[Contribution from the Wolcott Gibbs Memorial Laboratory, Harvard University.]

A CRITICAL STUDY OF THE CAPILLARY RISE METHOD OF DETERMINING SURFACE TENSION, WITH DATA FOR WATER, BENZENE, TOLUENE, CHLOROFORM, CARBON TETRACHLORIDE, ETHER AND DIMETHYL ANILINE.

[Second Paper.][1]

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The Contact Angle.

One of the moot points concerning the validity of results with the capillary rise method of determining surface tension is the question as to whether or not the meniscus of the liquid surface is exactly tangent to the inner wall of the capillary tube at its highest point. This is, of course, an important question, demanding definitive answer. Various attempts to settle it have been made with varying results.[2] The consensus of opinion seems to be that in most cases the angle of contact is zero; but more convincing evidence is needed.

The present method consisted in the direct observation of the angles of reflection of rays of light from the region immediately surrounding the line of union of the liquid and glass. A rectangular glass vessel (the lower part of a flat moulded bottle) was filled with the liquid to overflowing; and in it was stood vertically a piece of carefully cleaned plate glass. A fine bundle of horizontal parallel light rays (obtained by passing light from a Nernst glower through a collimator and then through an inclined spectroscope slit) was allowed to fall upon the plate glass in such a manner that the upper rays struck the glass above the liquid while the lower ones struck the liquid as it curved up to the glass. The rays striking the glass must be reflected horizontally, but those striking the liquid must be reflected upwards at angles equal to twice the departure of the liquid from the vertical. A discontinuity between the two reflections would indicate a contact angle between the liquid and the solid.

When in use the receptacle was enclosed in a blackened wooden box, the interior of which had been saturated with the vapor of the liquid by a dish of the slightly warm liquid. The reflected rays were usually caused

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[1] All the experimental work on this paper was finished early in 1917, long before the interesting and important paper on this subject was published by W. D. Harkins and F. E. Brown, This Journal, **41**, 499 (1919). It supports and supplements this paper.

[2] See for example, Quincke, *Wied. Ann.*, **2**, 145 (1877); **27**, 219 (1886); **52**, 1 (1894); **61**, 267 (1897); **64**, 618 (1898); Magie, *ibid.*, **25**, 432 (1885); Ramsay and Shields, *Z. physik. Chem.*, **12**, 452 (1893); Volkmann, *Wied. Ann.*, **53**, 633 (1894); Richards and Coombs, This Journal, **37**, 1668 (1915).

to fall upon a photographic plate; but instead of using the photographic plate, a clear glass could conveniently be used and the rays followed visually by means of a pin-hole placed in front of the eye.

Fig. 1 is a photographic record of rays thus reflected, made with water. The straight line is the reflection of the slit image from the glass, while the upper part of the curved line is the reflection from the liquid. If there had been an "angle of contact," the curved line would not have met the straight line, but would have began some distance above. A faint curve (continued below the straight line) was caused by the reflection from the glass below the liquid, the curvature being produced by refraction at the air-liquid boundary. The continuity is further evidence of the absence of a contact-angle. This lower curve is too faint to appear in the print.

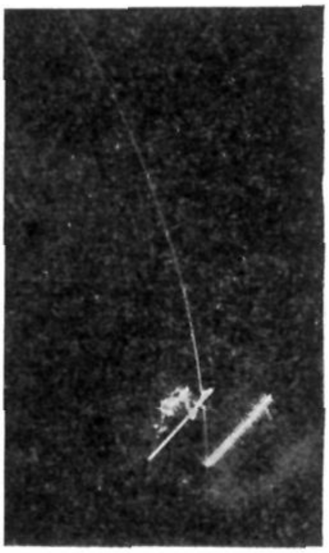

Fig. 1.—Showing contact between curved reflection from meniscus and image of slit reflected from glass plate. This indicates complete tangency at point of contact. (The images to the left were caused by irregular reflecting surfaces behind the glass plate and are to be disregarded.)

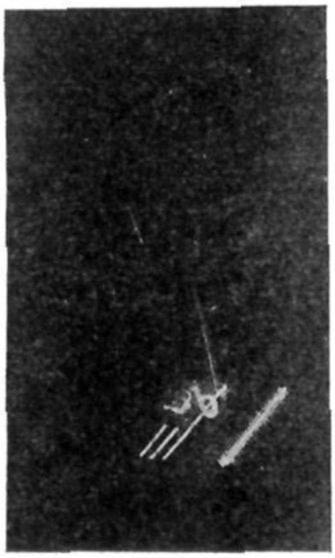

Fig. 2.—Showing break between curved reflection from meniscus and image of slit, with meniscus from which the edge had evaporated. This indicates a definite contact angle.

The foregoing experiment shows conclusively that when glass is thoroughly cleaned, and when no evaporation is taking place, there is no angle of contact in the case of water. Similar results were obtained with ethyl alcohol, benzene, carbon tetrachloride, chloroform, and ether. It seems safe to assume that there is no angle with any similar liquids which "wet" glass.

Fig. 2 is an exposure made intentionally when evaporation was taking place. Here the curve does not meet the slit-image; therefore, there must have been an angle of contact in this case. Evidently, then, the exclusion of evaporation is very essential.

The accompanying photograph (Fig. 3,) of a glass rod dipping in water (and surrounded above by moist air in an appropriate glass box) shows clearly the fact that the contact-angle with water must be very small, if existent at all, thus confirming the preceding method.

The outcome suggests (as has been surmised before)[1] that the different results sometimes obtained with tubes of different materials are due to incomplete adhesion of the liquid to the wall. This may be caused either by roughnesses, or by impurities, or by partial evaporation of the thinnest part of the film. In support of this conclusion, it may be mentioned that Volkmann[2] found that capillaries of different kinds of glass give essentially the same results for the surface tension of water.

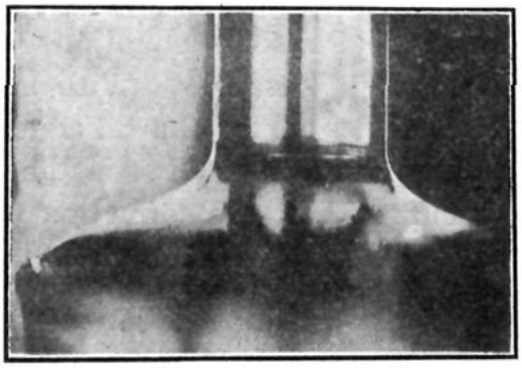

Fig. 3.—Photograph of glass rod in water, magnified 5 times. No contact angle is perceptible even with a magnifying glass on the original negative.

The Correction for the Small Meniscus.

The need of a correction for the weight of liquid above the bottom of the small meniscus in the capillary tube has given rise to a number of mathematical investigations, of which the equations of Poisson,[3] $h = h_\circ + r/3 - 0.1288\,r^2/h$, and of Hagen and Desains,[4] $h = h_\circ + a^2r/(3a^2 + r^2)$ (which latter represents an oblate hemispheroid) are held in best repute.

