highly compressible; and so might one much distended because not greatly pressed upon by outside cohesive pressure. Both of these tendencies would cause small density and accordingly large atomic volume; and the second of these tendencies would add low melting point. Therefore, the general form of the equation is plausible.

The case of tungsten is especially striking. The atomic volume is small, considering its large atomic weight (that is to say, its density is great) and its melting and boiling points are so high that this metal is now chosen as the most suitable for the filaments of electric lights. All these properties would seem to indicate cohesiveness; and a body under the pressure of such extremely high cohesion would be supposed to have a very small compressibility, which as a matter of fact it has—the value being 0.00000027, the smallest of any element thus far carefully studied.

In conclusion, the contents of this paper may be summarized by stating that the compressibilities of all the 38 elements determined at Harvard have been reduced to the new standard for the compressibility of mercury as determined at the Jefferson Physical Laboratory and the Wolcott Gibbs Memorial Laboratory of Harvard University. The new values for the compressibilities are now in accord with the less extended work of Bridgman, Grüneisen, and others. Attention is directed to probable relations between the compressibilities and the atomic volumes, densities, coefficients of expansion, and melting and boiling points of many of these elementary substances; and an approximate empirical equation is proposed for the calculation of these compressibilities.

CAMBRIDGE, MASS.

[CONTRIBUTION FROM THE WOLCOTT GIBBS MEMORIAL LABORATORY OF HARVARD UNIVERSITY.]

THE SURFACE TENSIONS OF WATER, METHYL, ETHYL AND ISOBUTYL ALCOHOLS, ETHYL BUTYRATE, BENZENE AND TOLUENE.

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This investigation is a part of a series of investigations having for their object the study of the fundamental properties of liquids. It is hoped that when a number of these properties have been determined with great accuracy, the essential relations between them may be discovered with greater certainty than is possible at present.

A glance at the published data[1] concerning surface tension leads one to conclude that much remains to be done. For example, the values

[1] See, for example, "Landolt-Börnstein Tabellen," p. 113 (1912). The recent interesting research of Morgan upon the drop-method has developed since that time (THIS JOURNAL, 30, 360 (1908), and many other references given in THIS JOURNAL,

obtained by experienced men for water at 20° vary all the way from 70.6 to 78, according to different methods. Even a single method, that of the rise in capillary tubes, has yielded results in the last twenty-five years varying from 70.6 to 72.7, and no satisfactory evidence is forthcoming as to the reasons for the difference.

To us it seemed, therefore, worth while, not only to study the surface tension of a variety of new liquids, but also to discover the reason for the divergences between different methods, and to obtain results of absolute as well as of relative accuracy for liquids already studied. The present paper is a preliminary attempt, which seems to have been successful in locating several of the heretofore not quite adequately heeded sources of error.

The method chosen was that of measuring the rise of liquid in capillary tubes, because this method seems to be one of the most direct and least likely to lead to insoluble mathematical complications. The method has been used by many experimenters in the past.[1] No attempt will be made to give a complete discussion of older work, partly because some of the papers are not at present accessible, except in the form of abstracts; and partly because it is difficult to do justice in the limited space available here; but from time to time special points in some of these papers will be mentioned in comparison with our own procedure.

There are, of course, a number of minutiae which may affect the accuracy of the outcome. Prominent among the points needing detailed consideration were the following: First, the precise determination of the diameter of the tubes; secondly, the method of determining the exact position of the bottom of the meniscus; thirdly, the discovery of the diameter necessary in order to attain the flat surface with which the capillary rise is to be compared; fourthly, the precise determination of the weight of liquid contained in the meniscus at the top of the capillary tube; and fifthly, the angle of contact of the liquid with the tube. These points are discussed in order below.

The Diameter of the Capillary Tubes.

This question involved nothing not already well known. Each capillary tube was selected as follows: An apparently suitable piece of tubing

35, 1821 (1913)). The work of Renard and Guye should also be noticed: *J. chim. phys.*, **5**, 81 (1907), and that of Kistyakovsky, *Z. Electrochem.*, **8**, 376 (1902); **12**, 513 (1906).

[1] For a summary of Quincke's very irregular results and a bibliography of his eleven papers, the reader is referred to "Landolt and Börnstein's Tabellen," pp. 103, 116 (1905). The method has also been used by Ramsay and Shields, *Z. physik. chem.*, **12**, 433 (1893); Weinstein, "Landolt and Börnstein's Tabellen," p. 113 (1912), quoted from *Metron. Beitr. No. 6 Norm. Eich.-Komm.*, 1889; Domke, *Ibid.*, quoted from *Abh. Eich.-Komm.*, III, p. 3, 1902; Grabowsky, Dissertation, Königsberg (1904). Renard and Guye (*Loc. cit.*) and many others.

was carefully cleaned with concentrated sulfuric acid and dichromate, washed with distilled water and carefully dried. A thread of pure mercury was introduced into it and the length of this thread was exactly measured by means of an accurate comparator or calibrating instrument, the magnification of the microscope of which was so high that 12.50 turns of the micrometer head equaled 1 mm. The tube was placed beside a rod graduated in millimeters (verified by the Bureau of Standards) and the readings were transferred by swinging the axis of the microscope. Next, the thread was moved, again and again, along the tube; and its length was each time remeasured. In a tube of uniform bore the various lengths should, of course, be equal. After very many pieces of tubing had been examined, two were found sufficiently uniform for the purpose of this work; the extreme values for the measured lengths differed by less than 1 part in 2000. In one of these tubes the average length of a thread of mercury weighing 0.8650 g. was thus found to be 20.47 mm., and subtracting from this length the correction of 0.54 mm. for the protrusion of the two meniscuses,[1] the corrected length 19.93 mm. of the cylinder of mercury was found, and hence its radius according to equation: $r = \sqrt{0.8650/13.546\ \pi\ 19.93} = 1.0099$ mm. This tube was used in Apparatus III.

Another tube, which was only about one-fifth the diameter of this, served in Apparatus IV. In it 0.3403 g. of mercury occupied 213.31 mm. —0.04 mm. (correction for two meniscuses)[2] = 213.27 mm., hence its radius was 0.1936 mm. It had been tested throughout its length by a short column of mercury in the same way as the other wider tube. This calibration tested not only equality of bore, but also the essential evenness of the glass walls—a very important matter, as will be seen.

At about the center of each capillary tube was etched a fine mark, which served as a reference mark, so that it was possible to fill the apparatus, if need be, to exactly the same point in successive settings. The tubes were fused to other parts to be described later.

The Lighting and Observation of the Meniscus.

