay the attainment of equilibrium, there is perfect freedom of motion, and the apparent contact angle is zero. If the thickness is less than the range of molecular forces, then the apparent contact angle may be different from zero but will be definite if sufficient time is given for the layer to drain to its equilibrium thickness. Before such drainage is complete the angle may be expected to vary as the layer thins. In this case, also, the motion of the boundary surface over the solid will be quite free, but the freedom will decrease as the time required for drainage increases. The drainage will be affected not only by the viscosity of the fluid forming the layer, but also by that of the other fluid which presses it against the solid. In all these cases the actual angle of contact of the fluid-fluid surface with the solid is to be found at the free end of the layer far beyond the region with which we are primarily concerned.

Any change in the surfaces, whether due to contamination or other cause, may be expected to cause a change in the angle of contact, except in the single case in which it is zero as the result of the solid being covered by a layer of fluid so thick that the molecular forces of the solid can not penetrate it.

The main facts brought out by the large amount of experimental work that has been done in the study of angles of contact justify these conclusions. It has been found that in many cases the solid surface can be so prepared that the liquid will truly wet it (81, 64), will slide freely over the surface; under these conditions the effective angle of contact is actually zero, the free surface passing by imperceptible degrees into the exceedingly thin film which remains coating the solid and extending to points far beyond the apparent line of contact. But when surfaces so prepared are allowed to dry, the liquid may then meet them at a finite angle and may no longer slide freely over them (64). In other cases it seems impossible to prepare a given surface in such a way that the liquid can truly wet it (12). Generally, in such cases the liquid will not move freely over the solid, and the angle of contact will be both finite and variable; but occasionally the motion may be free, and then the contact angle though finite is constant. For any solid and any liquid an inconstant finite angle appears to be possible, but the insuring of a zero or other constant angle is in many cases very difficult if not impossible.

For these reasons it is desirable to choose for the measurement of surface tension such methods as do not require a knowledge of the value of the angle of contact. Methods involving a knowledge of the angle of contact may, however, be safely used if care is taken to insure that the solid is perfectly wetted by the liquid at the time that the measurement is made. Or, if the liquid moves perfectly freely over the wall, although it does not wet it, provided that the angle of contact is certainly known to the necessary precision. A measurement of the angle of contact under the conditions of observation in surface-tension measurement involves many difficulties, not the least of which is the fact that the angle required is that made by the last infinitesimal element of the surface. To measure the angle under one set of conditions and to use it under another involves the unsound assumption that it is necessarily the same in both cases. (Quincke (55, 56), Volkmann (82, 83, 84, 85, 86, 87), Anderson and Bowen (4), Bosanquet and Hartley (7), Ablett (1), Ferguson (23), Dorsey (12), Devaux (95, 96).)

5. MATHEMATICAL

Of the many mathematical discussions of the problems that arise in connection with the measurement of surface tension, the most satisfactory and complete is probably that of Verschaffelt (78, 79, 80). It should be noted that his notation differs from those most commonly used. He deduces general equations which can be readily adapted to the various particular cases that arise in practice, but in only a few instances does he give an equation in the final form required for the reduction of observations.

As the derivations of the equations applicable to the several methods which we shall consider are readily available elsewhere, it will suffice to give here the final equations and references to where their derivations may be found. The equations given will not always be of the same form as those given in the corresponding citations but will be derivable therefrom. The change in form has been made for the purpose of securing greater uniformity.

6. NOTATION

Throughout the remainder of this paper the following notation will be used; when additional symbols are required they will be explained as introduced.

SUBSCRIPTS.—Whenever it is necessary to distinguish between the two fluids of which the surface is the interface it will be done by means of the subscripts 1 and 2. When the problem involves a reference to a portion of the surface which is horizontal and flat, the subscript 1 will be used to denote that liquid which lies below that portion of the surface. When a surface of revolution is under consideration the subscript 1 will be used to denote that liquid which is below the vertex of the surface. (See figs. 1, 2.) It will be noticed in Figure 1 that the fluid which is denoted by 1 when the meniscus in the tube is being considered is the same as that denoted by 2 when the suspended drop is being discussed. Quantities pertaining to the vertex of a surface of revolution will be distinguished, as necessary, by means of the subscript 0.

$A^2 = \pm \frac{T}{(\rho_1 - \rho_2)g}$, the choice of sign is determined by the fact that A^2 is essentially positive. A^2 is half the product of the radius of a tube multiplied by the height above a flat surface that the liquid would rise in the tube if the meniscus were hemispherical; it is numerically equal to half the height that the liquid would rise under such conditions in a tube of unit radius. In the literature the symbol a^2 is used to denote sometimes A^2 and sometimes $2A^2$; the latter is the usual custom of German and the former of English authors.

g=The acceleration of gravity.

$h = p/(\rho_1 - \rho_2)g$, by definition. It will be noticed that p is the difference in the pressures exerted by two columns of liquid of height h, the density of one liquid being ρ_1 and that of the other being ρ_2.

p=The amount by which the pressure at a point infinitely near the surface and in fluid$_2$ exceeds that at a neighboring point in fluid$_1$. It measures the discontinuity in the pressure on crossing the surface.

P=The total vertical pull exerted by a mass of liquid that is raised as a result of surface tension effects.

$2r$=The diameter of a tube, or the distance between two parallel plates.

R=Radius of curvature of the surface; R' and R'' denote the principal radii of curvature at the point where p is measured; R_0 is the radius of curvature of the vertex of a surface of revolution. A radius of curvature is to be considered positive if in the section to which it applies the surface is concave toward fluid$_2$. In Figure 2, R_0 is negative for the drop (D) and positive for the bubble (B).

T=The surface tension.

θ=The angle of contact of the surface of a fluid with another surface. In all cases considered in this paper the second surface will be that of a solid wall. In every case it is necessary to indicate to which of the two fluids θ applies.

ρ=The density; ρ_1 is the density of fluid$_1$ and ρ_2 that of fluid$_2$. (See figs. 1, 2.)

In dealing with surfaces of revolution, axes of coordinates will be laid so that the origin is at the vertex, the axis of X is in the tangent plane, and the positive direction of Y is upward. Other cases, of which there are but few, will be considered as they arise.

7. RESERVOIR CORRECTION

The fundamental equation in capillarity is

$$p=T\left\{\frac{1}{R'}+\frac{1}{R''}\right\} \tag{1}$$

or, if the surface is one of revolution,

$$p_0=\frac{2T}{R_0}$$

whence T may be obtained at once if p_0 and R_0, or p, R', and R'' are known.