In these equations h is the true corrected height of column, $h_\circ$ the observed height of column to bottom of meniscus, r the radius of tube, a^2 is equal to hr, the capillary constant of the liquid under examination.

In coöperation with L. B. Coombs,[5] one of us pointed out recently that Poisson's equation leads to an absurdity when the capillary becomes wide, whereas that of Hagen and Desains leads to no such self-contradiction and is therefore to be preferred. In this recent Harvard research just mentioned, the experimental method represented by the equation $h = h_\circ + h_m/3$ was used, in which h_m is the measured height of the meniscus from its lowest point to that where it becomes exactly tangent with the wall of the separating tube. This experimental method is closely, if not exactly, equivalent to the equation of Hagen and Desains, its chief difficulty being the uncertainty as to the exact position of the last named upper limit. It was shown that all of these three expressions reduce to the simple equation $h = h_\circ + r/3$, when r is very small.

In view of these considerations the late Lord Rayleigh[6] investigated

[1] For example, Richards and Coombs, *loc. cit.*, p. 1668.

[2] Volkmann, *loc. cit.*

[3] Poisson, "Nouv. Theor. d. l'act. capill.," Paris, 1831, p. 112.

[4] Desains, *Ann. chim. phys.*, [3] **51**, 417 (1857); see also Chwolson's "Physik," **1**, p. 598 (German edition) where the equation is incorrectly given.

[5] Richards and Coombs, *loc. cit.*

[6] The Rt. Hon. John William Strutt, 3rd Baron Rayleigh, *Proc. Roy. Soc.* A, **92**, 184 (1915).

further the difficulty with the Poisson equation and pointed out that it should be corrected for any but the smallest tubes by the addition of another term, $+0.1312\ r^3/h^2$. In a typical case in which $r = 1$ mm. and $a^2 = 3$ mm^2., the correction for the capillary meniscus becomes 0.290 mm. with Poisson's equation, 0.295 with Rayleigh's and 0.300 with Hagen and Desains's. With narrower tubes or with liquids having larger values for a^2 the differences between the results of the equation would be much less. For instance, with the same liquid and a tube with 0.5 mm. radius, the correction to h_0 would be: Poisson's 0.1613, Rayleigh's 0.1614, and Hagen and Desains's 0.1622. With water in the larger tube (1 mm. radius) the value becomes 0.324 with Poisson's, 0.324 with Rayleigh's, and 0.326 with Hagen and Desains's.

In the last examples the difference between the several expressions and doubtless also the deviation of any one of them from the true value is no greater than the possible error of the experiment. Obviously, for safety with regard to this matter, as well as to attain precision of measurement, a narrow capillary tube should be used, especially for a liquid with small surface tension. The difference between most of these values and the results of the experimental method used in the earlier Harvard work is less than the probable error of experiment.

Correction of the Large Meniscus.

In the earlier Harvard research it was shown that many previous experimenters had used tubes of inadequate size in the wide arm of the apparatus. In such tubes the base of the large meniscus is raised distinctly above its true position and, therefore, the rise in the small tube appears to be smaller than it really ought to be. Qualitative experiments led us to believe that the large tube in the case of water should be larger than 34 mm.; but the minimum width was not certainly established, and the matter was postponed for further study. A tube of 38.4 mm. diameter was actually used.

Subsequently, Lord Rayleigh[1] subjected the matter to mathematical analysis, and showed that even tubes of 38 mm. diameter, although wide enough with liquids like benzene, are probably not wide enough to take advantage of the experimental accuracy which had been attained in the case of water. His mathematical treatment took the same line as a similar study by Laplace[2] and led to a somewhat similar result, namely, the following equation,

$$r/\alpha - \log.\ \alpha/h_0 = 0.8381 + 0.2789\ \alpha/r + 0.5 \log \pi r/\alpha,$$

in which $\alpha^2 = {}^1/_2 a^2 = {}^1/_2$ hr. This equation gives a correction of 0.016 mm. for water in a tube of 38.4 mm. diameter such as was used by Rich-

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[1] Lord Rayleigh, *loc. cit.*

[2] Laplace, "Méc. Cél.," 4, suppl. to Book X, 1805, p. 59.

ards and Coombs. Walden and Swinne[1] used Laplace's formula to correct for the meniscus in their wide tube, which needed the correction more, however, because it was narrower than ours.

Since Lord Rayleigh was somewhat doubtful as to the accuracy of his equation[2] and since he showed that it could not hold with tubes as narrow as 10 mm. in diameter, experimental verification seemed desirable. In the previous Harvard research it had been pointed out that the small values concerned are not easily found with accuracy by direct measurement of capillary height because of the difficulty of obtaining very wide tubes with optically perfect walls. Therefore we sought to solve the problem by determining quantitatively the radius of curvature of the surface of water in a dish 38 mm. in diameter. In the earlier work this observation had been made in merely qualitative fashion.

Attempts to neutralize the distortion of the reflection of a small circular object in the liquid surface by means of concave lenses, yielded fluctuating and inconsistent results, but the method finally adopted was very satisfactory. It consisted in measuring the displacement of an inclined ray of light reflected first from one point near the center of the wide meniscus, and then from another point at the same distance on the opposite side of the center. The apparatus is depicted in Fig. 4.

The ray was reflected from the water surface either to a photograhic plate or to an observation pin-hole (E) in a card—which latter was hung firmly upon a pivot, and provided with a long pointer moving over a scale. A large swing of the pointer moved the pin-hole only a short distance, but that distance could be measured with fair accuracy. Guides and stops allowed the dish to be moved but a certain distance, and in only one direction (in the figure, at right angles to the plane of the paper).

From the distance through which the observation pin-hole was moved (or that between the photographic images) corresponding to two opposite settings of the dish, together with the displacement of the dish and the vertical distance from the pin-hole to the level of the water, the radius of curvature could be calculated. The dark-room was saturated with moisture before each measurement, in order that no angle of contact, with its consequent irregularities, should be formed. The dish was cleaned with hot sulfuric and chromic acids and much water, and refilled with purest distilled water before every measurement.

The method of calculation involves the assumption that the curvature at the bottom is a segment of a sphere. This is not exactly the case,

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[1] Walden and Swinne, *Z. physik. Chem.*, **79**, 705 (1912).

[2] The general integration of the differential equation for liquid capillary surfaces has not yet been satisfactorily accomplished. Lord Kelvin, *Proc. Roy. Inst.*, **1886**, Boys, *Phil. Mag.*, **36**, 75 (1893); and Pöckels, Winkelmann's "Handbuch der Phys.," [I] 2, 1908, 1131, have contributed toward this solution and Lord Rayleigh has probably gone further than any one else in its application.

but as the same curvature was found when the dish was moved 8 mm. as when moved 2 mm., we assumed that no large error was introduced by the assumption.