The second point may now receive consideration. Our tubes containing the liquid to be studied were placed in a square thermostat tank, with windows in front and behind. For defining and measuring the meniscus we used a development of the method long used for reading both burets and barometers. A movable black metal screen with a sharp horizontal upper edge was immersed in the thermostat tank, just

[1] L. W. Winkler, *Z. angew. Chem.*, p. 719 (1903); *Z. anal. Chem.*, 40, 403 (1901).

[2] The smallest diameter measured by Winkler was 1 mm., but his results are so consistent that they may safely be extrapolated to zero diameter, where the height of the meniscus also would be zero. On this basis the correction for a tube 0.2 mm. in diameter is found to be 0.02 mm., which is doubled for the two meniscuses above.

behind the tubes to be observed. This screen could be adjusted at any height at the will of the operator by means of a delicate mechanism consisting of a fine chain passing over a pulley and around a drum held by a variable friction clutch. When the screen had been raised until its edge appeared to be exactly tangent to the deepest point of the meniscus, the area of the meniscus was wholly darkened and its lower contour became entirely clear and sharp. The apparatus thus adjusted is shown in the photograph, Fig. 1. There is every reason to believe that the edge thus observed is the true boundary of the meniscus, and in all the work to be described, the above relative position of window, screen, apparatus and carefully leveled cathetometer-telescope was maintained.

Fig. 1.—Photograph of Apparatus III in thermostat tank. The screen behind the tube is raised so as to be exactly tangent with the meniscus (about half actual size).

The Necessary Diameter of the Wide Tube.

Turning now to the third point mentioned above, one soon finds, on studying earlier work, that not all of the experimenters have agreed as to the width necessary. Even in the best laboratory handbooks[1] the directions are somewhat vague. Magie,[2] working by another method under Helmholtz's direction, speaks of employing a tube 3 centimeters in diameter, but others have usually employed a smaller tube. The best of the recent work in this respect seems to have been that of Walden and Swinne.[3] Like Magie, they used a tube 3 cm. in diameter, but they admit that this was probably not quite large enough, and calculated a possible correction with the help of a somewhat doubtful equation of Desains. The assumption seems to have been usually made that a tube 2 cm. in diameter is wide enough.

On the other hand, it had become clear to one of us in preliminary investigations conducted some years ago with the help of the late Dr. C. L. Speyers that this question had been by no means settled. The

[1] See for example, Ostwald-Luther. On page 237 the statement is made that the tube should be "recht weit" (1912).

[2] Magie, *Wied. Ann.*, **25**, 421 (1885).

[3] *Z. physik. Chem.*, **79**, 700 (1912).

familiar fact that a drop of insoluble oil (such as that which separates from the dilute emulsion of "Sulphonaphthol") on water in a bottle will seek exactly the center unless the bottle is 4 to 5 cm. in diameter seems to suggest that there is a real depression, even in a fairly large surface, when it is surrounded by walls wet with the liquid. For an accurate estimation of the surface tension, the larger tube should obviously contain a perfectly flat surface; but we cannot find that the diameter necessary to insure this condition has ever been adequately investigated. The matter, although apparently simple, is not after all very easily tested because of the usual inequalities in the glass walls of wide tubes. A slightly prismatic vertical section of wall (that is, a wall thicker at one end of the tube than at the other) causes considerable shifting of the image. Moreover, it is necessary that both tubes to be compared should be in a perfectly vertical position, for otherwise the greater refractive index of the glass causes an important displacement. If one of the tubes is slightly inclined to the other, or if one of them is slightly thicker at one end, the effect of difference of level might appear when really none existed. The two tubes must be kept at exactly the same temperature, for obvious reasons.

Our first arrangement for testing the flatness of liquid surfaces in large tubes consisted in a three-fingered or double U tube, having its three fingers, respectively, 2.1, 2.54 and 3.8 cm. in diameter, which was partly immersed in the thermostat tank mentioned above. This tank consisted of a copper, tin-lined box, 25 × 25 × 30 cm. It was provided, as before stated, with two windows; of these, that at the back of the tank was made of common glass; but the other, opposite to it, at the front, was provided with optically ground plane glass, in order that no distortion, due to the irregularities always present in ordinary glass, might cause error in the readings. Of course both of these windows were placed near the top of the tank.

The regulator was of the ordinary toluene-mercury type, having two fingers; it easily kept the bath constant to within 0.01°. The bath was set at 20.0°, since many other physical properties have been determined at that temperature. There were also the customary devices for heating (by electricity), cooling by a slow current of cool water, and thoroughly stirring the water in the thermostat.

The double U-tube (see Fig. 2) was filled two-thirds full of distilled water and set in the thermostat, exactly vertically, by means of a plumb-line. The levels of the water within the tube were, of course, sufficiently below the water level of the thermostat so that the meniscuses could be readily observed through the telescope of the cathetometer.

Proceeding with the comparison of the three meniscuses in the U-tube, we observed immediately that the smallest tube of 2.1 cm. diameter

not only did not have a plane surface at the center of its meniscus, but also that it produced an appreciable rise of the water level above that of the largest tube. Therefore, because it was obviously too small, no further attention was paid to this tube. The large and medium tubes were very carefully compared. Not only were measurements taken with one side of the apparatus presented to the telescope, but also settings were made again after the tubes had been rotated in the horizontal plane through 180°. Thus by observing the meniscus through the two sides of the apparatus it was hoped to eliminate, or at least detect, any errors due to irregularities in the walls of the glass tubes. Afterwards more water was added and another set of readings made, the observations, of course, in this last case being made through a still different part of the glass walls. Before each reading was taken, the apparatus was inclined, so that the glass walls were well wetted above the meniscus, then clamped exactly vertically, and five minutes were allowed for complete drainage of the liquid from the walls of the tube, before readings were taken. Great care was taken to always have the cathetometer-telescope and column properly levelled.

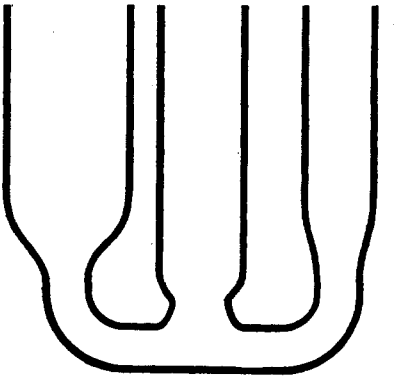

Fig. 2.—Diagrammatic section of double U-tube used for measuring levels in wide tubes (one-third actual size).

