of vibration, and a special flask, designed to give a clean liquid surface, buried under the water of a thermostat.

5. It was found that the accuracy of measurement of the dimensions of the rings depends greatly upon the method of illumination employed, and apparatus for these measurements was developed.

6. It was shown that at a certain height above the surface of the liquid the pull on the ring reaches a maximum. This maximum pull is what was determined in the measurements reported.

7. A necessary condition of the ring method is that the angle of contact between the ring and the liquid be zero.

8. Preliminary measurements indicate that the ring method may be used for the determination of interfacial tension.

CHICAGO, ILLINOIS

[CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY OF THE UNIVERSITY OF CHICAGO AND FROM ARMOUR INSTITUTE OF TECHNOLOGY]

A THEORY OF THE RING METHOD FOR THE DETERMINATION OF SURFACE TENSION

BY B. B. FREUD AND H. Z. FREUD

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The most convenient method for the determination of surface tension is perhaps what is known as the ring method. It has been used extensively, for example, by DuNoüy[1] in the case of numerous biological liquids. It is convenient because the experimental procedure necessary to obtain a fair degree of accuracy can be made very simple, although of course it becomes much more complicated when a higher degree of accuracy is sought. The essentials of the procedure are a ring, capable of being wetted by the liquid whose surface tension is to be measured, suspended horizontally in the flat surface of that liquid, and some device to measure the force necessary to separate ring and liquid. That the applied force may be changed gradually, a torsion balance is often used but a beam balance of the chainomatic type is also satisfactory. From this measured force, expressed as a weight, a quantity which many assume to be the value of the surface tension is often obtained from the relationship

$$W = 4\pi R\gamma \tag{1}$$

where R is the radius of the ring, γ the surface tension and W the maximum weight of liquid held up or the pull on the ring at the instant of rupture. Modifications have been introduced into this equation, such as the substitution of $(R_1 + R_2)/2$ for r, where R_1 and R_2 are the inner and outer radii of the ring. But the validity of this relationship is not at all obvious. An experimental study of it by Harkins, Young and Cheng[2] and

[1] DuNoüy, *J. Gen. Physiol.*, **1**, 521 (1918–1919), etc.

[2] Harkins, Young and Cheng, *Science*, **64**, 93 (1926).

a later one by Harkins and Jordan[3] indicate that it is in error in some cases by as much as 30% in either direction, plus or minus. The experiments of Harkins and his collaborators are expressed in the form of a series of empirical curves which involve the value of the surface tension as determined by a so-called absolute procedure and which must be used to correct the value given by the above relationship. It should be noted in this connection that a precisely analogous correction for the drop weight procedure for measuring surface tension was proposed by Harkins and Brown.[4] The purpose of this paper is to establish a theoretical basis for these empirical correction curves to the ring procedure, so that the values of surface tension as thus obtained may be accepted with that additional confidence which is given to a procedure based on a solid theoretical foundation. A similar study of the theoretical basis for the corrections to be used with the drop weight procedure made by Freud and Harkins[5] should be consulted for certain details of the mathematical analysis. These two studies are interrelated.

The ring method, and for that matter many other methods for the determination of surface tension, depends upon the equilibrium forms assumed by liquid surfaces under the combined action of their own surface tension and some external forces, of which gravity usually is the dominant one. The capillary rise method is usually considered an absolute procedure largely because it is affected by the shape of the liquid surface less than any of the others. In this procedure it enters only as a correction in estimating the volume of liquid in the meniscus. The shapes taken by liquid surfaces play a much more significant role in the bubble pressure, sessile drop, hanging drop and drop weight procedures, none of which accordingly have been regarded as fundamental. As was indicated in our study of the shapes of hanging and of detaching drops, the drop weight procedure alone of those just mentioned involves the properties of a dynamic system, the others being stable even though some of them are at the very limit of stability. It is only in drop weight procedure that the theory is not complete; in this case the weight of the detached drop involves changes in the shape of the drop during the process of detachment, which, of course, cannot be explained by any theory of static liquid surfaces. A dynamic theory has been proposed by us[5] but it proved much too complicated to be applied. The ring procedure, as this paper shows, is another that may be adequately based on sound theory. There is no fundamental reason why it too should not be regarded as an absolute method.