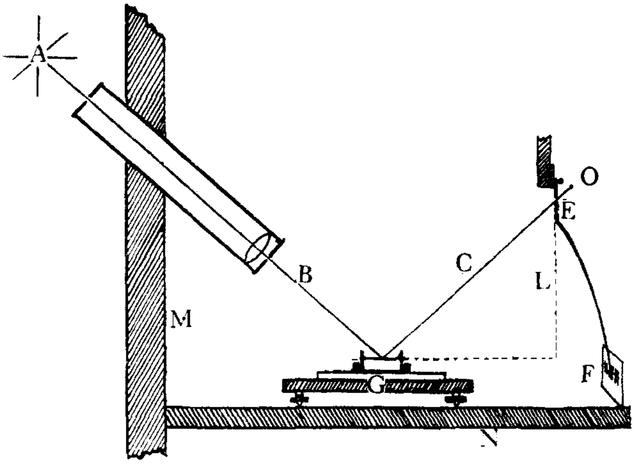

Fig. 4.—Apparatus for determining curvature of wide liquid surfaces, represented diagrammatically. A = Nernst lamp; B = incident ray of light through collimator with two pin-holes. C = reflected ray of light; E = pivoted card with observation pin-hole (sometimes replaced by photographic plate); F = index with scale (in perspective); G = dish of liquid resting on glass plate supported by levelled board; L = height of observation pin-hole above liquid; M = wall of dark room; N = table top; O = position of observer's eye.

Let L equal the vertical distance from the observation pin-hole to the water level. Let d be the distance through which the pin-hole must be moved, let c equal the distance through which the dish was moved, and let θ equal the arc of the sphere represented by the distance c.

Then $$\sin 2\theta = d/L$$

or, with sufficient approximation (since the angle is very small)

$$\sin \theta = d/2L$$

and

$$\sin \theta = c/R$$

where R = the radius of curvature of the bottom of the meniscus.

Combining these last two equations we get,

$$R = \frac{2Lc}{d}.$$

Now the height to which any liquid rises under a curved surface like this is equal to a^2/R where a^2 = the capillarity constant.[1]

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[1] This is obtained by considering the difference in pressure above and below the surface film, which difference is due to the weight of the liquid, pulling downwards, and is equal to $h_o Dg$ (h_o = height of liquid, D = density, and g = gravitational const.) In order to maintain this difference in pressure the surface must be curved so that

Thus we get

$$h_0 = \frac{a^2d}{2Lc}.$$

The results obtained are shown in the table following. ($a^2 = 14.88$). Although the variations are considerable, their average should be fairly near the truth. This average agrees remarkably well with the corrections calculated by the equations of Lord Rayleigh and Laplace.

CAPILLARY RISE IN 38 MM. TUBE.

No.	d(mm.).	c(mm.).	L(mm.).	h_0.
1	3.5	8.7	224	0.013
2	3.9	8.7	224	0.015
3	3.8	8.7	224	0.014
4	5.5	8.7	224	0.021
5	6.6	8.7	224	0.025
6	1.15	2.1	224	0.018
7	1.07	2.1	224	0.017
8	3.5	8.7	224	0.013
9	0.92	2.1	224	0.014
10	1.07	2.1	224	0.017
11	1.37	3.0	224	0.015
12	3.1	5.6	224	0.018

Average h_0 = 0.017
Calculated h_0 = 0.016

Thus, perhaps for the first time, the deductions of Laplace and Rayleigh concerning the corrections needed for wide tubes have been experimentally verified far within the limit of error of measurements of this kind. Desains's verification was indirect.[1] Theoretically no tube can be wide enough so that the water in it is absolutely flat until indeed the curvature of the earth counterbalances the effect of the walls.

The Correction for the Meniscus in Medium Sized Tubes.

All the formulas just given for very wide and for very narrow tubes fail in tubes of medium diameter, between 5 and 25 mm. That of Hagen and Desains is perhaps the best, but this equation can hold only so long as the wide meniscus is essentially a true oblate hemi-ellipsoid. Mathematically, this intervening range has not been satisfactorily solved, and although Lord Rayleigh was appealed to for help, he found himself unable to solve the problem in the time at his disposal. Accordingly, the experimental method alone is at present available. A number of determinations already made at Harvard by the late C. L. Speyers and by

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$\gamma (1/R_1 + 1/R_2) = h_0Dg$ when γ = surface tension; $R_1 + R_2$ are two radii of curvature in planes at right angles to each other. This is a well known general equation. In our case $R_1 = R_2$ so that we can write $h_0 = 2\gamma/RDg$ but $2\gamma/Dg = a^2$; therefore $h_0 = a^2/R$. See Tait's "Properties of Matter," 5th ed., London, 1907, p. 254.

[1] Desains, *Ann. chim. phys.*, [3] **51**, 417 (1857)

L. B. Coombs involved this range, because the small quantities of the rare liquids investigated by them did not permit the use of a very wide tube. It was worth while, therefore, to discover the correction needful for medium sized meniscuses, especially because these results were awaiting this knowledge for publication.

Winkler[1] made a number of determinations of the heights of meniscuses with various sized tubes, but his results do not lie on a perfectly smooth curve, and on repeating his work by his method we were unable to obtain better results. We turned, therefore, to another experimental method.

This other method consisted simply in measuring the capillary rise of 5 different liquids in the 2 pieces of apparatus used by Coombs (one (IV) having a meniscus 38.4 mm. wide and the other (V) a meniscus 9.32 mm. wide) and a 0.3798 mm. capillary.[2] The correction to be applied for these particular liquids could then be very simply found by assuming the larger meniscus (as corrected by Lord Rayleigh's correction, which is vanishingly small except with water) to give accurate results. From the results with Apparatus IV, the true capillary rises which should have been observed in a capillary 0.3798 in diameter were calculated.

The following table gives the capillary rise to the bottom of the meniscus in Apparatus V and that which would have been found in that apparatus if the large tube had been very large instead of only 9.32 mm. in diameter. The difference is the quantity sought, which could also have been found by connecting a 9.32 mm. tube directly with a wide tube.

Correction for the Rise in a Wide Tube of 9.32 mm. Diameter.

	Capillary constant[a]. (a^2).	Rise measured in App. V. Mm.	Rise calculated for this app. Mm.	h_0 Difference = rise in 9.32 mm. tube. Mm.
Water	14.877	76.08	78.26	2.18
Benzene	6.715	34.58	35.29	0.71
Ether	4.886	25.21	25.59	0.38
Chloroform	3.723	19.34	19.56	0.27
CCl_4	3.427	17.81	18.00	0.19

[a] These values were obtained with the standardized Capillarimeters IV and VI.

Fig. 5 plots the first column of figures in relation to the last, that is, the correction sought for the capillary rise of the large meniscus, and makes possible the finding of the correction for the large meniscus to be applied to any other liquid used in a tube of this diameter. For small deviations from this diameter an inversely proportional change in h_0 could be safely applied as a close approximation.