In making the measurement the fixed cross hair of the telescope was set on the largest meniscus, the telescope swung through a small arc, and the movable hair adjusted to the next smaller meniscus. Thus the difference in level of the meniscuses was recorded in terms of turns of the micrometer screw on the telescope. By later substituting a standard rule for the apparatus, the number of turns of the micrometer head corresponding to 1 mm. of the standard rule was determined.

In a preliminary series of not very concordant determinations, it was thus found that when viewed from one side, the largest meniscus appeared to be —0.09 turn of the micrometer lower than the middle one, and when viewed from the other side —0.14; average, 0.11 turn. Since 1 turn of the micrometer head was found to equal 0.67 mm., the difference in level between the lowest points in the meniscuses was 0.073 mm. It should be noted that there was a difference of 0.03 mm. between the observations made on the two sides of the tube. This was doubtless due to irregularities in the glass walls of the apparatus; the experimental error of setting should not be over 0.003 mm.

It occurred to us that if irregularity in the opposite walls of the tubes could cause such an error as appeared in these observations, there might be an error in both caused by a prismatic irregularity in both walls of one tube, an error which would not be eliminated by our simple precaution. A way to detect this error would be, of course, to invert the apparatus and make new settings; but this could not be done with the apparatus in the foregoing form. Hence in a new outfit a large U-tube with arms of unequal diameter was sealed at the top, and provided with a ground stopper for filling (Apparatus II, Fig. 3). With such an apparatus the tubes could be rotated not only through 180° horizontally, but also through 180° vertically. Thus any wedge-shaped places in the walls of the tube would become apparent; for by inverting the apparatus, keeping the same side always towards the telescope, identical readings could be obtained only if the surfaces of the tube were parallel. If the walls were wedge-shaped, readings would be obtained deviating from the truth in opposite directions. In this case the average would give the true value.

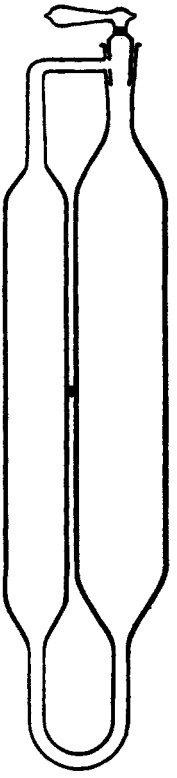

Fig. 3.—Diagrammatic section of reversible U-tube for discovering capillary effect in wide tubes (one-third actual size).

In this modified apparatus the large tube (I) had a diameter of 38 mm., the smaller (II) of 25.4 mm., *i. e.*, they were of exactly the same diameters as the large and medium tubes of the former apparatus. The glass was carefully chosen.

In every case the apparatus was set in a vertical position by means of a plumb-line and the meniscuses were carefully arranged, both exactly in focus of the telescope, which belonged to a first-rate, carefully leveled cathetometer. Two complete series were made, the apparatus being entirely dismounted between them. Adequate precautions as regards wetting of the walls of the tubes and drainage were carried out. The amount of water was so chosen that the water level came at exactly the same point on the large tube, no matter which position was adopted. The results of these experiments with pure water are tabulated in Table I. Readings were taken in four positions: Upright front (*a*), upright back (*b*), inverted front (*c*) and inverted back (*d*). The level in the larger tube was always set at 0.00 on the fixed spider-line of the cathetometer-telescope, and the readings of the level in the narrower tube, made with the movable spider-line, as already described, are recorded below in the table in fractions of a millimeter:

TABLE I.

	First series.	Second series.
Upright (*a*)	0.110	0.116
(*b*)	0.124	0.134
Inverted (*c*)	0.110	0.133
(*d*)	0.096	0.098
Average	0.110	0.120

From these readings it would appear that the front of the tubes (Readings *a* and *c*) possessed more nearly parallel-faced walls than the back (Readings *b* and *d*). Although the agreement is not perfect, it seemed, nevertheless, clear that the average of all the readings should give a value very near to the truth, and that the level of water in the tube of 25.4 mm. diameter was really 0.11 mm. higher than that in the tube of 38 mm. diameter.

The question then arose as to whether or not the tube of 38 mm. in diameter was large enough to obtain a perfectly flat surface. Of course, similar experiments could have been instituted with another reversible U-tube having one arm yet wider, but it proved to be difficult to obtain a sufficiently even tube of larger diameter. Moreover, qualitative observation seemed to show that 4 cm. is large enough. This observation was made in two ways: in the first place, the study of the meniscus in the experiment just recorded showed unquestionably that no part of the surface in the narrower tube (diameter, 25.4 mm.) was perfectly level. The curve was continuous from side to side. On the other hand, in the 38 mm. tube a portion in the middle, apparently about 5 mm. in length, appeared to be flat, coinciding exactly with the horizontal spider-line of the telescope. From this it would appear that a diameter 33 mm. might be enough, and that, therefore, 38 mm. should be ample. This conclusion is supported by observation of the reflection from the surface of water in a wider vessel. If a beaker of water 7 or 8 cm. in diameter is thoroughly cleaned, filled almost to the brim with pure water, and immersed in a large dish of water, the reflection in both surfaces of a vertical rod behind it is seen to be perfectly straight in the middle, but to bend when the image approaches nearer than about 1.7 cm. to the beaker wall. This indicates the need of a tube wider than 34 mm. A similar phenomenon is shown by mercury, of which a surface more than 40 mm. in diameter shows a small level spot in the center, approaching to within about 18 mm. of the edge. A surface less than 35 mm. in diameter shows no such level spot. These dimensions about coincide with those observed in the case of water. Therefore, we concluded that the error of level in a 38 mm. tube would be so small as to be outside the limit of our measurement. Accordingly, all our results recorded in the present paper were obtained with this large diameter—perhaps the widest unrestricted

tube which has ever been used in surface tension measurements. This matter will receive further study in order to discover if a yet wider tube may be necessary for the most exact result. At any rate, it is clear that any outcome obtained with the wider tube as narrow as 20 mm. must be far from the truth. This fact doubtless accounts, at least in part, for the low results for surface tension often obtained by this method.