A fundamental equation for the shapes of liquid surfaces, credited to Laplace, is

[3] Harkins and Jordan, This Journal, **52**, 1751 (1930).

[4] Harkins and Brown, *ibid.*, **38**, 246–252 (1916).

[5] Freud and Harkins, *J. Phys. Chem.*, **33**, 1217–1234 (1929).

$$\frac{1}{R_1} + \frac{1}{R_2} = \frac{P}{\gamma} \tag{2}$$

where P is the pressure and R_1 and R_2 are the two principal radii of curvature at any point in the surface. For $1/R_1$ and $1/R_2$ may be substituted their equivalents, $\mathrm{d}u/\mathrm{d}x$ and u/x, in the special case of liquid surfaces of revolution. Here x is the horizontal distance of the point from the axis of symmetry, and u is the sine of the angle which the tangent to the surface at the point makes with the x-axis. The latter is, in the notation of this paper, coincident with the level of the undisturbed surface of the liquid. For P may be substituted $\pm ygd$, the sign depending upon the particular surface involved. P is really a composite of several factors such as barometric pressure, gas pressure, head of liquid above the point and possibly others. All, however, may be included in the term ygd if the x-axis is taken at what may be termed the "ideal level" of the surface, and y is the vertical distance of the point from this level. The question of the proper sign for these terms is important. It has been found convenient, in this paper, to hold the convention that R_1 and R_2 are positive when the osculatory circle is on the liquid side of the surface, and negative when on the gaseous side. This usually can be determined by inspection. $\mathrm{d}u/\mathrm{d}x$ and u/x are numerically equal to $1/R_1$ and $1/R_2$ but are like them in signs only when the original choice of u or v, the cosine of the angle of which u is the sine, is such as to make them so. The signs of $\mathrm{d}u/\mathrm{d}x$ and u/x can also be told by inspection. If they do not agree with those of $1/R_1$ and $1/R_2$, this fact must be formulated by preceding $\mathrm{d}u/\mathrm{d}x$ and u/x, in the equation, with negative signs. The sign of the ygd term also can be told by inspection. It depends upon whether the "ideal level" is above or below the point in question. If the effect of the weight of the column of liquid is a push on the surface from the liquid side, the absolute value of the weight is positive; if it is a pull, the absolute value is to be given the negative sign. For the quantity gd/γ may be substituted its equal by definition, $2/a^2$, where a^2 is the capillary constant of the liquid; and a^2 may be eliminated by the device of changing the variables from x and y to $a\bar{x}$ and $a\bar{y}$, thus eliminating all characteristics of any particular liquid. The equation in this form becomes

$$\frac{\mathrm{d}u}{\mathrm{d}\bar{x}} + \frac{u}{\bar{x}} = \pm 2\bar{y} \tag{3}$$

This equation describes the surfaces of a very diverse set of phenomena: pendent drops, drops of fluid in a medium of greater density on a tip pointing upward, menisci, both convex and concave, the surface of a liquid surrounding a vertical rod whether or not the rod is wetted, the liquid surface raised by a disk, bubbles of a fluid in a heavier medium on a tip pointing downward, and sessile drops—in fact all liquid surfaces of revolution. The fact that this equation applies only to surfaces of revolution excludes its application to such forms, for example as are produced when a wetted rectangular plate is raised from the surface of a liquid.

The ring method involves two of these shapes, the meniscus and the surface raised by a disk. Shapes of menisci are not too difficult to obtain. They are determined by mechanical integration of the equation exactly as described in our previous study of hanging drops, with the difference that if u is considered positive, increasing from 0 to 1 as $\bar{x}$ increases from 0, $\bar{y}$ must be considered negative in the equation, as $du/d\bar{x}$ and $u/\bar{x}$ do not agree in sign with $1/R_1$ and $1/R_2$, and the weight of the liquid causes a pull on the surface. The tables of Bashforth and Adams[6] give the data for a few of the menisci in Fig. 1. Unfortunately these tables do not include data for menisci for which $\bar{y}$ at the $\bar{y}$-axis is smaller than 0.1414. The numerical integration is exactly as originally described by Lohnstein,[7] with the change in sign mentioned above.