For convenient use with wide tubes of other diameters, these figures

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[1] Winkler, *Z. angew. Chem.*, 1903, p. 719.

[2] This is the average value. The capillary was not perfectly cylindrical. All the needful corrections are applied, however, in the table below.

may well be generalized. The outcome is then comparable with the several formulas, for capillary tubes on the one hand and for wide tubes on the other hand. The data thus become generally useful; moreover, one can easily see how adequately they bridge the gap (hitherto defying mathematical treatment) between the extremes. The rational method of comparing different liquids in different tubes is to plot the number h_0/a in relation to the number r/a, r being in this case 4.66, and a being the square root of the capillary constant (having the dimension of length). This procedure is in accord with that adopted by Rayleigh in the table at the conclusion of his last paper on the subject.[1] It rests upon the fact that with a given value of r/a the meniscus has essentially the same geometric form whatever may be the value of r.[2] In Fig. 5 values for the r/a are plotted as abscissas, and the actual heights of the bottom of the meniscus above the true level, divided by a, are plotted as ordinates. The results indicated by the formula of Hagen and Desains for capillaries and Rayleigh for wide tubes are plotted also.[3] The experimental points derived from the foregoing table and graph are seen to coincide essentially with the mathematical outcome with very wide and very narrow tubes. More extended experimental work of the same kind is desirable—the present results are merely preliminary.

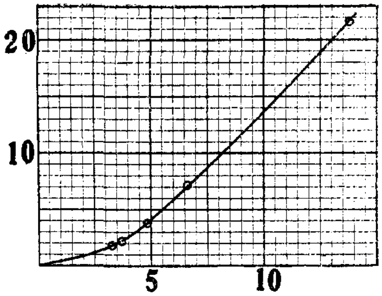

Fig. 5.—Capillary rise in 9.32 mm. tube. With liquids of different capillary rise. Rises of bottom of meniscus above true level are plotted as ordinates; capillary constant as abscissas.

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[1] Lohnstein, *Ann. Physik.*, [4] **20,** 237–68, and 606–18 (1906), **21,** 1030 (1907), *Z. physik. Chem.*, **64,** 686 (1908), and **84,** 410 (1913), *tacitly* makes a similar assumption with reference to r/a representing the same form of drop when hanging from a cylindrical tip. While he does not directly state his assumption, it was stated directly by Brown and Harkins, THIS JOURNAL, **41,** 521 (1919). (Editorial suggestion.)

[2] It might be worth while to test experimentally this well founded theoretical inference. See A. C. Lunn, *ibid.*, **41,** 620 (1919).

[3] The values of h/a for the Desains's equation are found as follows. Since the true capillary height h equals a^2/r, the height of the bottom of the meniscus above the height which would have been observed if the tube were very wide is $h_0 = a^2/r - m$, where m is the height of the cylinder which the liquid of the meniscus would occupy if it were flattened into a flat cylindrical form. Therefore $h_0/a = a/r - m/a$. From the equation of Hagen and Desains, the corresponding expression is $h_0/a = h/a - ar/(3a^2 + r^2)$ which (substituting $h = a^2/r$ and finally calling $r/a = x$ since that quantity is plotted in the direction of abscissas) reduces simply to the expression $h_0/a = l/x - x/(3 + x^2)$. The values for Rayleigh's equation have already been calculated by him (*Proc. Roy. Soc.* [A] **92,** 195 (1915)). In plotting them attention is directed to the fact that his "a" is $\sqrt{1/2}\,a^2$ instead of being $\sqrt{a^2}$ as defined previously.

The points for the curves h_0/a against r/a are

	h_0/a.	r/a.
Water	0.566	1.21
Benzene	0.274	1.80
Ether	0.172	2.11
$CHCl_3$	0.111	2.41
CCl_4	0.102	2.52

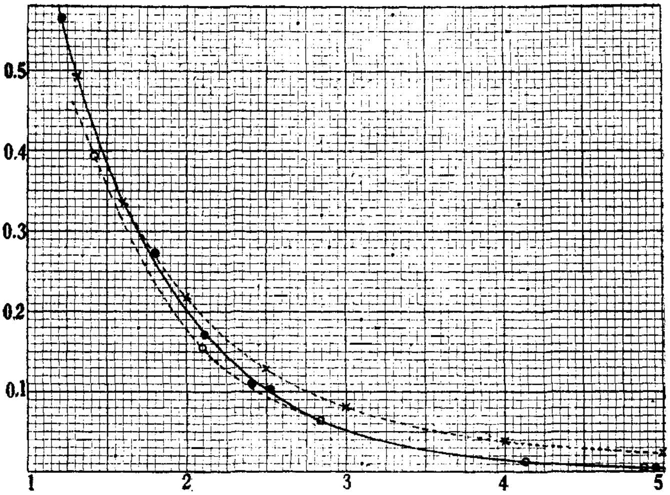

Fig. 6.—Relation of deductive equations to experimental results. The quantity h/a is plotted in the direction of ordinates and the quantity r/a in the direction of abscissas. The unbroken line shows the experimental results for the relation between these two quantities. The upper broken line gives the indications of the ellipsoid formula of Hagen and Desains for narrow tubes; the lower broken line the indications of the more complicated formula of Lord Rayleigh (for wide tubes). The experimental results bridge the recognized gap between the two curves and make possible the use of wide tubes of any diameter in surface tension measurements. By chance most organic substances lie in this intervening region with wide tubes of 6 to 15 mm. diameter.

The middle experimental curve, as has been said, covers the interval as yet inaccessible to mathematical treatment, and can be used for correcting the large meniscus in a tube of any reasonable size. If more time had been available, more points would have been secured between abscissas 2.50 and 4.20. This would be desirable but not very important, since the most important regions lie in the neighborhood of the points already found.

In order to present a better idea of the shape of the meniscus, many photographs showing the profile of this curved surface were taken. The liquid was enclosed in tubes of various sizes from one mm. diameter up to one cm. diameter. Microscope slides were cemented to the front and back of these tubes with Canada balsam, in order to reduce, as far as possible, the distortion of the image. In order to discover how great this distor-

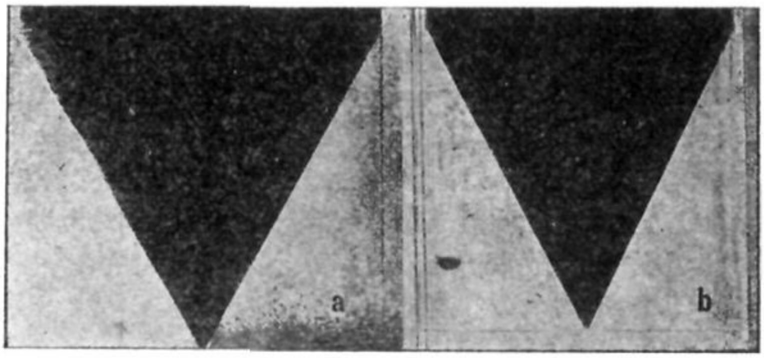

Fig. 7.—Photographs of an accurately turned brass cone in benzene (*a*) and water (*b*). By comparing the angle of the image of the cone on the photographic plate with the actual angle of the cone (59° 54′, determined by measurements with a micrometer caliper and a cathetometer), the lateral correction to be applied to the meniscus is obtained.