The error is magnified by the presence of a further point of support in the middle of the wide tube, such as the capillary usually employed. In some preliminary experiments of our own, it was found that when a fine glass rod is immersed in water in the middle of a tube 20 mm. in diameter, the capillary rise in this tube is about 0.31 mm. more than that without the rod. Because liquid in a tube of this diameter, even without the central capillary, is distinctly above a level surface, it will be seen that

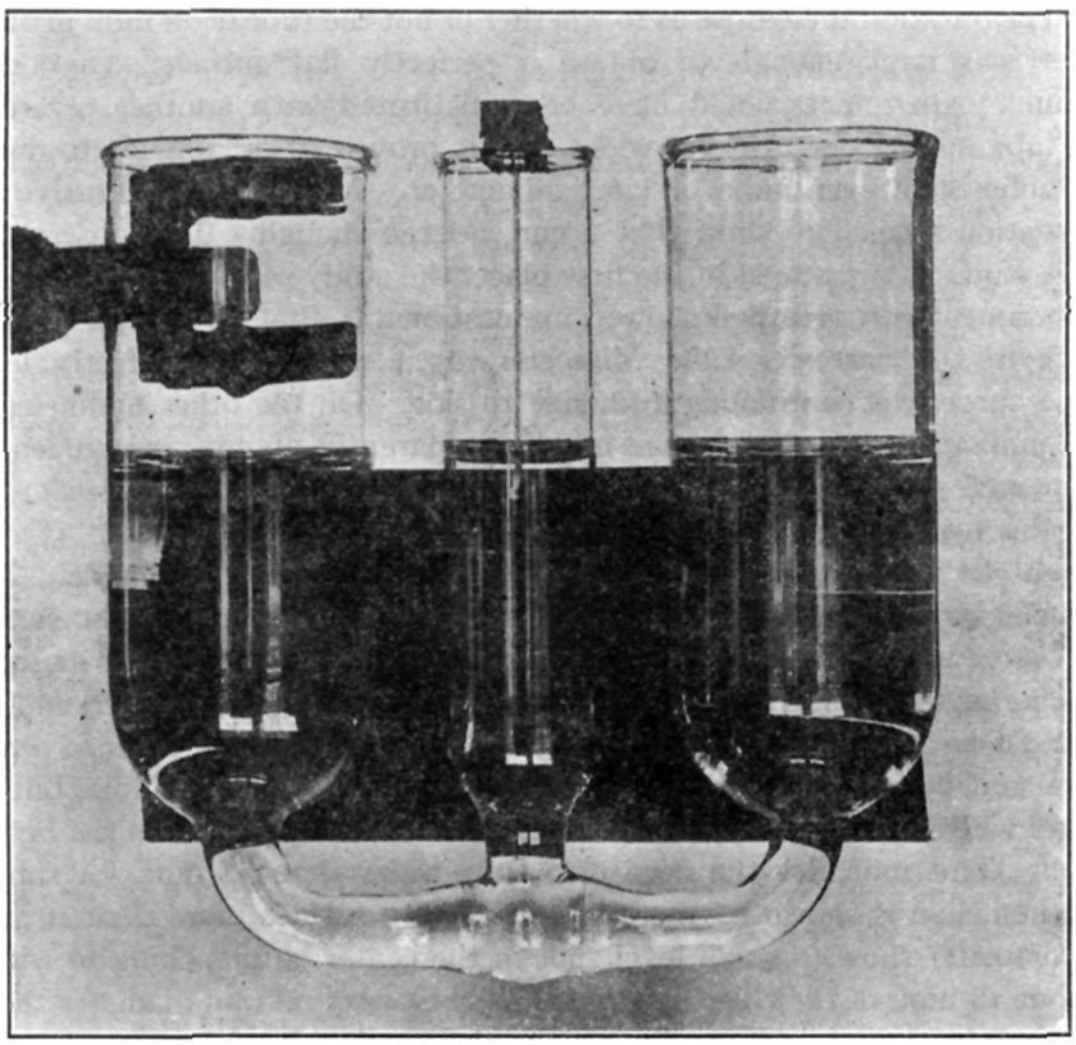

Fig. 4.—Photograph (seven-tenths actual size) of capillary rise in 20 mm. tube (with central rod) above level in two 36 mm. tubes. The straight-edged screen behind the tubes is exactly tangent to the larger meniscuses. This photograph shows the magnitude of the error in the usual surface tension apparatus, which is like that in the central tube.

the many experimenters who have used this arrangement must have obtained results much too low.

The combined effect is shown in the appended Fig. 4. This is a somewhat reduced photograph of a 20 mm. tube between two tubes, each 36 mm. in internal diameter. The middle tube has within it, in the center, a fine glass rod, which, as regards its exterior capillary action, would give the same effect as a fine capillary tube. The tube was carefully leveled and the lens of the camera placed exactly on a level with the meniscuses. A screen with a straight upper edge was then arranged behind the meniscuses in such a way as to be exactly tangent with the bottoms of the two larger ones. Any one can see how much the liquid in the middle 20 mm. tube is raised above the level in the wider tubes. This error, which does not need a micrometer to appreciate its magnitude, has entered into many of the earlier investigations, especially among the recent ones in that of Rénard and Guye.

The Correction for the Weight of the Meniscus in the Capillary.

The reading of the height in the capillary is made from the lowest point of the meniscus, and all the liquid above that level in the capillary, rising up to the walls of the tube, is, therefore, ignored in the simple reckoning. But the weight of the liquid in the meniscus itself may be very important unless the capillary is exceedingly fine.

The calculation of the exact shape of the meniscus is a mathematical problem of great intricacy, which has apparently not yet been satisfactorily solved.[1] Special assumptions have usually been introduced in order to effect integration, and terms of a smaller, but still possibly significant, order must be neglected. The usually assumed relation is that of Poisson,[2] who came mathematically to the conclusion that h is to be found as follows: $h = h_0 + r/3 - r^2/h_0$ 0.1288. This equation gives a reasonable result when the capillary is fine; but when the tube becomes wide, r^2 exerts too great an influence, and with a diameter approaching 1 cm., h becomes less than h_0—an obvious absurdity. Hagen and Desains[3] have proposed a widely different equation as follows: $h = h_0 + a^2 r/(3a^2 + r^2)$; in which a^2 is the capillarity-constant (the true height multiplied by the diameter of the tube). This expression (based upon La Place's reasoning) at least never makes the calculated value less than the observed value, and is, therefore, in this respect to be preferred to the

[1] La Place, Gauss, Young, Poisson, Maxwell, Rayleigh, Gibbs and others have attacked the problem. Lord Rayleigh's papers on the theory of capillarity are especially interesting. See Lord Rayleigh's collected works 1883–1892, II, 236, III, 397, 513, 562, 572 (1901). A historical and appreciative review of the work of these various investigators is forbidden by lack of space.

[2] Poisson, "Nouv. Théor d. l'act. capill.," p. 110 (Paris, 1831).