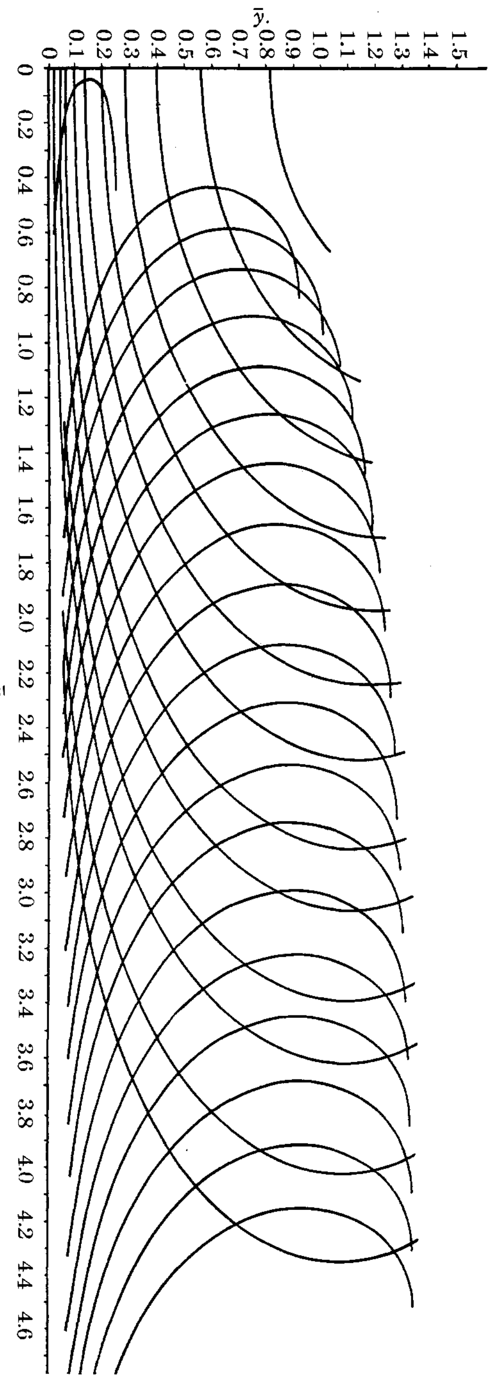


Fig. 1.—Meniscus and disk curves. Expansion of $du/d\bar{x} + u/\bar{x} = \pm 2\bar{y}$.

[6] Bashforth and Adams, "Attempt to Test Theories of Capillary Action," Cambridge University Press, **1888**.

[7] Lohnstein, *Ann. Physik*, [4] **20**, 237, 606 (1906).

In the case of the outside surface sloping away from the ring, however, the problem is less simple. It must be recalled that this equation cannot be integrated, and even mechanical integration requires that $\bar{x}$, $\bar{y}$ and u be known for some particular point in the surface. In the cases of a stable pendent drop and a meniscus, it is known that at the very bottom u equals zero because at this point the tangent to the surface is parallel to the $\bar{x}$-axis, and $\bar{x}$ and $\bar{y}$ may be known from a suitable choice of the coördinate system. In the case of the surface raised by a disk, however, no point is really known except at infinite distance from the disk, that is, in the undisturbed level of the surface. Here $\bar{x} = \infty$, $\bar{y} = 0$ and $u = 0$. Because one of the coördinates of this known point has the value of infinity, the method of numerical integration, using Taylor's theorem, is inapplicable. However, we also know that $\bar{y}$ and u become very nearly equal to zero before $\bar{x}$ becomes very large. We have considered it sufficiently precise to assume that $\bar{y}$ and u become equal to 0.00001 units at distances from the axis of symmetry varying from 7.5 to 12.0 units. These distances were chosen because the resulting curves lay in the region experimentally investigated by Harkins and his collaborators. One curve starting much closer to the $\bar{y}$-axis is given, but was not used in any of the calculations. This approximation involves an error so small that conclusions can nevertheless be made with a precision quite equal to that given by the best experimental technique.