Fig. 8.—Benzene in tubes (*a*) of 6 mm. and (*b*) of 12 mm. diameter magnified 5 diameters. Very little distortion of the image appears in these photographs, so that they give nearly the true profiles of the meniscuses; (*a*) is essentially elliptical, falling on Desains's curve; (*b*) is of the nondescript type treated only by our experimental curve (See Fig. 5).

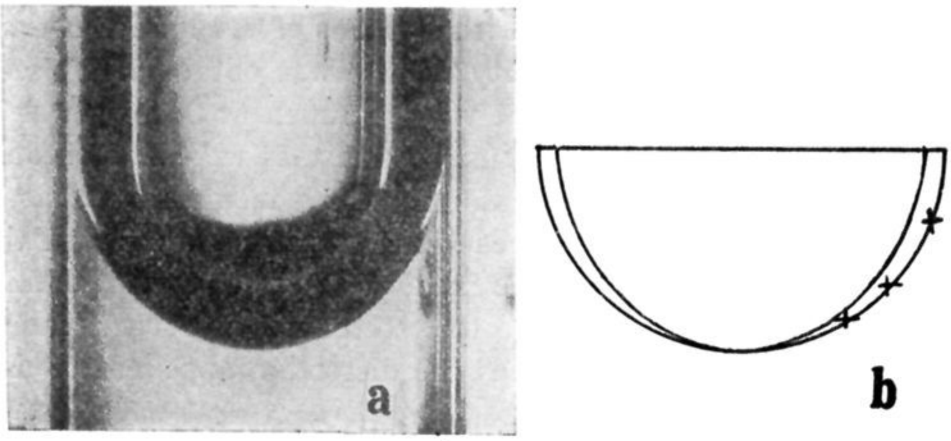

Fig. 9.—(*a*) Water in tube of 1 mm. diameter, magnified 40 diameters; (*b*) plots the apparent outline of the meniscus (inner curve) and shows the corrections (for refraction) to be applied to this outline, indicated by the crosses. Note that this meniscus must be very nearly hemispherical, as indicated by the outer curve, which is an exact half circle.

tion was, a brass cone of 58° 54′ apex-angle was put into a closely-fitting tube in each liquid and photographs of it taken when it was immersed in benzene and water. A correction derived from the measurement of the photographs of the cone could then be applied for every point on the profile of each meniscus. With benzene this correction was too small to be measured: the cone appeared truly conical, and not contracted in diameter. With water the cone appeared equally true, but somewhat more pointed, showing a contraction in the diameter of about 8% (see Fig. 7). Typical results are shown in Figs. 8 and 9. Careful examination of the negatives with a magnifier showed no evidence of any contact angle.

The Radius of the Capillary Tube, and the Construction of Another Capillarimeter.

The radii of capillaries are often determined by means of a mercury thread. Volkmann, whose measurements of the surface tension were very carefully made, states that a film of air (clinging to the walls of the tube between the mercury and the glass) changes the effective diameter of the tube by 0.004 mm. This seems excessive, if the tubes are smooth and clean. Determinations of the capillary rise with tubes of different bore would test this statement. In the earlier Harvard research, with benzene in tubes of radii 0.1936 and 1.0099 mm. (Capillarimeters III and IV) the values 6.714 and 6.728, respectively, were found for a^2, differing by 0.2%. The difference lies in the direction indicated by Volkmann, but is no greater than the possible error of experiment, with tubes as wide as 1 mm. radius, as the authors realized.

Therefore, a new capillary of a radius small enough so that the measurements of height could be made accurately, yet large enough so that any effect of the air cushion would be made apparent by comparison with the narrow tube of the earlier work, was prepared.

About 5 kg. of capillary tubing with a radius of 0.4 mm. was examined before a piece of sufficient regularity for use was obtained. A section 7 cm. long of which the bore did not vary as much as 0.05%, was found. For these measurements wholly consistent results were not obtained by using Winkler's[1] corrections for the mercury meniscus. Instead, we measured the linear protrusion of each meniscus and calculated the correction on the assumption that the meniscus was a segment of a sphere. In a recent paper Harkins and Brown[2] state that gravity distorts the meniscus; but with such small tubes the distortion appeared to us to be negligible.

The effect of ellipticity in the cross section of the tube needed attention.[3] An elliptical tube would cause a higher capillary rise than a tube

[1] Winkler, *Z. anal. Chem.*, 40, 403 (1901); also *Z. angew. Chem.*, *loc. cit.*

[2] Harkins and Brown, *loc. cit.*

[3] This point had been considered in a provisional manner before a courteous letter from Professor A. W. C. Menzies in 1918 kindly called our attention to it, with reference

of circular cross section possessing the same volume. A section was accordingly cut from each end of the new tube and the bore, greatly magnified, was measured on 4 diameters at 45° to each other by means of a filar micrometer. In no case did the diameter vary by more than 2%.

An elliptical tube having major and minor diameters $a = 4.100$ and $b = 4.000$ will have the same cross section as a circular tube $\sqrt{4.100 \times 4.00} = 4.04969$ in diameter. The weight of the liquid in the capillary may be considered as suspended from the inner circumference of the tube; and the height to which it will rise is inversely proportional to this circumference, provided the cross sections of the tubes are the same. The circumference of the above circular tube is 25.445, while that of the elliptical tube is 25.4476;[1] and the error is only 0.01%. As the ellipticity in our experimental case was less than in the typical case just considered, we may fairly neglect the corresponding error. The appended graph gives the correction for other extents of ellipticity (Fig. 10).

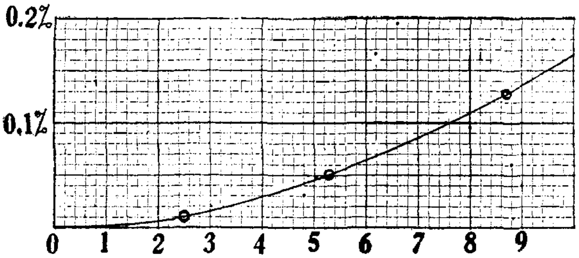

Fig. 10.—Error caused by ellipticity of capillary. Percentage excess of major axis over minor axis is plotted in the direction of abscissas; percentage error thereby caused in capillary constant is plotted in the direction of ordinates. Thus a capillary tube in which the major axis is 1.08 times the minor axis, causes a capillary rise 0.11% too great.

In order that no errors might be introduced through irregularities in the wide tube, the latter had been tested with great care. Within a long piece of 40 mm. tubing in a vertical position, was placed an exactly graduated brass meter rod of which each centimeter was then measured very exactly by means of a cathetometer. A piece of tubing about 11 cm. long was selected which was so true that the vernier readings varied by no more than 0.01 mm., showing sufficient optical constancy.

An error might yet be introduced if the walls of the tube were wedge-shaped—thicker at one end than at the other. Therefore the thickness was measured with a very accurate Brown and Sharpe caliper. The greatest difference in thickness between corresponding points 25 cm. apart was 0.05 mm., which, if equally distributed, would cause the two

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to the work of one of us with Mr. Coombs. The capillary of Capillarimeter IV in that work had been selected with especial care in this regard. We have recently remeasured its diameters in all directions and found the maximum variation to be less than 2%, which would cause (as will be shown), no appreciable error.

[1] See Baker's "Elliptical Functions," p. 116, New York, 1890. The values plotted in Fig. 9 were calculated by Desains's formula for the circumference of an ellipse, *loc. cit.*, p. 411.

sides of the tube to be at an angle of 40″ with each other. Ten times this angle would be needed to cause an error of 0.01 mm. in the observed height of a liquid within the tube.

Accordingly, the selected capillary and large tube, having radii about 0.4 and 20 mm., respectively, were built into a new Capillarimeter VI, essentially like those employed by Coombs.[1] This was especially desirable in order to verify the preceding work, which depended upon only two capillaries—carefully prepared and measured, to be sure, but nevertheless not absolutely infallible.

In this new apparatus, designated Capillarimeter VI, we obtained results constant (except at the extreme ends) to better than 0.02 mm. for the capillary rise of water in all parts of the tube. The result, applying additive corrections for both small and large meniscuses calculated in accordance with Rayleigh's investigation, was, at 20°:

Capillary rise in No. VI	34.33
Small meniscus correction	0.143
Large meniscus correction	0.013
Corrected height	34.49
Capillary constant	14.877 sq. mm.

The earlier Harvard result,[2] 14.861, with the much wider Capillarimeter No. III, when corrected for the large meniscus by Rayleigh's correction, gives 14.878 for the capillary constant. The agreement is better than is justified by the accuracy of the two measurements. Our value given above may be accurate to within 0.05%, and the validity of the earlier result is corroborated. The comparison of these two tubes tends toward showing that the suspected air cushion can hardly affect tubes as wide as these.

Benzene also was measured in this new tube, and compared with new measurements in the best (narrower) tube (IV) of the previous investigation:

Average capillary rise in No. VI uncorrected	15.425
Small meniscus correction	0.141
Large meniscus correction	0.000
Capillary constant (Capillarimeter VI)	6.715
Capillary constant (Capillarimeter IV)	6.707
Coombs (Capillary constant Capillarimeter IV)	6.714

The disagreement amounts to about 0.1%, but although it lies in the same direction as that which would be caused by an air cushion, it is not greater than a possible aggregate of errors of experiment. Evidently an air cushion cannot seriously affect the calibration. Of all the results we believe those with Capillarimeter VI to be the most accurate, because the

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[1] The form is illustrated in the preceding article. The new capillarimeter had too short a capillary to allow its inversion with liquids having high surface tension.

[2] Richards and Coombs, *loc. cit.*, 1674.

capillary was wide enough to avoid serious error from the air cushion (if such exists), and, on the other hand, was narrow enough to give a rise of sufficient magnitude for accurate measurement.

In the table immediately preceding it will be noted that two determinations are given with Capillarimeter IV, which was the one made and used by Coombs. The slight difference between these is due not to any difference in capillarity, which we found to be precisely the same as had been found in the earlier investigation, but rather to a slight correction of the calibration. A new and far more extended calibration of the capillary of No. IV was made by measuring the length of a very short mercury thread (about one cm. long) throughout its length. The minute drop of mercury, after expulsion, was weighed with the greatest care upon an exceedingly delicate assay balance. A much longer thread also was measured. The tube was found to be slightly constricted in the middle, the part most used for liquids of low capillary constant, leading to a slightly smaller estimate of its diameter in these places than had been assumed in the earlier investigation in which the mercury thread employed had been too long to discover this constriction. In subsequent use of the tube, the values as found by the new estimate were used, corresponding to the particular places on the tube at which the meniscuses appeared. The tube (which had been chosen as being very nearly cylindrical) was carefully measured as to ellipticity and found to be essentially circular in cross section.

Similar study was made of another capillarimeter, No. V, which was used in the earlier investigation. The results obtained with this capillarimeter had not been published because the necessary knowledge concerning neither capillary nor wide tube had then been acquired. Our new study has led, as will be seen, to a complete elucidation of the matter. In this tube there was distinct departure from a true cylinder, the ratio of the major and minor axes being 1.08 : 1. The error caused by this degree of ellipticity is 0.11%, as is seen in Fig. 10.

Observation and Lighting of the Meniscuses.

The general method adopted in the earlier Harvard research was employed, with further precautions to minimize optical defects. The capillarimeter, immersed exactly vertically in a thermostat at 20.000°, was observed through a window of plane optical glass adjusted in a perfectly vertical position by means of the reflection of a point of light exactly on a level with the telescope. Close behind the capillarimeter was placed a movable black screen which could be raised until its upper straight border was exactly tangent to the black image of the meniscus. Feustel[1] rightly points out that it is difficult to focus on the bottom of a horizontal meniscus. We were able greatly to reduce this uncertainty by placing a

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[1] Feustel, *Ann. Phys.*, 16, 61 (1905).

diaphragm, with an opening only 6 mm. in diameter over the objective of the telescope. This device was effective because the telescope at a distance of 7 cm. collects through it rays which are nearly parallel. With wider aperture the rays striking the top of the telescope objective come from a part of the meniscus different from that which emits the rays striking the bottom of the objective. The rays cannot then be brought to a point.

This more precise arrangement enabled us to verify yet more sharply the conclusion of the earlier work that the average of readings taken in 4 positions (2 being when the tube was inverted) gives exactly the true value, even when the large and fine tubes are not parallel.

Two consecutive readings taken a short time apart were found almost always to agree; but when 2 or 3 hours intervened, differences were sometimes observed. Values were accepted when they were not changed by repeated observations, with every part of the apparatus readjusted in the intervals and the capillary thoroughly wet.

The tubes were cleaned with scrupulous care before the introduction of the liquid. Warmed cleaning-solution and a great volume of water were employed because the experiments on contact-angle had demonstrated the necessity of very great care in this respect. The tubes were not, however, steamed before use. This is to be regretted since Harkins and Brown's[1] more recent work seems to indicate that steaming causes the tube subsequently to show a slightly higher capillary effect. Whether the difference is due to a slight contact-angle or to the effect of impurities dissolved from the glass is not known. But in any case the very close correspondence of our final result with Harkins's entirely independent value shows that in our tubes the cleaning was so thorough that the disturbing effect of the lack of steaming, if any, was exceedingly slight. This cause of trouble seems to appear even slightly only in the case of water, since Harkins and Brown's results on benzene agree with ours easily within the limit of the error of experimentation. In all cases (except with water) the tube was very carefully dried for at least 6 hours in a current of pure dry air.

The Effects of Air on the Capillary Rise.

The most obvious effect of air on the capillary rise is recognized in the surface tension equation

$$\gamma = {}^1/_2\, rhg\, (D - d),$$

where D is the density of the liquid and d the density of the vapor phase (including air). This effect in the presence of air for most liquids would amount to about 0.1% increase in capillary rise per atmosphere. Besides this effect another (lessening the observed rise) would be caused by the fact that as the vapor phase increases in density, the change from

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[1] Harkins and Brown, *loc. cit.*

liquid phase to vapor phase becomes less abrupt. A third effect would be due to the impurity in the liquid introduced by the dissolving of oxygen and nitrogen in it. Prediction as to the magnitude and sign of the total, net effect is difficult.

Ramsay and Shields[1] made some measurements of the capillary rise of several substances, showing great increase of capillary rise when air is present. The difference varied from 2 to 4% and they ascribed it to the formation of a contact-angle in the presence of air. It is difficult to account for these results unless due to misprint, or to the causing of a contact angle because of evaporation in a vacuum, since the change of capillary rise is in the wrong direction besides being much too large. Renard and Guye[2] in a more accurate research measured the capillary rise of a few liquids in air and in the presence of their vapor only, and found no difference greater than 0.5%.

Especially in view of the contradiction just mentioned it seemed advisable to test this question once more. The mode of experimentation was as follows.

The exact capillary rise was measured as usual in the presence of air. The air was then pumped out by means of a water pump, the stopcock being open. The apparatus was placed in warm water and the evacuation continued until the liquid had boiled for several minutes. Since the top of the apparatus had been sealed outside (to prevent leakage) either by hard paraffin or by a rubber tube, the stopcock was not disturbed, but the capillarimeter was closed by a pinchcock on the rubber tube connecting with the pump.

The rise in the capillarimeter was then measured in the two upright positions only, because the liquid would have come into contact with the rubber if the apparatus had been inverted. For measuring so slight a change, this gave the relative effect quite adequately. When measurements *in vacuo* had been taken, air was admitted and the change noted. This latter value was taken as indicating the true effect of the change produced by the air; the initial reading before evacuation was taken as the true capillary rise in air. We found differences varying from almost a zero change in surface tension up to as high as 0.5%. The surface tension was always greater in the absence of air.

A great source of annoyance during the measurements *in vacuo* was the condensation of the liquid on the parts of the apparatus that projected above the water of the thermostat. This caused evaporation from the surface and the formation of an angle of contact, with the consequent

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[1] Ramsay and Shields, *loc. cit.*

[2] Renard and Guye, *J. phys. chim.*, 4, 81 (1906). In the paper by Richards and Coombs the volume number of this reference was wrongly given because of an error on the cover of the separate copy which had been kindly sent by the authors.

lowering of the capillary rise. The trouble was obviated by keeping the projecting parts of the apparatus warm.

The Preparation of the Liquids.

Water was thrice distilled, once from alkaline permanganate, once from very dilute sulfuric acid, and at last directly into the apparatus.

Benzene was purified in the manner already described.[1]

Of *toluene*, two samples were used. One had been prepared by Dr. Shipley.[2] The other was made from a commercial C. P. toluene, by shaking with conc. sulfuric acid for 5 days, washing with alkali and water, drying over sodium, and fractionating by distillation. Each of these specimens was recrystallized thrice with liquid air. Toluene becomes viscous near its freezing point (—93°), hence its crystallization is less effective than that of benzene. The most satisfactory crystals were obtained when the liquid was supercooled several degrees and then touched to the side of the liquid air jacket to start crystallization. This liquid was then stirred violently by a glass screw propeller with many blades along its hollow shaft—which shaft served to suck out the discarded mother liquor. The crystallized toluene was dried over sodium for several days and then distilled into the apparatus. As nearly as could be determined, its boiling point was constant within about 0.1°. The product from the earlier preparation boiled 0.1° higher than that from the latter. All samples gave the same capillary rise to within 0.06%.

Chloroform (Commercial C. P.) was shaken with two portions of conc. sulfuric acid for several hours, and fractionated through a Glinsky tube 6 times. The portion employed came over almost entirely within 0.01°.

Carbon tetrachloride (the best obtainable in commerce) was fractionated 4 times. The purest fraction (boiling within 0.1°) was recrystallized 4 times in an apparatus similar to that used for the toluene, with solid carbon dioxide and ether as a freezing mixture.

Of *ether*, 3 samples were used, all prepared from a very pure commercial product. One sample was washed with water several times, shaken with solid sodium hydroxide for a few hours, dried over sodium, and fractionated twice, with preservation of each middle portion. The second sample was prepared by A. S. Coolidge, who employed many washings with water, and then dried the product over phosphorus pentoxide. It was distilled from phosphorus pentoxide directly into the apparatus. The third sample was prepared by treating the good raw material with many portions of sodium, until fresh sodium was not attacked. The middle fraction was then distilled from sodium directly into the apparatus. All these samples distilled within 0.01°, and all gave the same capillary rise.

Of *dimethyl aniline*, a dark brown sample was distilled. All came over within one degree and most within 0.1°. This latter portion, which was light yellow, was recrystallized thrice in a freezing mixture. It was kept over sodium for a day and redistilled under reduced pressure in the presence of nitrogen. By this means an almost colorless product was obtained. Quickly assuming a light yellow color on exposure to air, it nevertheless gave the same results for the surface tension then as when colorless before exposure.

The difficulty of preparing almost any organic substance in a state of purity is notorious. It would be well, therefore, as a rule, to determine other physical properties of the liquids employed, such as the density,

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[1] Richards and Shipley, This Journal, **36**, 1825 (1914); also Richards, Carver and Schumb, *ibid.*, **41**, 2026 (1919).

[2] Richards and Shipley, *loc. cit.*

freezing and boiling points, and the refractive index. These, if accurately measured, serve to define the grade of substance used and help to identify possible impurities. The density is, of course, the most important, since it is needed in the calculation of the surface tension. We regret that time was lacking for the determinations of these physical constants in this case, excepting in the case of the density of ether and dimethylaniline. The other densities were taken from older records.

The Measurements.

Measurements were taken with all 4 pieces of apparatus. Only 2 of the capillarimeters give absolute results for water: namely, Coombs's Capillarimeter III with a 2.0 mm. capillary and the new Capillarimeter VI with a 0.8 mm. capillary. The capillary rise with water in Coombs's Capillarimeter IV (capillary 0.2 mm. diameter) was so great that the small meniscus fell on an uncertain part of the tube. Apparatus V had a wide tube, so narrow that the measurements needed correction in the way already described, hence they were really referred to Capillarimeter IV. Capillarimeters III, IV and V were employed in all 4 positions, both upright and inverted; Capillarimeter VI, having been made with especial care, was read only in the two upright positions. Each figure given below

TABLE OF CAPILLARITY CONSTANTS (a^2) AND SURFACE TENSIONS OF VARIOUS SUBSTANCES IN PRESENCE OF AIR.

	r. Mm.	Height obs.	Height corr.	a^2.	D.	Effective density. ($D-d$).	Surface tension. Dynes/cm.
Water.........	1.0099	14.343	14.737	14.883	0.9982	0.9972	72.75
Water.........	0.43135	34.33	34.49	14.877	0.9982	0.9972	72.73
Benzene........	0.43135	15.425	15.568	6.715	0.08788[a]	0.8775	28.88
Benzene........	0.1934	34.62	34.68	6.707	0.8788	0.8775	28.79
Toluene........	0.1934	34.63	34.69	6.709	0.8657[b]	0.8645	28.43
$CHCl_3$.........	0.1932	19.21	19.27	3.723	1.4884	1.4869	27.14
CCl_4...........	0.1933	17.68	17.74	3.427	1.5947	1.5932	26.77
Ether..........	0.19325	25.12	25.18	4.866	0.7133[c]	0.7109	16.96
Dimethyl aniline	0.1935	40.32	40.38	7.813	0.9562[c]	0.9545	36.56

TABLE OF CAPILLARITY CONSTANTS (a^2) AND SURFACE TENSIONS OF VARIOUS SUBSTANCES IN ABSENCE OF AIR.

	Radius of tube. Mm.	Fall on admission of air. Mm.	Height corrected. Mm.	a^2.	Effective density. D.	Surface tension. Dynes/cm.
Water............	0.4313	−0.02	34.47	14.867	0.99823	72.75
Benzene..........	0.1934	+0.05	34.73	6.717	0.8787[a]	28.93
$CHCl_3$...........	0.1932	+0.05	19.33	3.735	1.4881	27.24
CCl_4.............	0.1933	+0.10	17.84	3.448	1.5944	26.95
Ether............	0.19325	+0.06	25.24	4.878	0.7115	17.01
Dimethyl aniline..	0.1935	+0.06	40.44	7.825	0.9556	36.66

[a] Richards and Coombs, *loc. cit.*

[b] Louguinine, *Ann. chim. phys.*, [4] 11, 453 (1867).

[c] These values were found with the particular samples employed.

TABLE OF CHANGE IN SURFACE TENSION CAUSED BY PRESENCE OF AIR AT ONE ATMOSPHERE.

	In vacuo.	In air.	Dynes/cm.
Water	72.75	72.73	+0.02
Benzene[a]	28.93	28.79	+0.14
$CHCl_3$	27.24	27.14	+0.10
CCl_4	26.95	26.77	+0.18
Ether	17.01	16.96	+0.05
Dimethyl aniline	36.66	36.56	+0.10

[a] Both values given here for benzene are those found with the smaller capillary, since these are logically comparable. Nevertheless we believe that the value with the wider tube (No. VI), is the more accurate as an absolute value in the presence of air, for reasons already given.

is the average of all measurements. Since different parts of the narrower capillary were used in different cases, a small correction for calibration was applied to *r*.

The comparison of these results with those of others is, for the most part, unnecessary, because nearly all of the earlier experimenters (excepting Harkins and Brown and the earlier Harvard workers) omitted essential precautions. The effect of removing the air, as shown in the above table, agrees fairly well in direction and magnitude with that found by Renard and Guye;[1] but, as already stated, it is entirely at variance with that of Ramsay. The value for water 72.75 dynes/cm. agrees very closely with Harkins and Brown's 72.80, as well as with Domke's 72.72 and Volkmann's 72.80. The average of all four is 72.77, which must be very near the true value. If Harkins and Brown's conclusions as to the necessity of steaming the tube in this case are correct, their value (the highest of the four), is probably the most accurate. The reason for the lower value, 72.61, published in the earlier Harvard research, is due to the fact that the result as published was not corrected for the rise in the wide tube, subsequently found by Lord Rayleigh.[2] When thus corrected (72.77) it approaches closely our more recent value. In the case of benzene, our old and new values, and Harkins and Brown's, are very close.

The value which we have found for toluene is somewhat less than that published in the earlier Harvard research, the new value being 28.43, the old 28.58. This is probably to be referred chiefly to the difference in the purity of the toluene. The specimen used in this research had been recrystallized three times at —93°. Accordingly, the present value is to be preferred.

We are glad to express our indebtedness to the Carnegie Institution of Washington for financial support in this investigation.

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[1] Renard and Guye, *loc. cit.*

[2] Lord Rayleigh, *loc. cit.*

Summary.

(1) It has been shown that the supposed finite contact-angle (reputed to be the weakest point in the capillary rise method), does not exist with the liquids studied if the glass be properly cleaned and if evaporation of the liquid be prevented.

(2) The correction for the capillary rise in the wide tube calculated by Rayleigh and Laplace has been experimentally verified.

(3) A preliminary experimental curve for the capillary rise in tubes that are not wide enough to come under these mathematical equations has been obtained. This experimental curve fits smoothly between the theoretical curve for very wide tubes and the theoretical curve for very narrow tubes.

It has been shown that the method of calibrating tubes by weighing a mercury thread is not affected to an important extent by a film of air between the mercury and the glass, except perhaps in very fine capillaries. The disturbing effect of ellipticity in the cross-section of the capillary is indicated.

The difference between capillary rise in air and *in vacuo* has been determined with 6 liquids. In most cases the effect on the surface tension is less than 0.5%.

The surface tensions of water, 72.73; benzene, 28.88; toluene, 28.43; ether, 16.96; chloroform, 27.14; carbon tetrachloride, 26.77; and dimethyl aniline, 36.56, have been measured in the presence of air. Removal of air caused increases in the surface tension as follows: water, +0.02; benzene, +0.14; chloroform, +0.10; carbon tetrachloride, +0.18; ether, +0.05; dimethyl aniline, +0.10.

CAMBRIDGE, MASSACHUSETTS.

[CONTRIBUTION FROM THE BUREAU OF STANDARDS, DEPARTMENT OF COMMERCE.]

THE DETERMINATION OF IRON BY THE CUPFERRON METHOD.[1]

BY G. E. F. LUNDELL.

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I. Introduction.

Archibald and Fulton in a recent article[2] on the determination of iron and the separation of manganese from iron by cupferron, have made the assertions that "the cupferron precipitate of iron is slightly soluble in the acid solution in which it is precipitated" (0.001 g. of ferric oxide when 0.1373 g. of ferric oxide was precipitated in 166 cc. of solution containing 5 g. of ammonium chloride, 4 g. of cupferron, and 15 cc. of conc. hydro-

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[1] Published by permission of the Director of the Bureau of Standards.

[2] Archibald and Fulton, *Proc. trans. Roy. Soc. Can.*, 13, III, 243-53 (1919); *J. Chem. Soc.*, 118, 512 (1920); *C. A.*, 14, 2454 (1920).