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

equation of Poisson; but it is doubtful if all the necessary quantities have been considered. However, the equation reduces to $h = h_o + r/3$ when h is very large (that is, when r is very small) as it should to correspond to the facts.

In view of this failure of both the usually accepted equations under common conditions, we sought to discover, if possible, further experimental light upon this vexed question.

Even superficial observation shows at once that the meniscus in a very small tube is almost hemispherical, and that this hemisphere becomes more and more oblate or flattened as the tube becomes wider. Obviously the short diameter of this pseudo-oblate spheroid ought to be an important help in solving the riddle. The measurement of the height of the meniscus between its lowest point and the point of actual contact with the glass walls of the tube was, therefore, carried out; it proved to be easier than had been expected.

In our apparatus, with the dark screen tangent to the meniscus, although the lower suface of the meniscus is very sharply defined, the extreme upper edge cannot be very easily identified. A simple device made it possible to determine exactly the position of this upper edge, nevertheless. If the screen is gradually raised above the position of tangency, its image becomes at first much refracted and distorted by the curved surface; but, as the screen is raised higher, its image approaches straightness again, until at a definite position the edge of the screen appears again entirely straight. This straightness must be attained at the level where the liquid meniscus is exactly in contact with the walls of the tube. The cross hair of the telescope can then be accurately set on the edge of the meniscus and screen, thereby giving exactly the position of the upper boundary of the meniscus.

Careful measurement thus made showed the height of the meniscus in a perfectly clean tube 0.4 mm. in diameter to be very nearly equal to the radius of the tube, varying but slightly with different liquids. Thus the shape of the meniscus in a fine tube of this sort is nearly spherical. If this were exactly true, the correction would be simply $^1/_3$ its height, because a hemisphere occupies precisely two-thirds of the volume of the circumscribed cylinder. Practically, the deviations from this simple expression are so slight with tubes of this very small bore that they may be neglected. Thus in such a tube the third term of the second member of the theoretical equation of Poisson should become so small as to be negligible.

The height of the meniscus in wider tubes next deserved attention. In the way just described the height of water in a meniscus within a tube 2.02 mm. in diameter was found to be 0.964 mm., a value near that of the radius, but slightly less. It seemed highly probable that within the limit of error of experiment it would be safe here to assume that this menis-

cus was a slightly flattened sphere (or oblate spheroid) with its shortest radius 0.964, and that the volume of the concave mass of liquid enclosed between the hemispheroid and walls was to be found by multiplying $2\pi r$ by one-third of its height. The various qualitative arguments which led to this conclusion need not be detailed, because a satisfactory quantitative support of the assumption is found in the data of Winkler,[1] determined by actually weighing the water in the meniscus. For such a tube the correction to the height given by Winkler is 0.32 mm. in very close agreement with one-third of the meniscus height, 0.321. Hence it seemed reasonable to use this simple method with other liquids and other tubes of small diameter. The equation, then, used throughout this paper for tubes of 2.02 mm. (or less) in diameter, is $h = h_o + h_m/3$, in which h = the true corrected height, h_o = observed height, and h_m = the height of the capillary-meniscus, as observed by the method described above. When the tube is very small this becomes approximately $h = h_o + r/3$, because h_m is then almost equal to r.

This equation, like that of Hagen and Desains, is evidently safer than that of Poisson, since it never leads to an absurdity, no matter how wide the tube may be; and with small tubes we have good reason to believe that it is better than either of the others. For tubes over 4 or 5 mm. in diameter, it doubtless needs modification. In a very wide tube, *e. g.*, of 30 millimeters, nearly all the liquid raised must be in the meniscus (measuring here with water about 4 mm. in height). In this case, the correction which should be applied to the bottom of the meniscus to obtain the corrected capillary rise (easily calculated to be about 1 mm.) would be about one-quarter of the meniscus height instead of one-third, as was found with very small tubes. It seems probable, then, that these two fractions (one-quarter and one-third) represent the limits of the variation of the correction for the meniscus as applied to the measured height of this raised mass of water, and that all values for tubes of less than 30 mm. diameter must lie between these rather close limits. The corrected value of the rise above the standard flat level in any tube less than 30 cm. in diameter would, therefore, be $h = h_o + nh_m$, where n varies from exactly one-third with very narrow tubes to about one-quarter with wide tubes. A more comprehensive study of the relation of the weight of the meniscus to its height will be carried out in the near future in this laboratory. For the present research this was not necessary, because only very narrow and very wide tubes were used, and each of these was treated adequately with the definite knowledge hereinbefore detailed.

The Angle of Contact.

This is a very important consideration, concerning which the evidence is conflicting. In this preliminary paper we have made no attempt to

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

add to the knowledge of it. The angle of contact enters into the complete expression for calculating surface tension in the form of its cosine, and must, therefore, assume a value of 2° 30′ in order to affect the result by 0.1%. It is true that early indirect results by Quincke seemed to show that the angle of contact, even with water, was as much as 25°, which would affect the result to the extent of 10%. More recent results, however, have discredited these conclusions. There is good reason to believe that, although in the case of mercury (where the tube is not wetted by the liquid) the angle of contact is considerable and important, in all those cases where the tube is fully wetted by the liquid, this angle is reduced to zero. Attention is especially directed to the careful and thoughtful work of Magie,[1] who found that some of the assumptions underlying Quincke's mathematical work were incomplete (as has so often been the case in discussions of this kind) and that there is really no basis for believing, at least as far as Quincke's results go, that any appreciable angle of contact exists. Ramsay and Shields[2] bring forward a very ingenious piece of evidence in favor of this thesis. They show that a completely spherical bubble, which has exactly the diameter of a small vertical tube, will not rise, but that a spherical bubble with a very slightly less diameter will rise in the tube. Because the spherical bubble must have its periphery tangent to the tube, and when it just fits the tube practically consists of two meniscuses, one concludes that the meniscuses are exactly tangent.

Nevertheless, the question is not wholly answered; and we hope before long to have further evidence to advance concerning it. Our experience thus far would seem to indicate that the large values for the contact angle found by some experimenters must have been due to impurities which prevented the liquid from truly wetting the walls; in such cases a large contact angle is evident even to a superficial observer.

Another question more or less connected with the contact angle is the question as to the effect of the material of the tube. Quincke[3] thought that the nature of the material of the tube produced an effect upon the capillary constant, but Volkmann[4] has disproved these conclusions. Here again, incomplete wetting was probably the cause of the deviations.

Preparation of the Materials.