In many cases the pressures p_0 and p are derived from the observed height of a column of liquid. In practice, the vertical height of the column is usually measured from the vertex of the surface of a liquid contained in a relatively large reservoir. Unless the sectional area of the reservoir exceeds a certain value, depending upon the liquid, the surface at the vertex will be appreciably curved. This curvature will introduce a pressure (equation 2). The total pressure corresponding to the observed height will be the sum of the pressure due to the curvature, taken with the proper sign, and the hydrostatic pressure due to the observed column. It is customary to express the pressure due to the curvature in terms of the equivalent hydrostatic column and to regard it as a correction to be added to the observed height. This correction may be denoted by the symbol h_c. Richards and Carver (64) have experimentally investigated the amount of this correction in the case of cylindrical reservoirs of circular section of radius r and have prepared a curve giving the values of $h_c/A\sqrt{2}$ corresponding to various values of $r/A\sqrt{2}$ lying between 1.25 and 4.30. They use the symbol a to denote $A\sqrt{2}$. An optical method was used for measuring the curvature of the surface at the vertex. Rayleigh (62), and also Verschaffelt (79), have deduced expressions by means of which the value of h_c/A may be computed when r/A is known, provided that r/A amounts to at least several units. Rayleigh gives a table of values of h_c/A corresponding to integral values of r/A lying between 6 and 10. Values may also be computed from the exact tables prepared by Bashforth and Adams (5), either directly or from the table which was prepared from these tables by Sugden (70). The values given in Table 1 were obtained from Sugden's table; they essentially agree with the values given by Rayleigh and by Richards and Carver.

TABLE 1.—*Reservoir correction*

[The capillary rise h_c in a cylindrical tube of circular section, radius r, the capillary constant, $\frac{T}{(\rho_1-\rho_2)g}$, being A^2]

$\frac{r}{A}$	$\frac{h_c}{A}$	$\frac{r}{A}$	$\frac{h_c}{A}$	$\frac{r}{A}$	$\frac{h_c}{A}$
1.75	0.76	3.25	0.19	6.0	0.015
2.00	.59	3.50	.15	6.5	.009
2.25	.46	4.00	.09	7.0	.006
2.50	.37	4.50	.054	8.0	.0023
2.75	.30	5.00	.035	9.0	.0009
3.00	.24	5.50	.022	10.0	.00034

In the same paper, Rayleigh shows that the equation of the surface near the vertex is

$$y=h_c\left\{J_0\left(\frac{ix}{A}\right)-1\right\} \tag{3}$$

where J_0 is the Bessel function of the first kind and zeroth order, i denotes $\sqrt{-1}$, and h_c is the correction required. From this it can be shown that at a point 1.8A distant from the vertex the surface will lie h_c higher, or lower, than it does at the vertex. This is Rayleigh's criterion for the flatness of a surface. If the difference in level between the vertex and a point 1.8A distant from it can not be detected, then the surface is flat within the limits of error in the vertical measurements. In order that h_c/A for a water-air surface shall be as small as 0.001, it is necessary for the reservoir to have a radius of about 2.4 cm. That the curvature of a water-air surface may be apparent at 2.5 to 3 cm from a plane vertical wall was pointed out by the author (12) many years ago.

In the further course of this paper we shall assume that this effect, arising from the curvature of the surface in the reservoir, has been considered and the proper correction applied. Where it seems desirable to emphasize the fact, we may speak of the height measured from a flat surface.

III. METHODS OF MEASUREMENT

If R_0 is sufficiently small, p_0 will be of such magnitude that it can be measured without serious difficulty. The determination of T by equation (2) then reduces to the problem of finding R_0. This can be done in some cases by means of optical methods (64); in other cases it may be determined by the measurement of a photograph or of an enlarged projection of the surface (8, 15, 91); but in most cases it is more satisfactory to deduce the value of R_0 from some other length that is more amenable to direct measurement. This is the usual procedure in the method of capillary tubes.

1. CAPILLARY TUBES

For capillary tubes the value of R_0 is deduced from the radius of the tube and the properties of the fluids. In this way equation (4) is obtained. In this equation θ_1 denotes the angle of contact of the lower fluid (fluid$_1$) with the wall.

$$T\cos\theta_1=\frac{p_0 r}{2}\left[1+\frac{1}{3}\left(\frac{r}{h_0}\right)\sec^3\theta_1\,(1-\sin\theta_1)^2\,(1+2\sin\theta_1)\right.$$
$$+\frac{1}{3}\left(\frac{r}{h_0}\right)^2\sec^2\theta_1\left\{\sec^4\theta_1\,(1-\sin\theta_1)^3\,(1+\sin\theta_1+2\sin^2\theta_1)\right.$$
$$\left.\left.+2\log\frac{1+\sin\theta_1}{2}\right\}+\cdot\cdot\cdot\right] \qquad (4)$$

or, if the angle of contact is zero,

$$T=\frac{p_0 r}{2}\left[1+\frac{1}{3}\left(\frac{r}{h_0}\right)-0.1288\left(\frac{r}{h_0}\right)^2+0.1312\left(\frac{r}{h_0}\right)^3+\cdot\cdot\cdot\right] \qquad (5)$$

The first expression, Verschaffelt (79), holds provided that the cube of r/h_0 is negligible in comparison with unity; the second, Rayleigh (62), holds if the fourth power of r/h is negligible. Even the first of these approximations is ample for most practical purposes. From its definition (see Notation) it is obvious that h_0 is the vertical distance of the vertex of the meniscus from the flat liquid surface in a connecting reservoir, the same body of overlying fluid being in contact with each of these surfaces. In designing the apparatus, an unnecessarily small r should not be chosen, as this limits the precision; T can not be determined to a higher precision than that to which r is measured. The disadvantages inherent in this method are: (*a*) The contact angle must be known; (*b*) there is difficulty in measuring r to the necessary precision; (*c*) as the surface in the tube is small, a very small amount of contamination may produce a marked effect; (*d*) the cleaning of a small tube is not easy; and (*e*) the meniscus lies in an exposed position so that its temperature has to be inferred rather than measured. Conditions can probably be adjusted so that the last-named disadvantage is more apparent than real.

Numerous modifications of the simple capillary-tube method have been proposed and occasionally used. One of the most recent was proposed by Ferguson (20). He suggests applying a pressure to the capillary column so as to drive the meniscus down until its vertex is just in the plane of the end of the tube, placed vertically. By this procedure the meniscus is always in the same section of the tube, thus obviating the necessity of calibrating a long section of tubing, and the cleaning of the tube and the control of the temperature are facilitated. Obviously, this method is not applicable to the measurement of the surface tension of a liquid in contact with only its own pure vapor.

For liquids that are obtainable in only very small quantities Kiplinger (38) proposed that a short column of liquid suspended in a capillary tube be used, the tube being tilted until the liquid surface at the lower end becomes plane. Then, if the contact angle is zero,

$$T=0.5(\rho_1-\rho_2)grl\cos A \tag{6}$$

approximately, where l is the length of the short column of liquid and A is the angle it makes with the vertical. His results run low by from 1 to 8 per cent. But, as Ferguson (22) has pointed out, the lower surface is never plane when the tube is tilted. Ferguson has proposed that the tube be left vertical and the pressure upon the suspended column be adjusted until the lower surface becomes plane, as optically tested. In this case the usual equation for capillary tubes applies. He found that individual determinations made by this method differed among themselves by as much as 7 per cent, but the probable error of a set of 28 observations amounted to only 0.25 per cent. Only a few cubic millimeters of liquid are required for the measurement.

Sugden (70) endeavored to eliminate the uncertainty of the effect due to the curvature of the surface in the reservoir by employing two capillaries and basing the computation upon the difference in the elevations of the vertices of the two menisci. He employed a method of approximation, using the tables computed by Bashforth and Adams (5). The increased difficulties introduced by the use of two capillaries would seem to offset by far any apparent advantage of the method.

Anderson and Bowen (3) proposed an optical method for measuring the curvature at the vertices of the surface in the capillary and in the reservoir. These values inserted in the obvious manner into equation (2) permit the surface tension to be evaluated at once. The realization of the method requires a knowledge of the index of refraction of the liquid and the ability to estimate accurately the difference in elevation of two images, one formed by refraction and the other by reflection. The determination is independent of the angle of contact but would seem to be difficult to employ with any considerable precision. For additional details the original paper should be consulted.

Bigelow and Hunter (5a) and Carver and Hovorka (10a) have used an interesting modification which is attributed to Oersted. In this the capillary consists of a perforated plate which rests on the top of a vertical tube of large diameter. The whole is immersed in a reservoir of liquid until the latter floods the plate; then the tube is raised slowly, or the level of the liquid in the reservoir is slowly lowered, until the meniscus which forms at the perforation breaks. This occurs when the distance from the surface of the liquid in the reservoir to the bottom of the meniscus at the perforation is equal to the height the liquid would rise in a tube of the diameter of the perforation. The method is said to be quite accurate and rapid. In this method the diameter is measured at the exact section at which the meniscus forms, and this section is the same for all liquids; the cleaning of the capillary is relatively easy. These are distinct advantages. The measurement, however, depends upon the determination of the incidence of instability, and this may introduce difficulties when exact determinations are desired; also, the perforating of the plate may present difficulties.

A problem which is of no little interest in connection with the determination of the surface tension by means of capillary tubes is the determination of the shape of the surface between two concentric cylinders, one of which is much smaller than the other. Apparently this problem has not been very completely solved even by approximations, but Verschaffelt (77) has shown that in the region approximately midway between the tubes the curvature of the radial section of the surface differs but little from that of the corresponding region (that at the extremity of its minor axis) of the ellipse of which the major axis is equal to the distance between the walls of the two tubes, the minor axis is equal to twice the height of the meniscus; that is, to twice the distance between horizontal tangent to the surface and the line of contact of the liquid with the outer tube. He tested this relation by measuring the changes produced in the height to which a liquid rises in the inner tube when the inner radius of the outer tube was changed from 1.04 cm to 0.745, 0.505, 0.325, and 0.295 cm, respectively, the external radius of the inner tube being 0.0464 cm. in every case. Excepting for the smallest tube, the observed changes differed from those calculated by not over 0.004 cm, which was considered satisfactory for his purpose.

2. VIRTUAL CAPILLARY TUBE (METHOD OF SENTIS)

Sentis (67, 68) employed a very ingenious modification of the capillary tube method. A modification which entirely eliminates the question of the angle of contact, provided that it is the same for each of two consecutive observations. His method has very appropriately been called the method of "virtual capillary tube." He introduced into a vertical capillary tube such a column of liquid that a drop formed on the lower end of the tube, and, with the column, was supported by the surface forces. (Fig. 1.) He measured the maximum horizontal diameter, $2r$, of the drop. Then a vessel of the liquid was brought up from beneath until the surface of the liquid just touched the bottom of the drop.

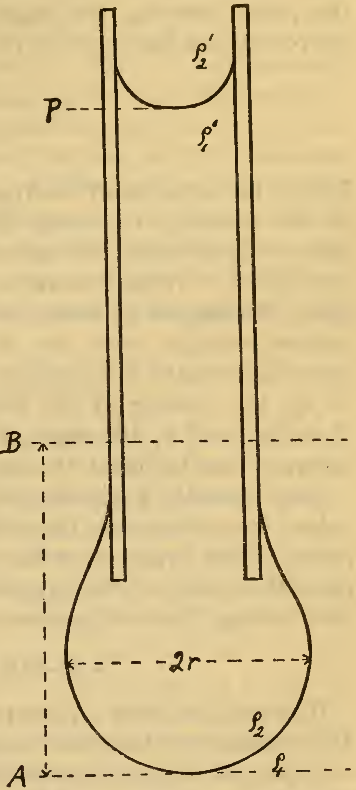

Fig. 1.—*Drop of liquid suspended from a tube*

Illustrating Sentis's method—the method of the virtual capillary tube

At this instant the column in the tube falls. The position (A) of the surface is noted, and the vessel is then raised higher until the meniscus of the column in the tube is restored to the position (P) which it occupied when the drop was measured; the surface is then in position B. The vertical distance (AB) between these two positions, corrected for the curvature of the liquid in the vessel, is the quantity which we have denoted by h_0 (See Notation); it measures the hydrostatic pressure which the column exerted upon the vertex of the drop. The problem is, therefore, exactly the same as that of a capillary tube with the denser liquid on the upper side of the surface at the vertex, the angle of contact being zero, and the diameter of the tube being equal to that of the maximum horizontal section of the drop. Equation (5) applies directly, but it should be noticed that in this case the quantity h_0 is negative. The approximations employed by Sentis were lower than that corresponding to equation (5).

3. VERTICAL PLATES

Closely related to the rise in tubes is the rise between vertical plates. When the plates are parallel and the angle of contact of fluid$_1$ is zero,

$$T = p_0 r \left[1 + 0.2146 \left(\frac{r}{h_0} \right) - 0.052 \left(\frac{r}{h_0} \right)^2 + \cdots \right] \qquad (7)$$

(Volkmann (81)) where the distance between the plates is $2r$, the other quantities having the same meaning as before. If the plates are inclined to one another at the angle ϕ, the line of contact of the plates with one another being vertical, and if the axes of coordinates coincide, respectively, with the line of contact of the plates and with the intersection of the flat surface of the liquid in the reservoir with the plane bisecting the angle between the plates, then to a first approximation the equation of the median section of the meniscus is

$$xy = \frac{T \cos \theta_1}{(\rho_1 - \rho_2)\, g \tan \frac{\phi}{2}} \tag{8}$$

This is the equation of an hyperbola. In order to facilitate the use of this method, Grunmach (26) engraved on one of the plates a series of hyperbolas, for each of which the value of the product xy was known. Then, to make a measurement, the angle between the plates is changed by means of a micrometer screw until the liquid surface coincides with one of the hyperbolas, the plates being so placed as to make this possible. The hyperbola determines the value of xy, the reading of the micrometer fixes the value of ϕ, hence if the value of θ_1, the angle of contact of the lower fluid (fluid$_1$) is known, T can be found at once.

Quite recently Ferguson and Vogel (23a) have suggested a procedure for determining the surface tension from the positions of the points of the hyperbola with reference to any set of axes which are parallel to those of the hyperbola. This eliminates the difficulty of determining the exact position of the latter axes.

4. PLATE AND CYLINDER

Wagstaff (88) used a plate pressed against the inside of a cylinder. The coordinates of a series of points upon the projection of the meniscus upon the plate were measured, and from these and the radius of the cylinder the value of T was calculated. The main advantages claimed for this method over the use of capillary tubes is the facility with which the apparatus can be cleaned and the fact that no very small distances have to be measured. The volume of liquid required is large.

Obviously in all these cases the surface in the reservoir must be plane or due allowance must be made for its curvature. In the case of plates, it is also necessary that observations be confined to those portions that are so far from the edges that the shape of the meniscus is the same as if the plates were of infinite extent. For these reasons plates are not so suitable as tubes.

In the use of the capillary rise methods for determining the tensions of liquid-liquid surfaces it is necessary that care be taken to superpose the liquids in such a way as to facilitate the drainage of the film that is trapped between the wall and the advancing liquid. On account of difficulties that may be produced by such trapping, it is frequently impossible to test satisfactorily the freedom of motion of the surface over the wall.

5. SMALL PENDANT DROPS

Very similar to the method employed by Sentis is that generally known as the method of small pendant drops. In this method a drop is formed, the pressure in it is measured, and its form determined, either by a direct measurement of the drop or by the measurement of an enlarged photograph or projection of it. The results, being obtained from a direct measurement of the curvature of the drop at the point where p is measured, are independent of the contact angle. Obviously the method is equally applicable to bubbles or drops, as of oil in water, that are pendant upward, due account being taken of the sign of h (8, 15).

6. LARGE PENDANT DROPS

In the case of large pendant drops the pressure is too small to be measured manometrically with precision. In this case measurements at two or more selected levels give the data required for computing the curvature at each level. This determines the difference in pressure from level to level, which, equated to the corresponding difference in hydrostatic pressure, permits the tension to be determined. Measurements are usually made upon enlarged photographs or projections of the drop or bubble. The method employed for reducing the observations is, in part, determined by the manner in which the measurements have been distributed over the surface (15, 91, 93). In some cases the tables of Bashforth and Adams (5) should be of much assistance. No knowledge of the contact angle is required.

Likewise, from any two suitable sets of measurements made at different levels upon the same surface, whatever its form, the tension can be computed. Such computation does not involve any angle of contact. Thus, Pekar (52) has studied the form of the surface in a cylindrical tube of circular section, and Eötvös (13) has studied a section of a large drop. It should be remembered that all such determinations are based upon the departure of the surface from a spherical form, thus resting upon just those factors that give rise to the correction terms in the equations applicable to the rise in a capillary tube. This indicates the limitation of the method; it rests upon the precise measurement of quantities which in other methods enter only as correction terms.

7. SESSILE DROPS AND BUBBLES

An essentially similar problem is involved in the method of sessile drops and bubbles. In this method the form of a drop resting upon a flat horizontal surface, or of a bubble formed under such a surface, is studied. The quantities that are usually measured are the maximum horizontal diameter ($2l$) of the drop or bubble, the distance (k) from the plane of maximum diameter to the vertex, and the distance (K) of the vertex from the plane upon which drop rests (fig. 2). From the first two the surface tension can be determined (99, 48) by means of the equation:

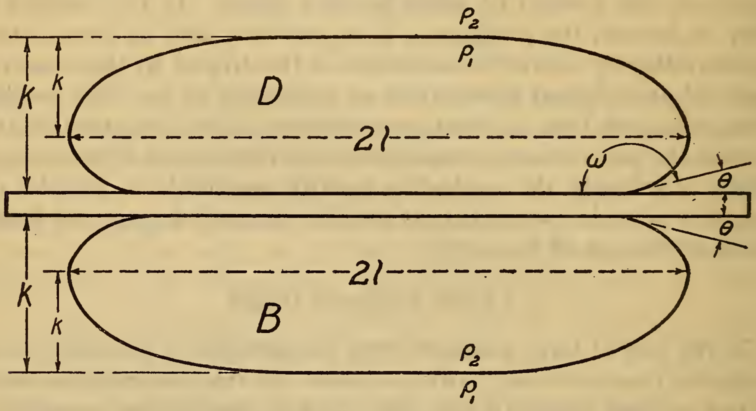

FIG. 2.—*Meridional section of a sessile drop (D) and bubble (B)*

$$A^2=\frac{k^2}{2}\left[1-1.724\frac{A^3}{lk^2}+\frac{4A^2}{R_0k}+\cdots\right] \tag{9}$$

in which R_0 is the absolute value of the radius of curvature at the vertex of the drop or bubble. From Verschaffelt's (80) equation (13) it follows that

$$\frac{1}{R_0}=\frac{1.16}{A}\sqrt{\frac{l}{A}}\cdot e^{-\frac{l}{A}} \tag{10}$$

approximately. Whence it is evident that this term in equation (9) will be very small indeed when the preceding term is small; we may omit it. The equation relating A, K, and θ, the angle of contact of the outer fluid with the wall is (48)

$$A=\frac{K}{2\cos\frac{\theta}{2}}\left[1-\frac{2A^2\left(1-\sin^3\frac{\theta}{2}\right)}{3lK\cos\frac{\theta}{2}}+\frac{2A^2}{KR_0}+\cdots\right] \tag{11}$$

It should be especially noticed that here θ is in every case the angle of contact of the outer fluid with the wall; when bubbles are considered, θ is the angle of contact of the surrounding liquid with the wall; when drops are considered, θ is, as before, the angle of contact of the surrounding fluid with the wall. The angle of contact of the liquid forming the drop is ω, the supplement of θ (see fig. 2).

By combining (9) and (11) the angle of contact can be determined. Equations equivalent to (9) and (11) are attributed (48) to Poisson. The approximation of neither of these equations will be satisfactory unless A/l is small as compared with unity. In much of the work that has been done by this method the drops or bubbles have been entirely too small for the approximations used to be satisfactory; in nearly all of the earlier work only the first term of each of these equations was used, thus making matters far worse. Quincke (54) determined experimentally, in both water and alcohol, the ratios of k and of K corresponding to air bubbles of various diameters to the corresponding quantities for bubbles 10 cm in diameter and attempted to correct his values by means of them.

Siedentopf (69) used drops about 1 cm in diameter and measured the maximum horizontal diameter and the curvature at the vertex, using an ophthalmometer. His observations were reduced by graphical methods.

Although the method of sessile drops is very convenient for determining the surface tension of fused materials at the instant of solidification, Verschaffelt (80) is probably right in saying that "a really practical importance can not be ascribed to them." Others who have used and discussed the method are Heydweiller (32, 33, 33a), Lohnstein (43, 44), and Worthington (94). Heydweiller (33a) gives a table which facilitates the reduction of observations.

8. JAEGER'S METHOD

When the column of liquid that rises in a tube dipping vertically into a liquid is slowly forced down by applied gas pressure, it is observed that the pressure steadily increases to a well-marked maximum just before a bubble escapes from the end of the tube. The value of this maximum depends upon the surface tension and the density of the liquid and upon the configuration of the apparatus. Jaeger (34, 35) first employed this phenomenon for measuring the surface tension, and the method is generally called by his name. He first employed it for the determination of the way in which the tension varies with the temperature; and as at that time the equation relating the maximum pressure to the radius of the tube and to other factors had not been developed, he attempted only relative measurements. He used two tubes of different diameters and adjusted the difference in the depths of their immersion until the maximum pressure was the same for each. Until the line of contact reaches the end of the tube, the condition is exactly the same as in the case of capillary rise; whence it is evident that, to a first approximation, the pressure will be proportional to the surface tension multiplied by a function of the radius of the tube. Hence, in the case of two tubes immersed to different depths, the hydrostatic pressure corresponding to the difference in immersion will likewise be proportional to the tension multiplied by a function of the radii of the two tubes. Furthermore, it is evident that the next degree of approximation will depend upon the density of the liquid. Jaeger assumed that it would be obtained by simply multiplying the first order approximation by a function of the density alone. Under the conditions of that work he found that this assumption fitted his observations within the limits of his experimental error, the density function being linear. Actually, the exact expression is not so simple. He emphasized the importance of the end of the tube being broken off perfectly smooth and flat and at right angles to the axis of the tube, and he comments on the advantage of using a broken, rather than a ground end.

The advantages of this method are: (*a*) The continual renewal of the surface reduces the troubles arising from surface contamination, (*b*) the temperature control is facilitated by having the surface surrounded by a large volume of liquid, (*c*) the use of a light manometric liquid, or of an inclined manometer, facilitates the measurement of the pressure, (*d*) the radius that is to be measured, in the case of absolute measurements, lies exactly at the end of the tube. While the use of a light manometric liquid is of advantage in the case of relative measurements, either after the manner of Jaeger or in the case of a single tube when provision is made for adjusting the depth to exactly the same amount in every case, its advantage is rather illusory in other cases, as the precision is limited by the accuracy with which the depth of immersion can be determined.

Since this early work, the equation relating the tension to the diameter of the tube, the maximum pressure, and the density of the liquid has been deduced by methods of approximation to a precision which is ample for experimental work. Unfortunately, several incorrect equations have been deduced and used, as pointed out by Schrödinger (66), and later by Verschaffelt (79). Four incorrect equations have been found in the literature (9, 24, 17, 10), viz:

$$T=\frac{\bar{p}r}{2}\left[1-\frac{2}{3}\left(\frac{r}{h}\right)-\frac{1}{3}\left(\frac{r}{h}\right)^2-\cdots\right] \tag{12}$$

$$T=\frac{\bar{p}r}{2}\left[1-\frac{2}{3}\left(\frac{r}{h}\right)-\left(\frac{r}{h}\right)^2-\cdots\right] \tag{13}$$

$$T=\frac{\bar{p}r}{2}\left[1-\frac{2}{3}\left(\frac{r}{h}\right)+\frac{1}{\sqrt{6}}\left(\frac{r}{h}\right)^2-\cdots\right] \tag{14}$$

$$T=\frac{\bar{p}r}{2}\left[1-\frac{2}{3}\left(\frac{r}{h}\right)-\frac{1}{2}\left(\frac{r}{h}\right)^2-\cdots\right] \tag{15}$$

The correct equation (66) is:

$$T=\frac{\bar{p}r}{2}\left[1-\frac{2}{3}\left(\frac{r}{h}\right)-\frac{1}{6}\left(\frac{r}{h}\right)^2-\cdots\right] \tag{16}$$

where $\bar{p}$ is the maximum excess of pressure in the bubble at the level of the end of the tube over that at the same level in the surrounding liquid and $h=\frac{\bar{p}}{(\rho_1-\rho_2)g}$. The equation assumes that static conditions exist, and that the internal circumference of the tube, on which the bubble forms, is circular and horizontal. Apparently no attempt has been made to determine how far these conditions may be departed from without introducing appreciable errors, although Martin (49) states that in purely relative measurements the horizontality and planeness of the contour of the end of the tube are of little importance. It is very important that all such questions be carefully studied.

For computing the tension from observations made with larger tubes, Sugden (71) has computed a table based upon those of Bashforth and Adams (5). Jaeger (34) has also compiled a table designed to aid in the reduction of observations. This table seems to be based upon the equations given by Fuestel (24), and consequently requires critical examination before it can be accepted with full confidence. (See Verschaffelt (79).)

The method is equally applicable to the case of drops of one liquid formed in another, provided that the drop forms on the inner circumference of the tube. The equation is the same in all cases, due attention being given to the sign of h. Verschaffelt's remarks (79) regarding the formation of drops and bubbles should be read by those interested in this method.

A modification of this method has been proposed by Whatmough (89). It has been criticized by Cantor (10) and appears to have little to recommend it.

9. DROP WEIGHT

In 1864 Tate (73) announced as the result of his observations that, "Other things being the same, the weight of a drop of liquid is proportional to the diameter of the tube in which it is formed." Four years later Quincke (53) undertook to estimate the value of the surface tension from the weight of a fallen drop of the liquid. He stated, quite correctly, that the weight of the suspended drop just before falling is $2\pi rT$, provided that the inflow of liquid into the drop is such that at the end of the tube the pressure in the drop is the same as if the surface were plane. But this condition is never fulfilled in practice. He also clearly recognized both that a portion of the drop remains adhering to the tube, causing an error which he thought would be negligible when the radius of the tube is very small, and that the conditions attending the breaking away of the drop are very complex; consequently, that the assumption that the weight of the fallen drop is equal to $2\pi rT$ can at best lead only to approximate values of the tension, and that the method should be used only when others are either not applicable or involve excessive experimental difficulties. Unfortunately, his followers have quite generally failed to recognize the limitations he pointed out and have endeavored to elevate to the dignity of an exact law the approximate numerical relation which he employed.

Worthington (91) in 1881 pointed out that the relation generally assumed

$$W=2\pi rT \tag{17}$$

could not be correct in any case, and that, in general, the relation between the weight (W) and the surface tension (T) would not be one of simple proportionality. Several writers have commented on the fact that the weight must depend upon how rapidly the drops form and must be sensitive to slight disturbances occurring at the instant in which instability is setting in; and Vaillant (76) Abonnenc (2), and Guye and Perrot (28b) have endeavored to determine experimentally the relation between the weight of the drop and the rate at which it forms. Even though the speed of formation were excessively slow, the effect of disturbances would persist, and, although the average of a number of drops formed under the same nominal conditions might under certain conditions exhibit a high degree of reproducibility, this would be no proof that the average is the same as would be obtained under other conditions, nor, in particular, would it be a proof that the average is the same as would be obtained in the absence of all extraneous mechanical jars, vibrations, or other disturbance.

Rayleigh (61), Kohlrausch (39), Harkins and Humphrey (31), and Harkins and Brown (104) have studied experimentally the variation of the ratio $W/(2\pi rT)$ with the value of r/A; and Lohnstein (45) has computed the same relation on the assumption that the residue of the drop left pendant to the tube was the stable drop for which the surface at the line of contact with the tube had the same inclination to the vertical as that of the unstable one which fell. The various tables thus prepared exhibit marked differences, due doubtless to the effect of slight mechanical and other disturbances upon the drop while passing through its condition of unstable equilibrium. These differences emphasize the weakness of the method as a means for obtaining reliable measurements of surface tension. The tables are, nevertheless, in agreement in showing that the ratio $W/(2\pi rT)$ varies markedly with the value of r/A and passes through a minimum when r/A is about equal to $\sqrt{2}$

Although these conclusions appear not to be accepted by Morgan (50), Lohnstein (47) has pointed out that his observations are actually concordant with them. In the progress of his work Morgan has been forced to limit the size of the tips he uses to those having radii that differ but little from $A\sqrt{2}$ for the liquids used for standardization; their use for liquids for which this relation is not approximately fulfilled is unjustified. He evades the point by demanding that the drop shall have a certain singular shape, described as bag-like. This limitation is closely equivalent to the former; but it is a criterion that can not be applied with rigor and leaves the observer uncertain whether the proper conditions have been satisfactorily met. The numerical relation leaves no such uncertainty; but in every case, whatever be the criterion, there remains the uncertainty arising from the effects of slight disturbances occurring while the drop is in its critical condition just preceding its fall.

The technique of this method, generally called the "drop-weight" method, is as simple as anyone could wish. For rapid work and within the limits of its reliability it would be the method of choice, especially when only small amounts of liquid are available, but it is not, and probably can not be made suitable for use where really accurate determinations are required. The reproducibility characteristic of averages is likely to lead to a very false estimate of the accuracy that has been attained. For example, Rayleigh (61) says:

> Successive collections, made without disturbance, gave indeed closely accordant weights (often to one-thousandth part), but repetitions after cleaning and remounting indicated discrepancies amounting to one-half per cent, or even to 1 per cent.

Although the method is not promising for accurate determinations, it is to be hoped that in Ferguson's proposed comparison of methods it will be compared with others under all the stringent requirements characteristic of precise physical work, so that its advantages as well as its disadvantages may be brought to light and that the conditions under which and the limits within which it can be trusted may be finally established.

Papers treating of this method and published prior to 1917 have been critically reviewed by Guye and Perrot (28a) and by Perrot (52a). Appended to their reviews are extensive bibliographies. In addition to the articles already referred to, the following should be consulted by those interested in this method: Davies (11), Ferguson (19), Guthrie (27, 28), Harkins and Brown (30), Lohnstein (46).

The methods so far considered have been based upon the measurement of the pressure exerted by a curved liquid surface. Obviously, it is possible to compute the tension from a direct measurement of the pull exerted by the surface under certain conditions. This is the basis of the numerous balance methods that have been proposed and used.

10. PULL OF VERTICAL FILM

Hall (29), Fahrenwald (14), Foley (24a), and Lenard, v. Dallwitz-Wegener, and Zachmann (42a) measured the pull exerted by the film formed upon a vertical rectangular frame when its uppermost side was raised above the flat surface of the liquid in the reservoir. The tension may be computed either from the maximum pull exerted by the film as the frame is raised or from the pull of the film after it has drained. Hall used both methods; the corrections to be applied are uncertain and troublesome.

11. PULL ON VERTICAL PLATE

Wilhelmy (90) weighed the pull upon a vertical plate dipping into the liquid. If the plate is very thin in comparison to its horizontal length, the pull is approximately equal to $T\cos\theta_1$ times the horizontal perimeter of the plate. Correction must be made for the effect of the liquid displaced by the submergence of the plate below the general level of the liquid. If the lower edge lies above the general level, there is likewise a correction for the liquid raised by adhesion to the bottom of the plate. Hall eliminated these hydrostatic corrections by making the weighing while the lower edge of the plate lay in the level of the undisturbed surface.

Worthington (92) rolled the strip into a cylindrical spiral, thus increasing the pull. He called this modification a "capillary multiplier."

12. PULL ON RING

Timberg (75) measured the maximum pull exerted by the surface as a thin horizontal ring of platinum was detached from the liquid surface. In reducing his observations he assumed that this pull is equal to the product of the surface tension times the sum of the outer and the inner perimeters of the ring. This approximation is of a low order. Cantor (9), and more recently Verschaffelt (80), have deduced a more exact expression for thin rings of rectangular cross section. Verschaffelt's equation, which is more exact than Cantor's, is equivalent to the following:

$$T=\frac{\overline{P}r}{4}\left[1-\left(\frac{\delta}{\overline{h}}\right)\sqrt{\frac{\overline{h}}{r}}\left\{2\sqrt{2}+\frac{2\sqrt{2}-1}{3}\sqrt{\frac{\overline{h}}{r}}\right\}+\left(\frac{\delta}{\overline{h}}\right)^2\left(\frac{\overline{h}}{r}\right)\left\{3+(4-\sqrt{2})\sqrt{\frac{\overline{h}}{r}}+\frac{9-4\sqrt{2}}{9}\frac{\overline{h}}{r}\right\}\cdots\right] \tag{18}$$

$$=\frac{\overline{P}r}{4}\left[1-\left\{2.8284+0.6095\sqrt{\frac{\overline{h}}{r}}\right\}\frac{\delta}{\sqrt{\overline{h}r}}+\left\{3+2.585\sqrt{\frac{\overline{h}}{r}}+0.371\frac{h}{r}\right\}\frac{\delta^2}{\overline{h}r}\cdots\right]$$

$$\overline{P}\equiv\frac{P}{\pi r^2}\qquad \overline{h}\equiv\frac{\overline{P}}{(\rho_1-\rho_2)g} \tag{19}$$

where P is the maximum pull, r is the mean radius of the ring, 2δ is the thickness of the ring, $\rho_1-\rho_2$ is the amount the density of the liquid exceeds that of the overlying fluid.[2] By the use of an indicating instrument, such as a torsion balance, for the measurement of the maximum pull, the value of the surface tension can be very quickly determined. The method has been used for the study of the progressive changes which occur in the surface tension of colloidal and certain other solutions (50a). It should be noticed that the equation (18) is derived on the assumption that the shortest distance between the ring and the wall of the vessel containing the liquid is so great that at a point midway between the two the surface is truly flat. If the vessel is cylindrical, the surface will not be flat unless this minimum distance amounts to some 2 or 3 cm, depending upon the surface tension and the density of the liquid. If the vessel is so small that the liquid surface between the ring and the wall is nowhere flat, then, in order to obtain the value of the surface tension, a correction will have to be applied to the quantity T computed in accordance with equation (18). It is believed that the mathematical expression for this correction has not been derived, but it appears evident that the amount of the correction will depend upon the properties of the liquid under study. When the vessel is small, it is not generally allowable to assume that the surface tension is proportional to the maximum pull, although such proportionality may practically exist for small variations in the tension. In much of the work done by this method the vessel has been too small.

The theory of various detachment methods has been discussed by Tichanowsky (74a, 74b), and a recent paper by Lenard, v. Dallwitz-Wegener, and Zachmann (42a) should be read by those expecting to use such methods.

13. ADHESION PLATE

In the method known as that of the adhesion plate, the force required to lift a horizontal circular plate from the surface of the liquid is measured. Two modifications of the method have been used. In one the maximum pull exerted as the disk is raised is measured. Ferguson's expression (16), slightly modified in form, for this

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[2] Since this paper was written there has appeared an important paper (31a) by Harkins, Young, and Cheng treating of the maximum pull upon a circular ring of circular cross section. They have determined experimentally the value of the factor F in the equation $T=PF/4\pi R$ for various values of A/R and of r/R, R and r being, respectively, the radius of the ring and of its cross section. They denote by V the total volume of liquid $(P/\rho_1 g)$ lifted by the tension and give four curves, each showing the variation of F with R^3/V for a different fixed value of r/R. Their F corresponds formally to the expressions in the square brackets in equations (18) and (19) but is not comparable with them because they are derived on the assumption that the axial width of the ring is effectively infinite.

maximum force (P) when the disk is perfectly wetted by the liquid is

$$h \equiv \frac{\overline{P}}{(\rho_1-\rho_2)g} \equiv \frac{P}{\pi r^2(\rho_1-\rho_2)g} = 2A\left\{1-\frac{A}{3r}-\frac{A^2\sqrt{2}}{3r^2}\right\} \tag{20}$$

Verschaffelt carries the expression only to the second term. The radius of the disk is assumed great. Ferguson says that in order to neglect the third term, r must be over 6 cm; he also calls attention to the fact that the r in this equation is not exactly the radius of the disk, but a slightly smaller one; the difference is negligible if r is sufficiently great to make the equation applicable.

In the other modification, the pull when the film is truly vertical where it meets the edge of the disk is measured. In this case the value of the angle of contact does not enter into the equation. This method was used by Gallenkamp (25). The expression for the pull (P_1) as deduced from the equation of Vershaffelt (80) is

$$h \equiv \frac{\overline{P_1}}{(\rho_1-\rho_2)g} \equiv \frac{P_1}{\pi r^2(\rho_1-\rho_2)g} = A\sqrt{2}\left\{1+\frac{7\sqrt{2}-4}{6}\left(\frac{A}{r}\right)\right\} \tag{21}$$

(There is an error, arising from an incorrect sign, in Gallenkamp's expression, p. 483.)

14. PULL ON SPHERE

Ferguson (16, 18, 21) has suggested the use of a sphere, the pull being measured when the lowest point of the sphere is in the plane of the undisturbed surface of the liquid. His expression, slightly modified, for the pull (P) in this case when the angle of contact is zero, is

$$\begin{aligned} \overline{P}R \equiv \frac{PR}{\pi R^2} &= 4T\left\{1-\frac{1}{3}\sqrt[4]{\frac{Th}{\overline{P}R^2}}-\frac{1}{3}\sqrt{\frac{Th}{\overline{P}R^2}}\cdots\right\} \\ &= 4T\left\{1-\frac{1}{3}\left(\frac{h}{4R}\right)^{1/4}-\frac{13}{36}\left(\frac{h}{4R}\right)^{1/2}\cdots\right\} \end{aligned} \tag{22}$$

where R is the radius of the sphere, and the other quantities have the same significance as formerly.

15. OSCILLATING DROPS AND BUBBLES

Owing to the capillary forces, a drop or bubble that is deformed from a spherical shape and then left to itself will execute periodic vibrations about its figure of equilibrium. These oscillations have been studied both mathematically and experimentally by Rayleigh (57, 58, 59, 63).

From a study of such vibrations the surface tension can be determined. For success a rather elaborate technique is required. The amplitude of vibration must be very small. The method is especially valuable, in that it permits the tension to be observed within a very short interval after the surface is formed. Lenard (42) employed the method as applied to freely falling oscillating drops. He found that the tension decreased as the age of the drop increased; this he attributed, probably correctly, to the contamination of the surface. Recently Kutter (40) devised a very simple, but probably not very precise, method for determining the period of the drops. He made use of the phenomenon described by Thomson and Newall (74) in 1885. When drops of one liquid fall into another with which it mixes, they form vortex rings that travel a greater or lesser distance into the second liquid. The depth to which they penetrate depends upon the form of the drop at the instant of impact; as the distance the drops fall before striking the liquid surface is progressively increased the depths reached pass through a succession of maxima and minima. The distance from one maximum to the next is equal to the distance that the drop falls while it is executing one complete vibration. His observations indicate that he can determine this distance with considerable precision; but it would appear to be necessary for the vibrations to have quite an appreciable amplitude, as compared with the radius of the drop, if the phenomenon is to be sharply defined, and the mathematical relation connecting the period with the surface tension and other quantities assumes that the amplitude is small in comparison with the radius. For this reason confidence can not be placed in the results, although those displayed appear to lead to nearly the correct values.

16. VIBRATING JETS

If at any point fixed with reference to its source a jet of liquid is subjected to a periodic change in form, it will be thrown into oscillations, which will exhibit themselves as stationary waves in the jet. Such vibrations have been studied both mathematically and experimentally by Rayleigh. His observations (57, 58) did not yield very satisfactory values for the tension. The subject was taken up again by Pedersen (51) with a very greatly improved technique. He showed that the method was capable of a precision that is comparable with those of other methods. The following year it was employed by Bohr (6). He elaborated Rayleigh's mathematical treatment and developed expressions that take account of the amplitude of the vibrations and of the damping of the waves. He obtained for the tension a value somewhat lower than that found by Pedersen and more nearly in agreement with the best of those found by other methods. He thinks that Pedersen's values are too high because he worked too near the orifice, obtaining measurements before the vibration had settled down to its normal condition.

17. RIPPLES

The velocity with which waves travel over the surface of a liquid depends upon the surface tension as well as upon the acceleration of gravity. The relative importance of these two factors depends upon the length of the wave. When the wave length is so short that the surface tension is the more important, the waves are commonly called ripples. Under suitable conditions the surface tension can be determined from the wave length and the period of ripples. This is known as the ripple method. The effect of the surface tension upon the velocity of surface waves was investigated by Kelvin in 1871 (37). The ripple method was used first by Rayleigh (60) in 1890 in his study of the contamination of water surfaces. (See also Lamb (41), Tait (72), Rayleigh (63).)

If the amplitude of the waves is so small that the square of the slope of the surface is at every point negligible in comparison with unity, if the waves are plane, and if the depth of the liquid is great in comparison with the length of the waves, then Kelvin's equation (23) is applicable

$$T=\frac{(\rho_1+\rho_2)\,\lambda^3}{2\pi\tau^2}\coth\frac{2\pi l}{\lambda}-\frac{(\rho_1-\rho_2)\,g\lambda^2}{4\pi^2} \tag{23}$$

where λ is the wave length, τ is the period, g the acceleration of gravity, T the surface tension, and l is the depth of the liquid; ρ_1 is the density of the lower liquid. Since T varies as the cube of the wave length and inversely as the square of the period, these quantities must be measured with extreme accuracy. This, however, can be done without great difficulty. The method obviously requires a large surface of liquid in order (*a*) that the waves reflected from the walls shall die out before reaching the portion under observation, and (*b*) that the undisturbed surface shall be truly plane. This large surface invites contamination, but has the advantage of distributing any small amount of contamination over a large surface, thus reducing its effect. In addition, it permits of a mechanical cleaning of the surface, thus enabling the observer to speak with confidence regarding the possible effect of the contamination that exists. The last is very desirable. The method is thoroughly trustworthy, but measurements must not be made too near the source, because, owing to the small amplitude of the waves, a very slight curvature of the surface will cause an appreciable relative displacement of the crests.

The necessity for considering this source of error, which has been quite generally ignored, was pointed out by the author a number of years ago. In that work (12) it was found that the curvature as far as 3 cm from the plate used for generating the waves was sufficient to displace the apparent crests by an appreciable amount. Consequently, no measurement should be made closer to the generator than 3.5 or 4 cm. Several experimenters have, however, employed observations made within a few millimeters of the generator. Some investigators, instead of using plane waves, have used the interference pattern produced by two sets of circular waves, assuming that the effects of the two sets of waves are directly additive; it is not evident that this is permissible, as here we have to do with a surface curvature, not with a mere surface elevation. (For experimental details and data see Rayleigh (60), Dorsey (12), Kalähne (36), Bohr (6), Grunmach (101, 102).)

Of the methods that have been considered a knowledge of the angle of contact is not required in (*a*) Sentis's method of virtual capillary tube, (*b*) pressure in a pendent drop, (*c*) measurement of the form of the surface so as to get the curvature at two different levels (this includes the method of Anderson and Bowen), (*d*) sessile drops or bubbles when the maximum horizontal diameter and either the distance from the vertex to the plane of the maximum diameter or the curvature at the vertex are used, (*e*) Jaeger's method, (*f*) pull of a true film, (*g*) maximum pull upon a thin ring, (*h*) pull on an adhesion plate when the surface is vertical at the line of contact, (*i*) oscillation of drops, (*j*) vibration of jets, and (*k*) ripples.

Those that require a knowledge of the angle of contact are (*a*) all others involving capillary rise in tubes, between plates, or against solid walls, (*b*) sessile drops or bubbles when the total thickness is used, (*c*) pull upon a vertical plate (Wilhelmy's method), (*d*) maximum pull upon an adhesion plate, and (*e*) pull upon a sphere.

The drop-weight method stands by itself as one involving undetermined factors.

Before closing, reference should be made to a few other articles. Those interested in capillary phenomena themselves will wish to read the article on "capillarity" in the Encyclopedia Britannica, and along with that Kelvin's comments (105) should be read. Boys's article (97) on the drawing of curves by their curvature, Pockels's article (107) on capillarity, and Maxwell's chapter on capillarity (106) should also be read. These and a few others that have not been referred to in the preceding portions of this article have been placed in a supplementary list at the end of the bibliography. The entries which are unnumbered have not been recently verified; they are believed to be correct.

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