It will be observed that our choice makes the sign of u positive for these outside surfaces, and thus fixes the signs to be used in Equation 3. As $\bar{y}$ and u both increase with decreasing $\bar{x}$, the tangents u/v and $\mathrm{d}u/\mathrm{d}\bar{x}$ are both negative, thus making v also negative; $u/\bar{x}$ is positive. Inspection shows that $1/\bar{R}_1$ is negative and $1/\bar{R}_2$ is positive according to our convention. Since these agree in sign with $\mathrm{d}u/\mathrm{d}\bar{x}$ and $u/\bar{x}$, and the weight of the liquid column causes a pull on the surface, the equation to be used for these outside surfaces, thus, is

$$\frac{\mathrm{d}u}{\mathrm{d}\bar{x}} + \frac{u}{\bar{x}} = -2\bar{y} \tag{4}$$

Had a negative sign been chosen for u, $d\bar{y}/d\bar{x}$ and $u/\bar{x}$ would have been negative and $\mathrm{d}u/\mathrm{d}\bar{x}$ and v positive. In this case $\mathrm{d}u/\mathrm{d}\bar{x}$ and $u/\bar{x}$ do not agree in sign with $1/\bar{R}_1$ and $1/\bar{R}_2$, so the equation would have been

$$-\frac{\mathrm{d}u}{\mathrm{d}\bar{x}} - \frac{u}{\bar{x}} = -2\bar{y}, \text{ or} \tag{5}$$

$$\frac{\mathrm{d}u}{\mathrm{d}\bar{x}} + \frac{u}{\bar{x}} = 2\bar{y} \tag{5'}$$

Mechanical integration of Equations 4 and 5 gives the same curve.

The two families of surfaces obtained in these ways are given in Fig. 1. The left edge of the figure, the $\bar{y}$-axis, is the axis of symmetry, and the lower edge, the $\bar{x}$-axis, is the level of the undisturbed liquid. The family of curves crossing the axis of symmetry represents the shapes of the menisci obtained with various rings for the different heights to which they are raised above the surface. The family reaching apparently to infinity at the right edge of the figure represents the shapes of the outside surfaces formed by the raised rings. If a ring made of wire with a rectangular cross section, one of whose edges is in the plane of the ring, is lifted from the $\bar{x}$-axis in such a way that its lower edge alone is wetted, the plane of the ring remaining parallel to the flat surface of the liquid, the various portions of the family of meniscus curves intersected by the lower left corner of the wire give the shapes of the crater-like formations at the center of the raised liquids. Similarly, those portions of the other family of curves intersected by the lower right corner of the wire give the outside slopes of the mountain-like formations pulled up by the ring.

If the ring is made of wire having a circular cross section and is pulled out, keeping the plane of the ring parallel to the undisturbed surface, the two curves, one from each family, which are at any particular position tangent to it, the meniscus on the inside and the other on the outside, give the shapes of the inner crater and the outer slope of the liquid raised by the ring in that particular position. The last statement involves an approximation. It is assumed that the material of the ring is wetted by the liquid. While it is accordingly to be expected that a film of liquid covers the whole of the ring, this film must be very thin where the ring is not immersed, for the attraction which causes it to adhere extends only a very short distance from the surface. The volume of this film, then, must be small. It is assumed in this discussion that it is negligible in comparison with that held up by the surface tension itself. Those curves that are tangent to the ring are the ones selected because the fact that the ring is wetted implies a zero angle of contact.

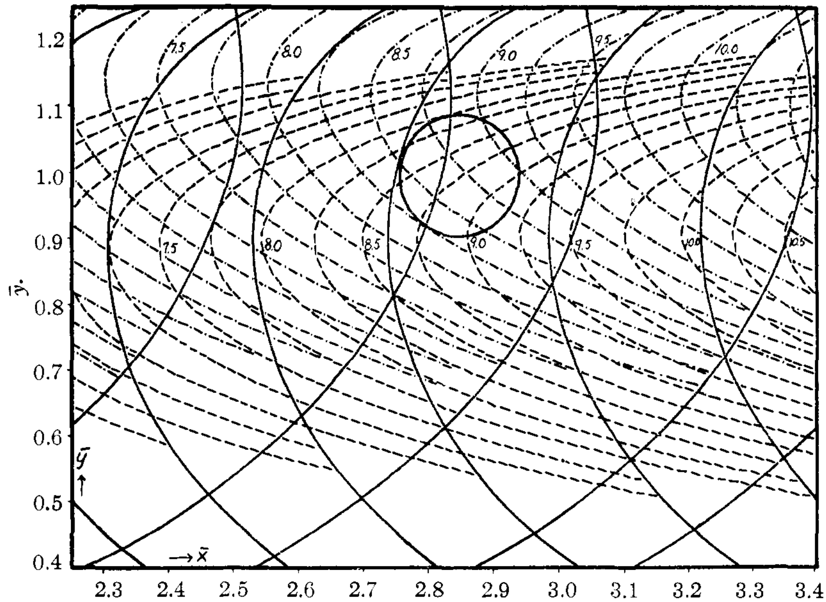
The quantity measured in the experimental procedure of the ring method is the weight necessary to cause the ring to break away from the liquid. This is usually the maximum weight of liquid held up by the ring. It may be calculated from our graphs of Equation 3. After the capillary constant has been eliminated from the equation, that which corresponds to the volume of the liquid held up by the ring in a particular position will be designated by $\bar{V}$. Its value is found as follows. Integration of Equation 3 gives for the volume below any horizontal section through the outer surface, for example, below the section through the point of tangency of curve and ring

$$\bar{V}_1' = \pi\bar{x}_1^2\bar{y}_1 + \pi u_1\bar{x}_1 \qquad (6)$$

and for the volume below any similar horizontal section cutting the meniscus surface

$$\bar{V}_2' = \pi\bar{x}_2^2\bar{y}_2 - \pi u_2\bar{x}_2 \qquad (6')$$

where subscripts 1 and 2 refer, respectively, to the points of tangency of the outer and meniscus surfaces with the ring, and the corresponding $\overline{V}'$ accordingly represents the volume below this section. For the outer curve it is the volume generated by revolving about the axis of symmetry the area bounded by the $\bar{x}$-axis, the $\bar{y}$-axis, the line $\bar{y} = \bar{y}_1$ and the curve; for the meniscus it is the volume generated similarly by the area bounded by the $\bar{y}$-axis, the line $\bar{y} = \bar{y}_2$ and the curve. This is shown in Fig. 3. $\overline{V}_1$, the volume outside of the line $\bar{x} = \bar{x}_1$ corrected as discussed below, is obtained by subtracting the volume of the cylinder $\pi\bar{x}_1^2\bar{y}_1$ from $\overline{V}_1'$. From Equation 6 $\overline{V}_1$ is thus seen to be equal to $\pi u_1\bar{x}_1$. From Equation 6′ it is seen that $\overline{V}_2$, the volume held up by the ring inside of the line $\bar{x} = \bar{x}_2$ properly corrected, is given by subtracting $\pi\bar{x}_2\bar{y}_2$ from $\overline{V}_2'$, and making the necessary change in sign.



—— Meniscus and disk curves; - - - constant $\pi u_1\bar{x}_1$ (disk); — - — constant $\pi u_2\bar{x}_2$ (meniscus).

Fig. 2.—Portion of Fig. 1 with constant $\pi u\bar{x}$ lines.

The volume labeled $\overline{V}_3$ in Fig. 2, between the limits $\bar{x} = \bar{x}_2$ and $\bar{x} = \bar{x}_1$, is obtained, allowing for a small correction, by finding the volume generated by revolving the area under a curve about an axis. In this case the curve is the cross section of the wire between the points $\bar{x}_2$, $\bar{y}_2$ and $\bar{x}_1$, $\bar{y}_1$ and the axis of revolution is the $\bar{y}$-axis. It is accomplished as follows. For convenience the bars above all symbols are dropped in the following derivation. R is the radius of the ring, r is the radius of the wire and h is the height of the bottom of the ring above the x-axis.

$$V_3 = 2\pi \int_{x_2}^{x_1} x\{(h + r) - \sqrt{r^2 - (R - x)^2}\}\mathrm{d}x$$

$$\int_{x_2}^{x_1} x(h + r)\mathrm{d}x = \left.\frac{x^2(h + r)}{2}\right]_{x_2}^{x_1}$$

$$\int_{x_2}^{x_1} x\sqrt{r^2 - (R - x)^2}\,\mathrm{d}x = -\int_{x_2}^{x_1} (R - x)\sqrt{r^2 - (R - x)^2}\,\mathrm{d}x + \int_{x_2}^{x_1} R\sqrt{r^2 - (R - x)^2}\,\mathrm{d}x$$

$$= -\frac{1}{3}\{r^2 - (R - x)^2\}^{3/2}\Big]_{x_2}^{x_1} - \frac{R}{2}(R - x)\{r^2 - (R - x)^2\}^{1/2}\Big]_{x_2}^{x_1} - \frac{R}{2} r^2 \sin^{-1}\frac{R - x}{r}\Big]_{x_2}^{x_1}$$

$$\therefore V_3 = \pi\{(h + r)(x_1^2 - x_2^2) + \frac{2}{3}[(h + r - y_1)^3 - (h + r - y_2)^3] + R(R - x_1)(h + r - y_1)$$
$$- R(R - x_2)(h + r - y_2) + Rr^2\left(\sin^{-1}\frac{R - x_1}{r} - \sin^{-1}\frac{R - x_2}{r}\right)\} \qquad (7)$$

Of the terms in Equation 7 only the first and last are of appreciable significance in most cases, and just these two were usually used in the calculations. In some cases, however, it was necessary to use the third

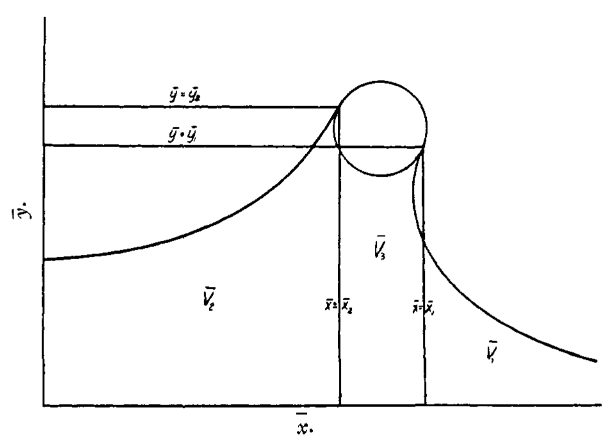


Fig. 3.—Vertical section of liquid raised by ring.

and fourth. It may seem that another correction should be made for the small volume of the ring which may be inside of the line $\bar{x} = \bar{x}_2$ or outside of that $\bar{x} = \bar{x}_1$. However, this is already allowed for in the calculation of $\bar{V}_3$, when $\sin^{-1}\frac{R - x_1}{r}$ or $\sin^{-1}\frac{R - x_2}{r}$, as the case may be, is greater than $\pi/2$. When these angles are less than $\pi/2$, the lines $\bar{x} = \bar{x}_2$ and $\bar{x} = \bar{x}_1$ cut the surfaces, and the correction is made in the corresponding value of $\pi u\bar{x}$, that is, $\bar{V}_1$ or $\bar{V}_2$. These corrections are, in general, so small as to be negligible in all cases except when R/r is very small.

The total volume held up by the ring in any position is given by

$$\bar{V} = \bar{V}_1 + \bar{V}_2 + \bar{V}_3$$

To facilitate the use of Fig. 1 in these calculations, constant $\pi u\bar{x}$ curves, isochors, for the two families of surfaces have been calculated, and superposed upon Fig. 1. Thus at any point on the map $\overline{V}_1$ and $\overline{V}_2$ may be read off. Unfortunately the necessary interpolations are such as to introduce an error into the conclusions, but this is inherent in the graphical method of solution. Of course, the error may be reduced below any desired limit if enough surfaces are calculated. To attain the precision of the experimental values of Harkins and Jordan more curves than we have provided are needed, although it is estimated that our procedure gives results of the same order of precision as their experimental method. We have been sufficiently precise to convince ourselves of the adequacy of the underlying theory proposed.

A small portion only of the map is reproduced in this paper as Fig. 2. The whole would be quite unintelligible, as well as unusable, because of the reduction necessary for publication, but the portion reproduced serves adequately to demonstrate our procedure. The heavy circle is the cross section of the wire of the ring. In the actual procedure we lay upon the map, which is an enlarged Fig. 1 bearing the constant volume lines, a metal template of this cross section made, of course, to scale, and place its center at a distance from the $\bar{y}$-axis equal to $\overline{R}$ for the ring. The points of tangency of the two curves, one from each of the two families of surfaces, with the wire are noted. These points are $\bar{x}_1$, $\bar{y}_1$ and $\bar{x}_2$, $\bar{y}_2$, respectively, and $\overline{V}_1$ and $\overline{V}_2$ are read from the map. $\overline{V}_3$ is calculated approximately from the formula $\pi(\bar{x}_1^2 - \bar{x}_2^2)(\bar{h} + \bar{r})$, thus using merely the first term of Equation 7, which is written as $\overline{V}_{3a}$. $\overline{V}_1 + \overline{V}_2 + \overline{V}_{3a}$ gives an approximate value of the total volume held up. The procedure is repeated, varying $\bar{h}$, that is, moving the template parallel to the $\bar{y}$-axis. It is found that as $\bar{h}$ increases, the approximate value of $\overline{V}$ goes through a maximum. This maximum value and a few on either side of it are recalculated more precisely using additional terms of Equation 7. The maximum thus precisely calculated is taken as the maximum volume capable of being held up by the ring, and its weight is what is measured by the ring method.

Harkins and his collaborators plot their values for the corrections to be applied to the usual ring method on a diagram using R^3/V and γ/p as the coördinates, where R is the radius of the ring and $p = W/4\pi R$, a procedure quite analogous to Harkins and Brown's correction curve for the drop weight determination. The corresponding terms in our procedure are $\overline{R}^3/\overline{V}$ and $2\pi\overline{R}/\overline{V}$. $\overline{R}^3/\overline{V}$ is identical with R^3/V because the a^3 in numerator and denominator cancels. $2\pi\overline{R}/\overline{V}$ corresponds to γ/p by virtue of

$$\frac{\gamma}{p} = \frac{4\pi R\gamma}{W} = \frac{4\pi R\gamma}{Vgd} = \frac{4\pi Ra^2}{2V} = \frac{2\pi\overline{R}a^3}{\overline{V}a^3} = \frac{2\pi\overline{R}}{\overline{V}}$$

These quantities have been calculated by the procedure just outlined. The curves given by these variables are found to coincide with the experimental curves within the accuracy of the calculations. For comparison particular points so calculated are shown in Fig. 4. We are certain that any discrepancies are due entirely to the difficulties inherent in a graphical method and in the fact that enough surfaces have not been calculated; but only those who have made such numerical integrations can appreciate the labor involved in producing even a single curve.

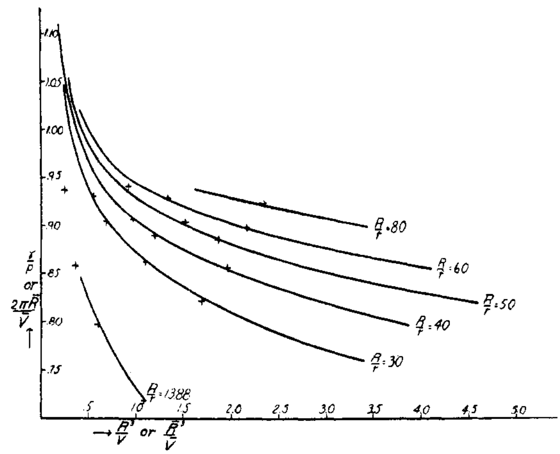


Fig. 4.—Comparison of theory and experiment: ——, experiment (Harkins and Jordan); +, theory (Freud).

The remarkable agreement between the calculated and the experimental values shows that, within the small error of both methods, the same values of the surface tension are obtained, whether the relative corrections of Harkins and his collaborators, or the absolute corrections as calculated by us are used. Thus the ring method, as described by Harkins, Young and Cheng, may now be considered as an absolute method, since by it the surface tension may be determined without reference to any other method.

Conclusions

1. A theory for the ring method of determining surface tension, based on the fundamental Laplace equation describing stable liquid surfaces, has been proposed.

2. This equation has been integrated numerically, thus giving data describing the shapes of the surfaces formed by raising a wetted ring out of a liquid. These data are represented in the paper by a graph of two families of curves. They may be used to supplement the tables of Bashforth and Adams.

3. From these curves it is possible to find certain ratios which are analogous to the dimensions of any particular ring and to the volume of any liquid held up by it. The relationship between three suitable functions of these ratios gives a set of curves which are analogous to those

determined experimentally and which are quite independent of any measurement of surface tension.

4. These curves are found to agree with the analogous experimental curves.

5. The ring method may thus be considered an absolute one for the determination of surface tension.

CHICAGO, ILLINOIS

[CONTRIBUTION FROM FERTILIZER AND FIXED NITROGEN INVESTIGATIONS, BUREAU OF CHEMISTRY AND SOILS]

EQUILIBRIUM IN THE SYSTEM $Co-CO_2-CoO-CO$. INDIRECT CALCULATION OF THE WATER GAS EQUILIBRIUM CONSTANT

BY P. H. EMMETT AND J. F. SHULTZ

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Introduction

A survey of the literature reveals marked disagreement concerning the value of the equilibrium constant K_1 for the reaction

$$CO + H_2O = CO_2 + H_2 \quad K_1 = (P_{CO_2})(P_{H_2})/(P_{CO})(P_{H_2O}) \qquad (1)$$

Hahn,[1] Haber and Richardt,[2] and finally Neumann and Köhler[3] have obtained directly values for the equilibrium constant. However, Eastman[4] and his collaborators, by measuring the equilibrium in each of the reactions

$$FeO + H_2 = H_2O + Fe \quad K_2 = P_{H_2O}/P_{H_2} \qquad (2)$$

$$FeO + CO = CO_2 + Fe \quad K_3 = P_{CO_2}/P_{CO} \qquad (3)$$

$$SnO_2 + H_2 = Sn + H_2O \quad K_4 = P_{H_2O}/P_{H_2} \qquad (4)$$

$$SnO_2 + CO = Sn + CO_2 \quad K_5 = P_{CO_2}/P_{CO} \qquad (5)$$

and by making use of the relations $K_1 = K_3/K_2 = K_5/K_4$, obtain indirectly a value for the water gas equilibrium constant that differs by about 40% from the directly determined one. The evidence for the validity of the indirect calculation has seemed particularly strong in view of the fact that the results obtained in the $Sn-SnO_2$ system agree so excellently with those in the $Fe-FeO$ system. Accordingly, since we have already determined and published[5] the value of the equilibrium constant for the reaction

$$CoO + H_2 = Co + H_2O \quad K_6 = P_{H_2O}/P_{H_2} \qquad (6)$$

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[1] Hahn, *Z. physik. Chem.*, **44**, 513 (1903); **48**, 735 (1904).

[2] Haber and Richardt, *Z. anorg. Chem.*, **38**, 5 (1904).

[3] Neumann and Köhler, *Z. Elektrochem.*, **34**, 218 (1928).

[4] (a) Eastman and Evans, THIS JOURNAL, **46**, 888 (1924); (b) Eastman and Robinson, *ibid.*, **50**, 1106 (1928).

[5] Emmett and Shultz, *ibid.*, **51**, 3249 (1929).