The benzene used in this work was freed from thiophene by prolonged shaking with several portions of sulfuric acid. It was then washed with water until there was no further test for acid, thoroughly dried over sodium wire, redistilled once, and recrystallized four times (until the

[1] Magie, *Wied. Ann.*, **25**, 432 (1885).
[2] *Z. physik. Chem.*, **12**, 452 (1893).
[3] *Wied. Ann.*, **61**, 267 (1897).
[4] Volkmann, *Ibid.*, **53**, 633 (1894).

freezing point became constant). The benzene was preserved over sodium.[1]

The toluene was best "chemically pure" preparation made commercially in Germany. It was treated with concentrated sulfuric acid for a long time, washed with caustic alkali and water, and then shaken up with mercury until the mercury was no longer discolored. Finally it was fractionated (boiling at 110.4°–110.6° under 768 mm.) and preserved over sodium.

Methyl alcohol was prepared water-free by refluxing first with fresh lime and finally for a long time with metallic calcium. It had a boiling point of 64.65°–64.75° under 767.5 mm. pressure.

"Absolute" ethyl alcohol, obtained from a trustworthy American firm, and purporting to have only 0.2% of water, was refluxed with metallic calcium for a day, and then redistilled. During the distillation the receiver was well protected from moisture by a tube of freshly ignited lime. The boiling point of the fraction taken was 78.55° at 763.7 mm. The liquid was distilled directly into the surface tension apparatus, with every precaution to exclude moisture. This precaution is essential—a preliminary determination with alcohol which had been exposed to the atmosphere gave a value for the capillary constant appreciably too high.

Our isobutyl alcohol had been carefully fractionated in this laboratory by Dr. H. S. Davis, and had a boiling point of 107.2°–107.3°, under normal pressure.

Ethyl butyrate was purified by five fractional distillations, and boiled at 120.8° at 756.6 mm.

The water used was all twice distilled, first from alkaline permanganate, and then from a trace of sulfuric acid.

The Execution of the Determinations.

The essential preliminary details having been settled, it was now possible to proceed to develop an apparatus by which the capillary rise of liquids could be accurately measured. The first form which this apparatus took is illustrated in Figs. 1 and 5 (Apparatus III). Except that the narrower tube was very much smaller, the general design was the same as that in Apparatus II (Fig. 3). In Apparatus III the larger tube was 38 mm. in diameter, while that of the smaller was 2.0198 mm. This apparatus was made more compact than No. II, but it still demanded a rather large bulk of liquid (36 cc.), since we dared not soften the glass near the center of the large tube, where the meniscus was to be read. The difficulty was overcome in Apparatus IV (Fig. 6) by sealing into the large tube a closed sinker of glass (partly filled with lead shot), which displaced most of the liquid. The tube above was also filled with a loose plug of glass rod for the same purpose and the total bulk of liquid needed

[1] See Richards and Shipley, THIS JOURNAL, **36**, 1825 (1915).

was thus reduced to ·12 cc. In Apparatus IV the wide tube had the usual diameter of 38 mm. and the capillary tube a diameter of 0.1936 mm., as already stated. The presence of the sinker, with its top very near but fully below the surface, had the important incidental advantage of much diminishing the slight but irritating vibration which the liquid sometimes suffered in the wide tube. This vibration came chiefly from a distant engine in the Engineering Building of the University, and was especially noticeable when the ground was frozen.

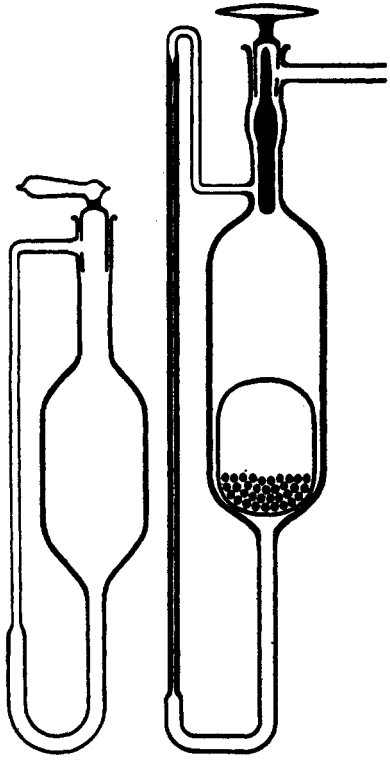

Fig. 5.—Apparatus III in diagrammatic section (about one-third actual size).

Fig. 6.—Apparatus IV in diagrammatic section (about one-third actual size). The loaded sinker is to diminish the necessary volume of liquid.

Obviously the first thing to do with each apparatus was to test it by means of some convenient liquid, taking readings at short intervals and in all the four possible positions. Thus any deceptive regions could be detected, and henceforth avoided in the actual use of the apparatus. Each apparatus had a mark etched upon it, for reference as to position.

Apparatus III was the first to be studied in this way. It was carefully cleaned with fresh sulfuric and chromic acid cleaning solution, thoroughly washed with purest water, and filled with water to the desired point. The importance of perfect cleanliness cannot be overemphasized. The apparatus was set in a precisely vertical position with the help of a plumb-line, and after sufficient time had elapsed for the liquid to take the temperature of the thermostat, the meniscus levels were carefully read by means of the cathetometer. Then the position of the meniscus in relation to the reference mark was noted, more water put in and new readings taken as before.

At first the readings were not concordant. It was found that the capillary rise was too small when liquid was being added to the large tube. Thus there was a slight lag in the fine tube,[1] probably due to increase

[1] Lord Rayleigh's interesting work on changing surface effects applies only to mixed solutions, such as oleates and saponin. (*Proc. Roy. Soc.*, 47, 281 (1890).)

of the contact angle with a rising thread. Only when the liquid is run rapidly up and down the capillary tube so as to wet thoroughly the walls (of course allowing sufficient time for drainage) are the readings consistent and trustworthy.

A few data may be given to show the importance of this precaution. For example, a preliminary observation with Apparatus III gave an uncorrected (and incorrect) capillary rise of 1.406 cm. On adding 3 cc. of water to the wide tube (a change of level of 2.8 mm.) the capillary rise was only 1.365; and upon adding a little more water the rise was still further diminished to 1.349. On the other hand, when the water in the wide tube was brought back to the original level, the reading was 1.437, which was regularly attained in this way on repetition. This is a total range of six per cent.—an altogether inadmissible irregularity. Hence special precautions must be taken about wetting the capillary before each reading, running the liquid back and forth, and giving plenty of time for drainage. The reading should be approached with a *falling* capillary thread—accomplished by suitably inclining the apparatus for a moment. In this way consistent and satisfactory readings may always be obtained, if the capillary is clean and the liquid pure. One notes that this is precisely the opposite procedure to that necessary in the case of mercury, which must be read in a capillary with a *rising* thread.

The technique having been settled, the calibration of Apparatus III could be undertaken. This was done by making many readings of the height of the water level at frequent intervals and in all the four possible positions. Thus it was found that with this particular apparatus sufficiently concordant results could be obtained only if the liquid level in the wide tube occurred between +0.4 to +1.3 mm. from the mark for all four positions; hence, this limited range was always adhered to. The precaution was important, for a great error may be introduced because of irregularities in the walls of some parts of the tubes. We are inclined to rate this as one of the most serious of the heretofore comparatively unheeded details.

In order to illustrate more fully the method employed, a series of readings in a single setting chosen at random, will be given in full detail. For this reading the apparatus happened to be placed in the thermostat in position *d* (that is, inverted, and viewed from the back, with the larger tube to the left). When the fixed spider-line of the micrometer eyepiece was set on the large meniscus, the reference mark on the smaller tube (2) corresponded to +0.400 on the micrometer scale. The positions of the two meniscuses were then read by measuring in turns of the micrometer the distance of the respective positions from the nearest millimeter as read off from the very carefully graduated scale of the cathetometer. It will be observed that the individual readings varied in maximum less

than 0.01 mm. on each side of the average. This may be taken as about the possible error of a single observation. The mean was doubtless considerably nearer the truth than this.

TWO PARALLEL SERIES OF READINGS: WATER IN APPARATUS III. (20°.)
Position (*d*) apparatus inverted, back.

		Micrometer scale settings.							
		In turns.					Ave.	Same in mm.	Total reading, mm.
	Mm. scale.								
(2)	919.00	+0.458	0.451	0.450	0.457	0.450	0.453	0.376	919.376
(1)	904.00	+1.185	1.183	1.188	1.186	1.186	1.185	0.983	904.983
									14.393
(2)	912.00	+0.461	0.468	0.448	0.459	0.452	0.457	0.376	919.376
(1)	904.00	+1.185	1.189	1.189	1.195	1.197	1.191	0.989	904.989
									14.390
							Average observed rise,		14.391

This table gives readings only in a single position. In order to be sure that inequalities in the tube caused no error, it was necessary (as already pointed out) to make readings also in the other positions, and the following table contains not only the two averages just given, but six other averages, two for each of the positions (*a*), (*b*) and (*c*), as already defined—*a* being always the position when the tube was erect, with the larger tube to the left.

RESULTS FOR WATER IN APPARATUS III.
Readings in all four positions.

	(*a*)	1.4378	(*b*)	1.4416	(*c*)	1.4389	(*d*) 1.4393
		1.4379		1.4427		1.4380	1.4390
Av....	(*a*)	1.4378	(*b*)	1.4422	(*c*)	1.4384	(*d*) 1.4391

Average of (*a*) and (*b*) = 1.4400; average of (*c*) and (*d*).. =1.4388
Total average..... =1.4394

It will be noticed that the readings in any one position are fairly consistent, but that there is considerable variation even in this very carefully selected and elaborately studied tube between the settings in different positions. Position (*b*) appears to be the most widely deviant, giving the highest results. (*d*) and (*c*) agree very closely with each other and with the average. On the whole, therefore, they are to be looked upon as the more accurate. The average of the eight figures has a probable error (according to the theory of least squares) of 0.0004, or 0.03%. Thus, the result is of a degree of accuracy consistent with that of the rest of the problem. Similar deviations were found with other liquids. Usually position (*a*) gave the lowest results and (*b*) the highest. Something depends, of course, upon the exact level of the liquid in the tube. With this apparatus determinations of the capillary constant not only of water, as just given, but also of benzene and toluene were made.

Apparatus IV (Fig. 6) (which had a much finer capillary and a sinker occupying most of its bulk, so that less liquid was needed) was calibrated and tested in exactly the same way as Apparatus III. Ethyl alcohol was used for this purpose, because the capillary rise with water was so great in this tube as to take the meniscus out of the range of the small window of optical glass in the thermostat. The results obtained in the various positions are recorded below:

RESULTS FOR ETHYL ALCOHOL IN APPARATUS IV.

Readings in all four positions.

(*a*)	(*b*)	(*c*)	(*d*)
2.9723	2.9713	2.9734	2.9700
2.9710	2.9713	2.9744	2.9701
2.9704	2.9715	2.9735	2.9702
2.9712	2.9714	2.9738	2.9701

Average of (*a*) and (*b*) = 2.9713; average of (*c*) and (*d*)..... =2.9720

Total average..... =2.9716

The agreement between the different positions is here much better than in the case of Apparatus III; it leaves nothing to be reasonably desired. The "probable error" is so small as to be negligible.

Benzene was again determined (so as to relate the results of one apparatus with the other). In addition isobutyl and methyl alcohol were likewise studied in this apparatus, as well as ethyl butyrate.

Before any new liquid was introduced, each apparatus was always cleaned with cleaning solution, thoroughly washed with nothing save the best distilled water and finally dried by blowing air dried by phosphorus pentoxide through it for a long time (two to four hours). No grease was used upon the stopcock, which was very finely ground and was moistened with the liquid within. To keep out water and withstand hydrostatic pressure when the apparatus was inverted, the top of the joint of the stopcock was carefully coated with hard paraffin, just before the immersion.

In the two tables which immediately follow there are recorded the successive determinations of the several liquids with Apparatus III and IV. In every case air at atmospheric pressure was present in each of the tubes, with the saturated vapor. Apparatus IV had been arranged so that the air could be removed, but lack of time prevented our making the experiment. The results of Rénard and Guye[1] show, nevertheless, that the effect of the air must be slight.

The tables contain in each case the mean value, obtained by averaging

[1] T. Rénard and P. A. Guye, *J. chim. phys.*, **5**, 81–112. Ramsay and Shields's method was employed to measure the rise of liquids in capillary tubes. Measurements were made *in vacuo*, and in the presence of air at atmospheric pressure. The difference between the surface energy in the two cases does not differ by more than 0.5%.

many determinations, in the way already explained in the case of water and benzene.

The tables for the most part explain themselves. The first column names the substance; the second records the observed height (average of at least four averages) of the column between the bottoms of the two meniscuses; the third gives the correction which must be added to this height on account of the weight of liquid in the capillary meniscus; the fourth gives the sum of the two preceding, or the corrected height; and the fifth gives the density of each substance.

The last two columns perhaps require slightly more detailed description. In the sixth, or the next to the last column of the table is recorded the so-called "capillary constant," usually expressed by the symbol a^2, which has the dimension of surface, but numerically represents the corrected height in millimeters to which the liquid would rise in a tube of exactly 1 mm. radius. It is calculated according to the equation

$$a^2 = r \times (h + h_m/3),$$

h_m being the height of the meniscus; which is very nearly the radius of the tube in a small tube of this sort.

The last column of the table gives the surface tension computed in terms of dynes per centimeter. These values for surface tension are calculated on the supposition that the angle of contact of liquid in the capillary tube is zero. They can be easily revised in the future provided it is found that this is not the case. The equation used is, of course,

$$\gamma = {}^1/_2\, a^2(S_1 - S_2)g,$$

the value of g at Cambridge being 980.4, a^2 being expressed in sq. cm., and S_1 and S_2 being the densities of liquid and vapor, respectively.

CAPILLARY CONSTANTS AND SURFACE TENSIONS.

Data obtained with Apparatus III (20.00°), radius of capillary = 1.0099 mm.

Substance.	Average observed height in millimeters.	Correction for small meniscus $= {}^1/_3\, h_m$.	Corrected height in millimeters.	Density 20°/4.	Capillary constant a^2 (in presence of air). (Sq. mm.)	Surface tension dynes per cm.
Water	14.394	0.321	14.715	0.9982	14.861	72.62
Benzene	6.351	0.311	6.662	0.8788	6.728	28.94
Toluene	6.366	0.311	6.677	0.8658	6.743	28.58
Data obtained with Apparatus IV (20.00°), radius of capillary = 0.1936 mm.						
Benzene	34.620	0.061	34.681	0.8788	6.714	28.88
Methyl alcohol	30.063	0.061	30.124	0.7918	5.832	22.61
Ethyl alcohol	29.719	0.061	29.780	0.7892	5.765	22.27
Isobutyl alcohol	30.016	0.061	30.077	0.8019	5.823	22.85
Ethyl butyrate	29.403	0.061	29.464	0.8789	5.704	24.54

Only one pure substance was determined by both tubes, namely, benzene. It will be noticed that the results for benzene are very nearly the

same in both cases, 6.728 and 6.714, the average value for the capillary constant at 20° being 6.721.

This close agreement of the two results with benzene seems to show that there is no essential flaw in the method, and that the radii of the tubes, the correction for each meniscus and the other details have been properly determined.

Our new values for the capillary constant and surface tension of these substances will be seen, on comparing them with the results of others, to be higher than most of the values found by this method already recorded in physico-chemical literature. For example, Quincke[1] found only 14.47 as the capillary constant of water, while Rénard and Guye[2] found only 6.47 for benzene, instead of 6.72, etc. One of the best of the older results is that of Frankenheim and Sondhauss,[3] who found 14.84 for water, a number very near our 14.86; Domke's[4] more recent result, 14.85, is even better. The carefully obtained results of Walden and Swinne[5] are doubtless correct relatively to one another, but they all depend upon a value of the capillary constant of benzene which is doubtless too low. Their results would have been much more like ours if they had accepted their own measurement of the diameter of their capillary, and even more consistent with ours if this measurement had been further corrected for the apparently omitted correction for the meniscuses of the thread of mercury used in calibration. If, as we think, the capillary constant of benzene at 20° is 6.721 instead of the value 6.515 assumed by them, all their results should be increased by $\left(\frac{6.721}{6.515} - 1\right) = 3.16\%$, and a similar, if not always quite equal, correction should probably be applied to all the results of Ramsay and Shields and Aston, and of Rénard and Guye.

In general it should be noted that higher results obtained by this method are probably to be considered, *à priori*, more accurate than lower ones, because most of the errors in the determination tend to diminish the observed value. If the tube is not perfectly clean, or if the flat surface used for comparison is not large enough, or if the correction for the capillary meniscus is omitted, the observed capillary constant will be too small; and usually at least one of these precautions has not been heeded in the earlier work.

This paper is only a preliminary communication. A large amount of further work upon the subject has already been finished, and more is in prospect. We hope that yet greater accuracy may be attained in the

[1] Quincke, *Pogg. Ann.*, **139**, 1 (1870); Brunner's old value (1847) is much better.

[2] Rénard and Guye, *Loc. cit.* This value for 20° is interpolated from their figures.

[3] Frankenheim and Sondhauss, *Pogg. Ann.*, **122**, 177 (1864).

[4] Domke, *Wiss. Abh. d. K. Normal-Aich. Komm.*, III, 1 (1902). He found 14.920 at 18.2°, which would correspond to the above value at 20°.

[5] *Loc. cit.*

future, bearing in mind the precautions to which attention has been called in this paper.

In conclusion, we are glad to express our indebtedness to the Carnegie Institution of Washington for some of the apparatus employed in this research.

Summary.

In the course of a series of determinations of capillary constants by measuring the capillary rise in fine tubes, the following precautions have been esspecially emphasized:

First, inequalities in the glass tubes employed were detected and corrected by the use of reversible apparatus.

Secondly, the capillary rise was referred to an unrestricted flat surface 38 mm. in diameter, which is larger than that usually used. It was shown that smaller surfaces are too small and that the insertion of a capillary in the middle of a larger tube causes appreciable error by increasing the capillary effect of the large tube.

Thirdly, special care was taken that the true bottom of the meniscus should be read.

Fourthly, the weight of the fine meniscus was in each case allowed for, and a new approximate formula suggested for its calculation, depending upon the observed height of the meniscus.

Heeding these precautions, determinations of the capillary constants of several important liquids were determined at 20° as follows: water 14.861, benzene 6.721, toluene 6.743, methyl alcohol 5.832, ethyl alcohol 5.765, isobutyl alcohol 5.823, ethyl butyrate 5.704.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.]

THE POTENTIAL OF SILVER AGAINST SILVER ION IN CONCENTRATED SOLUTIONS OF POTASSIUM AND OF SODIUM CHLORIDE, AND ITS RELATION TO THE ACTIVITIES OF SUCH SOLUTIONS.

BY GEORGE SHANNON FORBES AND FREDERICK OSBAND ANDEREGG.

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The present paper records the measurement of the potential of cells of the type Ag | dilute $AgNO_3$ | KNO_3 | AgCl in conc. MCl | Ag, and an attempt to calculate from the data the activity of chloride ion at high concentrations—a problem of great importance. This work, carried out in the academic year 1912–13, has been left unpublished in the hope of an opportunity to extend the experiments. Because this hope has not yet been fulfilled, the following statement of results is to be regarded, in a sense, as preliminary in character: