Summary.

The precipitation of zinc from solutions of formic acid by means of hydrogen sulfide has been studied with special reference to the conditions affecting the accuracy of the determination. It has been shown that:

(1) The range of hydrogen ion concentration between 10^{-2} and 10^{-3} is the most favorable for quantitative precipitation of zinc sulfide in a form suitable for rapid filtration and washing.

(2) The concentration of hydrogen ion may be kept within this range during precipitation by the use of buffers, as described, namely ammonium citrate and "formic mixture," this latter being a solution containing ammonium sulfate, ammonium formate and formic acid.

(3) The precipitation of granular zinc sulfide is favored not only by a concentration of hydrogen ion within the limits 10^{-2} to 10^{-3}, but also by a high concentration of an ammonium salt of a strong acid, by a volume of 100 cc. for every 0.1 g. of zinc present, and by a temperature of 95° to 100°.

(4) The passing of hydrogen sulfide under pressure is desirable both for rapid saturation, and for avoidance of loss of formic acid by evaporation.

(5) The conversion of zinc sulfide to the sulfate, a modification of the method of Sullivan and Taylor,[1] is accurate and satisfactory where precise determinations are desired.

(6) The method recommended is applicable to the separation of zinc from iron, manganese and nickel, and to the analysis of zinc alloys and ores.

(7) For the conditions discussed in this paper the method is accurate to within one part per thousand.

NEW YORK, N. Y.

[CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY OF THE UNIVERSITY OF CHICAGO.]

THE DETERMINATION OF SURFACE TENSION (FREE SURFACE ENERGY), AND THE WEIGHT OF FALLING DROPS: THE SURFACE TENSION OF WATER AND BENZENE BY THE CAPILLARY HEIGHT METHOD.

BY WILLIAM D. HARKINS AND F. E. BROWN.

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The accurate determination of surface tension is of importance in investigations on theories of surface structure, the structure of liquids, molecular cohesion, in the study of colloids, especially in physiological work, and in various lines of technical chemistry. It is, therefore, unfortunate that almost all of the surface-tension data in the literature are

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[1] *Loc. cit.*

3% or more too low, as has been shown by Richards[1] and also in a former paper from this laboratory. This error is all the more remarkable in that it would not be difficult to eliminate it almost entirely. The values for the surface tension of water reported by different observers using different methods vary by more than 6%.[2] Thus, while the most precise work by the capillary height method has given values very close to 73 dynes per cm. for the surface tension of water at 18°, the extremely careful experiments of Grunmach, using the capillary wave method, gave 76 dynes per cm. Now, it is not sufficiently realized that a considerable part of this deviation is due to the fact that *the theoretical basis of some of the methods is not sufficiently exact.*

The capillary rise is the only method for the determination of surface tension which has a mathematical theory so simple that the principal errors are experimental. There are, however, some serious objections to this method: first—it is very difficult to get capillary tubes of uniform bore; second—readings of high accuracy are not easily obtained even with a pair of reading telescopes, or a cathetometer; and third—the results obtained with some liquids are not consistent, but depend on the grade of glass composing the tube, and the length of time during which the liquid is left in contact with the glass; this method may give values 20% or more too low if a solution with a basic reaction is used. Viscous liquids and solutions of certain organic compounds also give incorrect results; on the other hand, excellent results are obtained with water, benzene, the lower alcohols, and similar liquids.

There is, moreover, a very simple, rapid, and accurate method for the determination of surface tension which usually gives excellent results. The theory of this, the drop-weight method, has been worked out in a preliminary way by Lohnstein;[3] but, unfortunately, the surface tension of a liquid calculated by the aid of his theoretical curve can diverge 4% or even 30 or more per cent. if the right-hand branch of his curve is used. Rayleigh,[4] in 1896, determined the weight of water drops falling from tubes of various diameters and his data could be used to standardize the method if he had used perforated discs instead of open, thin-walled tubes, for all of his measurements.[5] It is also essential that more

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[1] THIS JOURNAL, **37**, 1656–76 (1915).

[2] Freundlich, *Kapillarchemie*, Leipzig, **1909**, p. 27.

[3] *Ann. Physik*, [4] **20**, 237–68, 606–18 (1906); **21**, 1030 (1907); *Z. physik. Chem.*, **64**, 686 (1908); **84**, 410 (1913). See also Kohlrausch, *Ann. Physik*, **20**, 790 (1906). For a bibliography of the drop-weight method see a paper by Perrot, *J. chim. phys.*, **15**, 164 (1917).

[4] *Phil. Mag.*, [53] **48**, 321–37 (1899).

[5] Table IV and V of this paper are calculated from Rayleigh's data; Guye and Perrot, *Arch. sci. phys. nat.*, [4] **11**, 225, 345 (1901); **14**, 699 (1902); **15**, 132 (1903); *Compt. rend.*, **135**, 458 (1902); and Guglielmo, *Rend. R. Accaddei Linecei*, **12**, 462 (1903) have also worked on this correction.

than one liquid should be used in the standardization. Morgan determined values for drop weights which are seemingly experimentally accurate, but he has paid no attention to the theory of drop formation, and his calculations are carried out by a method which insures that at least a part of his surface-tension values must be incorrect. In other words, the Morgan method of calculation does not give the *relative* values correctly,[1] and the errors are such that if glass tips of convenient size were to be chosen for the determination of interfacial tension the error might be quite large. Even with single liquids the results deviate as much as 3 or 4% from the correct values. Thus, almost all of the surface-tension values for organic liquids are much too low, while those for water are very good.

Six years ago Harkins and Humphery carried out a preliminary standardization of the drop-weight method for the determination of surface tension over a limited range. The present work, for which we made about 30 new extremely accurate dropping tips, was undertaken to extend their investigations to such an extent as to make the data a basis for a method of calculating accurate values of surface tension from drop-weight data.

While the law of Tate ($W = Mg = 2\pi r\gamma$) considers that the weight[2] of a drop is proportional to the radius r of the tip, and to the surface tension γ, it fails to recognize the fact that it is also a function of the shape S of the drop. The shape depends on the ratio between some linear dimension of the tip, such as r, and a linear dimension of the drop l, or

$$W = Mg = 2\pi r\gamma f(r/l). \qquad (1)$$

Now, the cube root of the volume of the drop $V^{1/3}$ varies as a linear dimension of the drop, so

$$W = Mg = 2\pi r\gamma\psi(r/V^{1/3}) = 2\pi r\gamma\phi. \qquad (2)$$

In place of $V^{1/3}$ any other quantity which varies as a linear dimension of the drop, such as a, the square root of the capillary constant a^2, may be used. Here a should be expressed in centimeters.

$$W = Mg = 2\pi r\gamma f(r/a) = 2\pi r\gamma\phi. \qquad (3)$$

This has the form of Lohnstein's equation, but it may be deduced without the use of the objectionable hypothesis introduced by Lohnstein, that

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[1] The very considerable value of Morgan's work lies therefore not in his results for surface tension, but in the experimental results for the weight of drops. Fortunately the present paper gives a method of translating drop weight into surface tension, provided the radius of the tip employed is known. While, in general Morgan's papers do not give the radii of the tips used, they give data from which the radius of each tip may be calculated.

[2] The weight which the drop from any tip would have if Tate's law were valid will be called the weight of the *ideal drop*.

the angle of contact of the hanging drop with the tip, is the same immediately before and after the detachment of the falling drop. Indeed, this assumption seems to have no real meaning, since after the fall of the drop the remaining liquid changes its form with extreme rapidity, and it seems difficult to determine at just what instant to determine the angle of contact.

For any special drop the values of $r/V^{1/3}$ and r/a are in general different, but $\psi(r/V^{1/3})$ and $f(r/a)$ are the same. The purpose of this research is to determine the value of the function, either in terms of $r/V^{1/3}$ or of r/a. Of these two sets of variables $r/V^{1/3}$ is the more convenient, since both r and V are determined in the experimental procedure, but a is not, and hence must be calculated by methods of approximation, which, however, does not reduce the accuracy with which it may be computed.

Outline of Procedure.

Water and benzene[1] were chosen as the liquids to be used in the standardization; first, because they are easily secured and purified; second, because there is little doubt that the capillary rise method gives accurately their surface tension; and third, because several careful determinations of their surface tension are available for comparison. The surface tension of water and of benzene was determined by using the capillary rise method, and the value of a for each of these liquids was calculated. 28 tips of glass, brass, and monel metal, varying in *radius* from 0.09946 to 1.0028 cm. were carefully prepared. The value of r/a was calculated for each tip when used with water and when used with benzene. The weight of the *ideal* drop corresponding to Tate's law $2\pi r\gamma$ was then calculated for each tip with each liquid. The weight of the drop of benzene and of the drop of water which actually falls from each tip was determined experimentally. The cube root of the volume of this drop was calculated and from this result $r/V^{1/3}$ was determined; and finally $f(r/a)$ and $\psi(r/V^{1/3})$ were calculated by dividing the weight of the drop which actually fell by the weight of the *ideal* drop for the same tip with the same liquid. In Fig. 3 the values of r/a are plotted as abscissae and $f(r/a)$ as ordinates, and graph $r/V^{1/3}$ is plotted against $\psi(r/V^{1/3})$.

Preparation of Substances.

The water was prepared by redistilling distilled water in a copper still with a block tin condenser. The distillation was slow and only about one-half of the steam was condensed, so the steam escaping from the bottle used in collecting the water prevented contamination with dust or gases. Only the middle portion of each run was collected and the containers were resistance glass bottles which had been used exclusively for conductivity water for at least two years.

The benzene was Kahlbaum's best grade. It was treated with conc. sulfuric

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[1] Carbon tetrachloride and ethylene dibromide were used also, and were chosen on account of their high density.

acid until a sample did not darken on standing for 6 weeks in contact with the acid. The acid was neutralized with sodium hydroxide, and the benzene repeatedly washed with conductivity water. After drying over calcium chloride, it was distilled 3 times, and each time the first and last one-tenth of the liquid were rejected. The entire amount saved from the last distillation, about 8 liters, came over between 79.99 and 80.05° (corrected to 76 cm.). This was 3 times fractionally crystallized, each time rejecting the first and last portions. About 6 liters remained, and this was divided in two parts, and the part used in this research was stored in a resistance glass bottle. Into this bottle were dropped sticks of metallic sodium (which had been shaved free from all oxidized surface material) on 4 successive days, and which between shavings, had been immersed in fresh portions of this purest benzene. More than one year from their introduction into the benzene, the sodium sticks retained their metallic luster. It should be noted that this purification of the benzene was unnecessary from the standpoint of the standardization of the drop-weight method, since all that was necessary to secure good results was to use the same sample of benzene in all of the measurements. The purification was of use, however, since we wished to determine the surface tension of *pure* benzene.

The carbon tetrachloride used was made by Kahlbaum. This was washed with water, sulfuric acid, water, sodium hydroxide, and finally, water. It was then dried over calcium chloride and fractionally distilled 3 times. The fraction used in this research distilled over at 75.2°, when the barometric pressure was 74.85 cm.

The ethylene dibromide was Kahlbaum's best grade. It had been carefully purified by Dr. George L. Clark for the determination of its surface tension, and was not purified further.

The Surface Tension of Water and Benzene by the Capillary Height Method.

After examining[1] about 500 feet of capillary tubing, two pieces, each about 20 cm. long were chosen as having practically a constant diameter throughout a length of 10 cm. These tubes were washed with sulfuric acid-dichromate solution, and rinsed carefully. Then they were steamed out by the following method: A glass tube, whose internal diameter was slightly larger than their external diameter, was slightly constricted at one end, and this end inserted through a rubber stopper into a steam can. A capillary tube was inserted in the constricted tube with the capillary tube resting on the constriction. Conductivity water in the steam can was boiled, and the vapor forced through and around the capillary tube for about one hour. The tube was permitted to cool slowly and was then dried by means of washed filtered air. A short column of mercury was then drawn into the tube and its length read by means of the micrometer in several positions, chosen so that almost the entire length of the tube was included. For Tube No. 1, the lengths in cm. were (1.6790, 1.6777),[2] 1.6763, 1.6764, 1.6759, 1.6761, 1.6761 (1.6750, 1.6731, 1.6724). The space on the tube included in the first two, and

[1] This examination and the accompanying measurements took the time of two workers for two months.

[2] The data in parenthesis are for portions of the tube which were not used in the measurements.

last three of the readings was not used in our determinations. The tube, containing this column of mercury, was weighed. Then a column of mercury, which filled almost the entire length of the part of the tube having a uniform cross section, was introduced, and its length was read in three positions. The readings were 7.0473, 7.0473, 7.0470. The tube, with this column of mercury, was then weighed and this last weight, diminished by the weight of the tube and the first column of mercury gives the weight of a column of mercury 5.3713 cm. in length, with the menisci eliminated by the subtraction of the two menisci of the smaller column from the two of the larger column.

This method of eliminating the meniscus was used, because all meniscus corrections, published in the literature, are determined on menisci of vertical columns. The corrections in the two cases may be the same, but the shapes of the menisci are certainly different. When the tube and mercury column are horizontal, the lower side of the column is in contact with the glass, through a greater length than is the upper side; the meniscus shows a nipple-like protrusion[1] at the end; and the upper face of the meniscus is distinctly concave at one point.

The radius of capillary tube (No. 1) was found to be 0.26344 mm. More than a year later, Dr. Davies made an entirely independent series of measurements, and found the radius to be 0.25350 mm. This shows that standing a year after steaming out does not produce an appreciable change of diameter in the capillary tube.

In this laboratory we had been using, for reference level, an outer tube[2] whose diameter was about 10 cm. The capillary was inserted, so that the narrowest dimension of the free surface was more than 6 cm. This seems to be of ample size,[3] but the glass was blown or drawn, and the sides of the apparatus were not necessarily of uniform thickness. Any variation from uniformity in the thickness of glass in this wall, or the wall of the thermostat, would produce a refraction of the light and a consequent error in capillary height reading. To guard against this difficulty, the glass wall of the thermostat was first tested. Two hair lines were ruled on a glass plate by means of a dividing engine. The glass plate was set in a vertical position in air, and the distance between the ruled lines measured with a cathetometer. The ruled glass plate was then transferred to the thermostat and this distance again measured in various parts of the thermostat. The distance between the lines, as measured in air, was 7.3745 cm. A section of glass plate of the thermostat, large enough for our purpose, was found, behind which the distance between the lines, varied only between 7.3720 and 7.3740.

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[1] This protrusion has a definite form for a definite tube only when both the tube and the mercury are very clean.

[2] Harkins and Humphery, THIS JOURNAL, 38, 240 (1916).

[3] Richards and Coombs, *Ibid.*, 37, 1663–5 (1915).

The capillary height apparatus (Fig. 1) was a box with two tubes projecting from the top, with a plate of metal designed to be set horizontally, firmly attached to the last three which was used to support a level. The top, bottom, and two sides of this box were made of *heavily* gold-plated brass; and the other two sides, which were opposite each other, were made of French plate glass, made optically plane by Mr. Petididier and tested for us by Mr. Pearson of the Physics Department. The two lower tubes were closed at the bottom, and two of the upper tubes were directly above them so that a capillary tube[1] inserted into an upper tube, and its corresponding lower tube, would be perpendicular to the horizontal metal plate which carries the level, thus assuring the vertical position of the capillary tubes. The third tube made it possible to increase or decrease the pressure on the reference surface, and thus to elevate or depress the liquid in the capillary tubes.

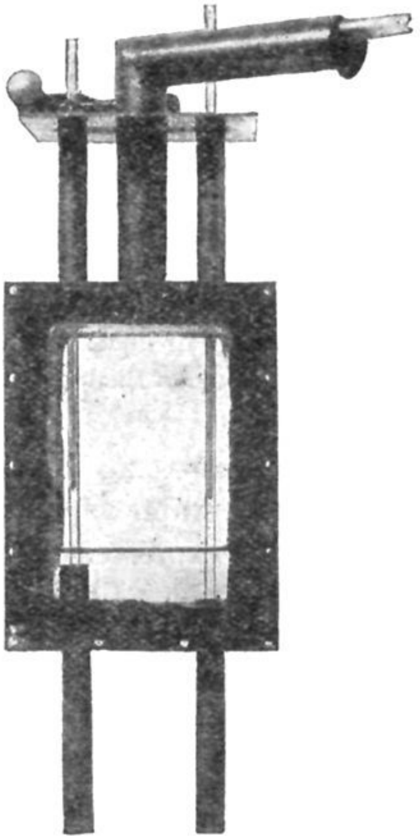

Fig. 1.—Gold-plated capillary height apparatus with faces of optically plane glass.

The Determination of the Surface Tension of Water and Benzene by the Capillary Rise Method.

Four separate determinations of the surface tension of water were made, using three different samples. The box of the capillary height apparatus, which was kept full of conductivity water when not in use, was carefully washed, partly filled with fresh, pure water and mounted in the thermostat at 20°, with the metal plate horizontal. The capillary tubes were cleaned and *steamed* exactly as they had been before being measured. Then each one was dipped into conductivity water, freshly drawn from a supply bottle, the upper opening was closed by pressing a piece of tin foil upon it with the finger, and the tube and water were transferred to the reference level box. By this means the surface tension was determined, using a sample of water which had been in contact with nothing but resistance glass containers and freshly steamed tube. After about 15 minutes a reading was taken. The meniscus was lighted by the method of Richards and Coombs.[2] The heights were read on a cathetometer graduated to

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[1] Each capillary tube was provided with a close fitting gold-plated collar fitting closely into its upper brass tube and another fitting into its lower brass tube, in order to insure a vertical setting of the capillary.

[2] THIS JOURNAL, 37, 1656–76 (1915).

0.02 mm., and 0.01 mm. was estimated. Readings were taken with an alternately rising and falling meniscus. In all about 75 readings were made on each of the two tubes in various positions. The rise for a falling meniscus was always greater than for a rising meniscus in the same sample of water so only the former was measured.

The greatest rise for Tube No. 1, with any sample of water was 5.650 cm. and the smallest was 5.642. The averages for the 4 samples of water are 5.6474 cm., 5.6467 cm., 5.6433 cm., and 5.6440 cm., respectively. The average of these averages is 5.6456 cm. These are all uncorrected for meniscus. The correction for a tube of this size is very close to $^1/_3$ of the radius of the tube. Then, the corrected rise is $5.6456 + {}^1/_3 \times 0.026344 = 5.6544$ cm.[1]

The capillary constant a^2 and surface tension γ of water against air saturated by water vapor were calculated by the formulas $a^2 = rh$, where r and h are expressed in millimeters; and $\gamma = {}^1/_2 a^2(D - d)g$, where *all* linear magnitudes (including a) are in centimeters, D is the density of water at 20°, d is the density of the air saturated with vapor, and g the value of gravity in dynes at the University of Chicago. The results obtained from this tube are

$$a^2 = 14.896 \text{ sq. mm.} = 0.14896 \text{ sq. cm.} \quad \gamma = 72.796 \text{ dynes/cm.}$$

The second tube was calibrated in the same manner as the first and used in the same reference box with the same samples of water at the same time. Its radius was found to be 0.25520 mm.

The greatest rise recorded was 5.836 cm.; the smallest, 5.827 cm.; the averages for the 4 samples of water are 5.8284 cm., 5.8330 cm., 5.8300 cm., 5.8290 cm. The average of these averages is 5.8301 cm. The rise, corrected for the meniscus, is 5.8301 cm. + 0.0085 cm. = 5.8386 cm. so $a^2 = 14.900$ and $\gamma = 72.816$.

Dr. Davies made an entirely independent determination of the values of a^2 and γ for a separate sample of water. His values are

For the first tube.................... $a^2 = 14.894$; $\gamma = 72.783$.
For the second tube................. $a^2 = 14.898$; $\gamma = 72.805$.

The average of all of the determinations made by us is $a^2 = 14.897$ sq. mm., and $\gamma = 72.800$ dynes cm. for water against air saturated with its own vapor and 20°. Richards' value[2] for γ at 20° is 72.62, Domke's is 72.72 and Volkmann's is 72.80.[3]

The surface tension of benzene was determined by the same general method as that employed for water. The tube used was prepared by

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[1] The use of the method of least squares makes no significant change in these results.

[2] THIS JOURNAL, **37**, 1674 (1915). When we used unsteamed tubes our results agreed even more closely with Richards' value, but since the diameters of the tubes did not change this indicates that steaming is essential for the perfect cleaning or removing of the surface of the glass. This is confirmed by the experience of Haber.

[3] See *Abhandlungen der Kaiserlichen Normal Aichung's Kommission*, **3**, **4**, 138 (1902).

carefully cleaning and drying; and then the vapor from boiling benzene was passed through it.

The data for benzene are

Average rise in capillary (corrected for meniscus) = 2.5482 cm.
Radius of capillary.......................... = 0.026344 cm.
a^2 for benzene at 20° against air saturated with benzene vapor.......................... = 6.7131
γ for benzene at 20° against air saturated with benzene vapor.......................... = 28.880

Richards' values[1] for γ at 20° are 28.88 and 28.94.

Drop-Weight Apparatus.

The apparatus (Fig. 2) used for the determination of the drop weight was a modified form of that described by Harkins and Brown.[1] The stoppers on which the Pyrex glass weighing bottles hang should be made of invar (or of glass). The monel metal and also the brass tips, from which the drops of liquid were allowed to fall, were of the interchangeable type. They were turned on a precision lathe, and the lower face was roughened by grinding on a steel block with medium carborundum powder. This roughening is necessary to secure good wetting.

To prepare the *glass tips*, suitable Jena glass capillary tubes were clamped in a high speed precision lathe and rotated. A very fine carborundum disc was also rotated at high speed so that the adjacent edges, the disc, and the tube were moving in opposite directions. Thin layers of the glass tube were ground off until about two centimeters in length at one end was of the diameter desired for the tip. The ground sides were then polished with rouge in oil. A *thick* (2 cm.) cylindrical brass block 10 cm. in diameter, was then perforated with a hole perpendicular to one of its *plane* faces, and of such a diameter that the cylindrically ground end of the tube would fit into it very exactly. The capillary tube was inserted into this hole and cemented in by using a mixture of beeswax and rosin, made up in such proportions as to have a hardness of the proper order to prevent any chipping of the edges of the glass tip. The glass, cement, and brass are ground away together by rubbing the plane face

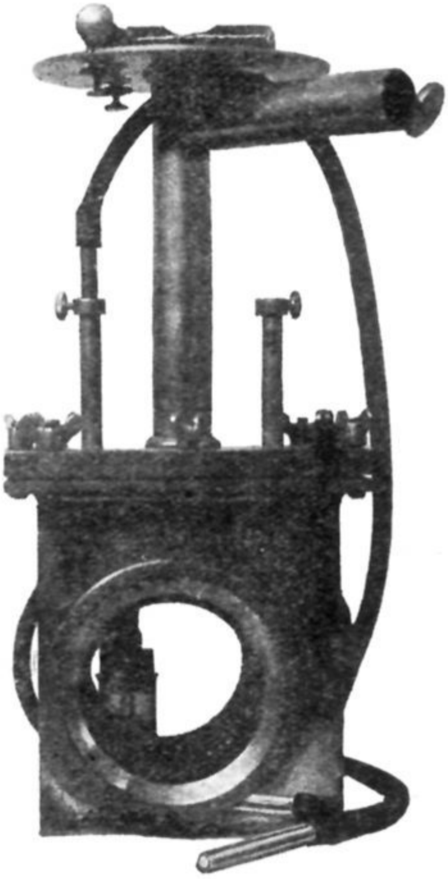

Fig. 2.—Drop-weight apparatus.

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[1] This Journal, 37, 1656–76 (1915).

on a plane steel block covered with fine, wet carborundum powder. Since it is somewhat difficult to determine the proportions for such a mixture of beeswax and rosin, Dr. Davies, working in this laboratory, devised a method of cutting the brass away around the bottom of the tip, and filling the hole thus made with molten Wood's metal, which was allowed to harden around the tip. When an examination with a magnifying glass shows that the surface of the tip is plane and free from flaws and chipped edges, the brass block and tip are placed on a beaker of water and warmed. The cement of the Wood metal melts below the boiling point of water and the tip is easily withdrawn. This method gave tips of excellent quality, such that various diameters of the same tip rarely differed from each other by 0.1%. The ends of the tips were plane, perpendicular to the sides, roughened enough so that liquids wet them readily; and, even under a magnifying glass, the edges of the better tips had NO FLAWS prominent enough to be visible under a magnification of 10 DIAMETERS.

The diameters of the tips were measured with a screw micrometer carrying a microscope which gave a magnification of 10 diameters. One division of the screw head corresponded to 0.0005 cm. and the micrometer readings were corrected by comparison with an invar scale which had been calibrated by the Bureau of Standards. From 5 to 14 readings were made on each of 4 different diameters for each tip. The quality of these tips is indicated by the measurements of Tip No. 1, which was of about the same grade as the others. The circle at the end of this tip was evenly divided by 4 diameters and 11 measurements were made on each diameter. The deviations from the average were: —0.00019 for the first diameter, +0.00010 for the second, +0.00005 for the third, and 0.00004 cm. for the fourth, and the average diameter was found to be 0.19893 cm. The complete set of 44 measurements was repeated the next day, choosing 4 different diameters. The average diameter obtained was 0.19889, so the final value used was 0.19891. This was the smallest glass tip with a circular end we have been able to obtain.

Control of the Drop.

The setting up and leveling of the apparatus and an apparatus for controlling the speed of formation of the drops, has been described in a previous[1] article. This method of controlling the speed of the drop was used in only a small fraction of the runs of this series, because, while it usually insures a slow growth of the drop during the last stages of its formation, the exact speed cannot be measured in any case.

A second method of control was devised, and was used in the greater part of the determinations described in this paper. Gravity alone is allowed to control the formation of the last tenth of the drop. To accomplish this, the level of the liquid in the supply bottle is made just a little

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[1] THIS JOURNAL, 38, 246 (1916).

higher than the level of the tip and by applying suction the drop is drawn over to as nearly full size as is possible without causing the drop to fall under the influence of the suction. How nearly the full size may be approached depends on the skill of the operator. Then the drop is allowed to complete its growth and fall under the influence of gravity. A second drop is allowed to form and fall under the influence of gravity alone. The time between the fall of the first drop and the fall of the second drop, when the whole drop is allowed to fall by gravity alone, is called the drop time. A supply cup 2 to 3 cm. in diameter was used, and the change in the rate of formation of drops during a 30-drop run, was very small. Frequently 3 successive runs were made from one filling of the supply cup, with correspondingly slower rates of formation for the drops of the later runs.

Speed of Formation of the Drop.

When the rate of formation is faster than a drop in 3 minutes, on ordinary sized tips, some of the liquid streaming from the tube seems to force its way into the falling drop during the time of detachment, and consequently, a drop formed rapidly is heavier than one formed slowly. The following series of runs was made by dropping water from a glass tip whose radius was 0.24456 cm.:

Drop time.		Drop weight in grams.
Min.	Sec.	
1	20	0.07191
1	45	0.07187
3	30	0.07179
6	00	0.07172
9	00	0.07174
10	00	0.07175
11	20	0.07173
Slower than 11	00	0.07172

The variation in the weights of the last 5 runs is probably due to experimental errors. The drop weight rises rapidly as the time of formation is reduced below that given in the above table. It will be seen that on a tip of this size three minutes is too short a time for the formation of the proper drop.

Collecting and Weighing the Drops.

In our experiments, before the apparatus was put in the thermostat, the level of the liquid in the supply cup was adjusted so that the drop time was about 5 minutes for small and medium sized drops, and up to 12 and 15 minutes for large drops. The time required for a 30-drop run, when the drop time was 15 minutes, would have been 7.5 hours, had we permitted gravity alone to form the drop. The possible errors due to evaporation would more than compensate for the accuracy gained by slow formation; so the drops were drawn to nearly full size and only the last fraction of each drop formed slowly. The average time required for an experienced operator to draw over and drop 30 drops is 30 minutes. Any form of suction apparatus, which is susceptible to quick and accurate control, can be used, but we found that suction with the mouth was satisfactory. A soda-lime tube was inserted in the rubber tube connecting the dropping cup and the mouth, if danger of contamination was apprehended.

Our method of making a run is: clean, mount and level a tip (see previous paper);[1] adjust the level of the liquid in the supply bottle, so that the drop time is about 5 minutes, force the liquid back through the capillary, so that no drop is on the tip, place a clean weighing bottle on the plug[2] around the dropping tip, adjust the protecting box of the apparatus in the thermostat. In our work, depending on the difference in temperature between the thermostat and the room, a period varying from 15 to 40 minutes was allowed for the liquid to reach the proper temperature. Then the first drop was drawn over, and, by suction or pressure, kept at full size for 5 minutes. The purpose of this was to saturate the space in the dropping cup with vapor, so that the first drop, as well as all others, would fall in its own saturated vapor. 30 drops were drawn successively, to as nearly full size as the operator could judge, and then allowed to detach and fall under the influence of gravity. The residual drop was forced back into the supply cup, the apparatus removed from the thermostat, and finally, the weighing bottle was cooled with ice water for $^1/_2$ minute, to prevent loss of vapor, and then removed from the plug and stoppered; another weighing bottle was put on the plug, the protecting box replaced, and the apparatus again immersed. As the apparatus was out of the thermostat 3 minutes or less, it would return to the desired temperature in a very short time. The bottle and drops were weighed while we were waiting for the apparatus to reach temperature equilibrium. This procedure was repeated for the second weighing bottle and the first weighing bottle was returned to the apparatus for the blank run. The blank run was made exactly like the others, except that the same length of time was taken for dropping 5 drops into the weighing bottle, as had been required to drop 30 drops into the same bottle in the ordinary run. After this run, the second bottle was returned to the apparatus and a blank run made in it. The weight of the bottle and 30 drops, diminished by the weight of the bottle and 5 drops, gives the weight of 25 drops. The distillation from the convex drop to the concave surface in the bottle, the weight of the vapor in the bottle, and all other causes for loss or gain in weight, are nearly the same in both cases, and are approximately

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[1] This Journal, 38, 246 (1916).

[2] This weighing bottle should be so ground to the plug as to give a very tight fit. Otherwise air is drawn through the crevice and this may evaporate some of the liquid which has dropped into the weighing bottle.

eliminated. This differs from Morgan's method of determining the weight of a drop, in only a few particulars.

When work was done under *unfavorable* conditions individual determinations of the weight of the drop falling from a single tip frequently differed among themselves by as much as 0.1%, and this occurred when the room temperature differed from that of the thermostat by more than 5 degrees and the humidity was high. However, no point on the curve was located where any point considered varied from the average more than 0.1%, and in these cases the weight of drop used for the determination was the average weight of one to 20 independent runs. *Most of the work was done under more favorable temperature conditions, and in these cases agreement to a unit in the fourth decimal place of the correction was not uncommon.*

Drop-Weight Corrections.

From the data secured by the capillary rise method the weight of the *ideal drop* ($2\pi r\gamma$) of water and of benzene may be calculated for any tip of known radius. And, since $f(r/a)$ and $\psi(r/V^{1/3})$ are merely the fraction of the *ideal drop* which actually falls, they too can now be calculated as soon as actual falling drops have been weighed. It will be noted that the values of $f(r/a)$ and $\psi(r/V^{1/3})$ for the same drops of liquid falling from the same tip are the same, but that r/a and $(r/V^{1/3})$ have different values.

In obtaining the data for the following tables, the radius of the tip was measured directly, the drops were collected and weighed to determine the weight of the drop, a was determined by the capillary rise of water and of benzene, and r/a was calculated from r and a. The value of $f(r/a)$ and $\psi(r/V^{1/3})$ were found by dividing the weight of the falling drop by the weight of the *ideal drop*. The fraction $r/V^{1/3}$ was calculated from the value of r and the cube root of the volume of the falling drop, and V in turn was found from the weight of the drop and the density of the liquid.

Table I contains data observed and calculated for drops of water falling from glass tips. Table II contains similar data for drops of water falling from brass tips. Table III contains the data for drops of benzene falling from glass tips. Table IV contains, in the first and third columns, Rayleigh's data, as published, for drops of water falling from glass tips and, in the second, fourth, and fifth columns, values derived from the first and third columns, but changed so as to make them as nearly like the data in the other tables as is possible. Even this reduction does not make them completely comparable to those of the other tables, for Rayleigh used glass tips with a large bore and thin walls, while the data in all of the other tables were secured by using tips which were practically discs perforated at the center by a capillary opening.

Table V differs from Table IV only in that the drops of water fell from perforated metal discs instead of thin-walled glass tips. The constants used in calculating Tables IV and V are given with Table VI. Rayleigh's data when obtained by the use of the perforated discs are both more consistent and in better agreement with our curve than his results from the thin-walled tips.

TABLE I.—DROPS OF WATER FROM GLASS TIPS 20°.

(a^2 water = 0.14897 sq. cm.)

Radius of tip. Cm.	Wt. of drop. G.	r/a.	$f(r/a)$ or $\psi(r/V^{1/3})$.	$r/V^{1/3}$.
0.09946	0.03345	0.25770	0.72080	0.30838
0.14769	0.046901	0.38265	0.68076	0.40819
0.19666	0.059700	0.50939	0.65081	0.50253
0.23052	0.068026	0.59728	0.63246	0.56413
0.23790	0.069869	0.61640	0.62944	0.57703
0.26802	0.077553	0.69444	0.62015	0.62787
0.27605	0.079680	0.71525	0.61862	0.64087
0.29423	0.084270	0.76235	0.61383	0.67045
0.29694	0.084880	0.76937	0.61266	0.67500
0.31891	0.090467	0.82630	0.60797	0.70970
0.32362	0.091620	0.83850	0.60676	0.71715
0.34188	0.096392	0.88581	0.60427	0.74491
0.34385	0.096918	0.89092	0.60409	0.74783
0.37964	0.10623	0.98365	0.59971	0.80080
0.39262	0.10966	1.0172	0.59864	0.81944
0.44755	0.12522	1.1596	0.59967	0.89368

TABLE II.—DROPS OF WATER FROM BRASS TIPS 20°.

Radius of tip. Cm.	Wt. of drop. G.	r/a.	$f(r/a)$ or $\psi(r/V^{1/3})$.	$r/V^{1/3}$.
0.13062	0.042347	0.33844	0.69483	0.37437
0.17750	0.054678	0.45990	0.66020	0.46719
0.25135	0.072682	0.65124	0.61974	0.60169
0.35022	0.09868	0.90741	0.60388	0.75712
0.39968	0.11161	1.0356	0.59852	0.82929
0.42765	0.11957	1.1080	0.59924	0.86729
0.44980	0.12575	1.1654	0.59921	0.89690
0.50087	0.14142	1.2977	0.60516	0.96040
0.55009	0.15750	1.4253	0.61381	1.0176
0.59703	0.17403	1.5469	0.62474	1.0658
0.59916	0.17460	1.5524	0.62456	1.0709
0.65031	0.19240	1.6849	0.63411	1.1253
0.69883	0.21083	1.8107	0.64658	1.1730
0.72229	0.22006	1.8714	0.65299	1.1952
0.74784	0.22626	1.9376	0.64843	1.2164
0.74822	0.22881	1.9386	0.65540	1.2221
0.77329	0.23517	2.0036	0.65182	1.2516
0.79915	0.23984	2.0706	0.64321	1.2849
0.84894	0.24617	2.1996	0.62148	1.3532
1.0028[a]	0.2486	2.604	0.5352	1.5992

[a] The tip used for the measurements on this point was made of monel metal and the runs were of only one drop each, and made in open air at 24°, consequently the accuracy of this point is rather uncertain.

TABLE III.—DROPS OF BENZENE FROM GLASS TIPS 20°.
(a^2 benzene = 0.067131 sq. cm.)

Radius of tip. Cm.	Wt. of drop. G.	r/a.	$f(r/a)$ or $\psi(r/V^{1/3})$.	$r/V^{1/3}$.
0.09946	0.012652	0.38380	0.68705[a]	0.40884
0.14769	0.017512	0.56991	0.64040	0.54473
0.19724	0.022413	0.76112	0.61372	0.67009
0.23052	0.025783	0.88955	0.60408	0.74742
0.24456	0.027204	0.94372	0.60078	0.77888
0.26802	0.029742	1.0342	0.59933	0.82859
0.27605	0.030628	1.0652	0.59923	0.84511
0.29694	0.032938	1.1453	0.59910	0.88729
0.31891	0.035502	1.2306	0.60124	0.92943
0.32362	0.036072	1.2488	0.60200	0.93816
0.34188	0.038320	1.3193	0.60548	0.97132
0.34385	0.038606	1.3279	0.60639	0.97450
0.37964	0.043277	1.4650	0.61541	1.0358
0.39262	0.045012	1.5151	0.61919	1.0572

TABLE IV.—DROPS OF WATER FROM GLASS TIPS. (RAYLEIGH.)
γ water 15° = 73.41. a^2 water 15° = 14.985 mm². = 0.14985 cm². $g = 981$. Density of water = g. 99126. Density of (water — air) = 0.9979.

Diam. in inches.[1]	Drop wts. G.	r/a.	$f(r/a)$ or $\psi\, r/V^{1/3}$.	$r/V^{1/3}$.
0.088	0.0375	0.2887	0.7136	0.3338
0.134	0.0526	0.4397	0.6574	0.4542
0.191	0.0712	0.6265	0.6243	0.5851
0.200	0.0755	0.6560	0.6322	0.6008
0.256	0.0923	0.8397	0.6038	0.7192
0.354	0.1151	1.161	0.5448	0.9240
0.383	0.1362	1.256	0.5955	0.9451
0.406	0.1461	1.332	0.6026	0.9787
0.459	0.1703	1.506	0.6213	1.051
0.465	0.1698	1.525	0.6115	1.066
0.521	0.1969	1.709	0.6329	1.137
0.523	0.2023	1.716	0.6478	1.131
0.566	0.2210	1.857	0.6539	1.189
0.584	0.2339	1.916	0.6707	1.203

Fig. 3*a* gives the correction curves plotted from our data, the former with r/a, and with $r/V^{1/3}$, as abscissas. It will be seen that they have almost exactly a form corresponding to a cubic equation. *In this particular the curves do not agree at all with that deduced by Lohnstein:* the left hand branch being almost exactly the same as his curve, *but the right hand branch of an altogether different form.*

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[a] The values of $f(r/a)$ for the first two points are too high, due to the fact that the benzene climbed up the side of the tip. While a means of preventing this might have been found, there was no necessity of so doing, since our results on water determine these values with sufficient accuracy. It is evident that such small tips of this form should not be used for benzene unless the climbing up the side of the tip, which increases the effective tip diameter, is prevented in some way.

[1] While the radii of the tips are given in inches, r in r/a is expressed in centimeters.

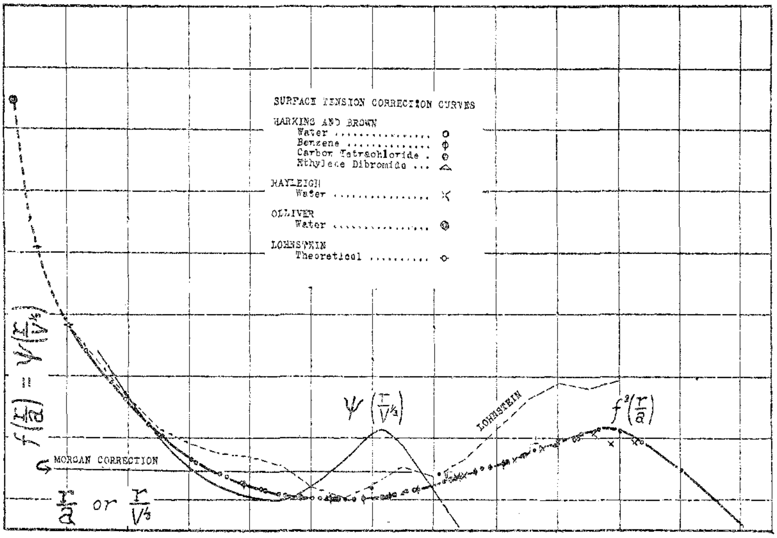

Fig. 3*a*.

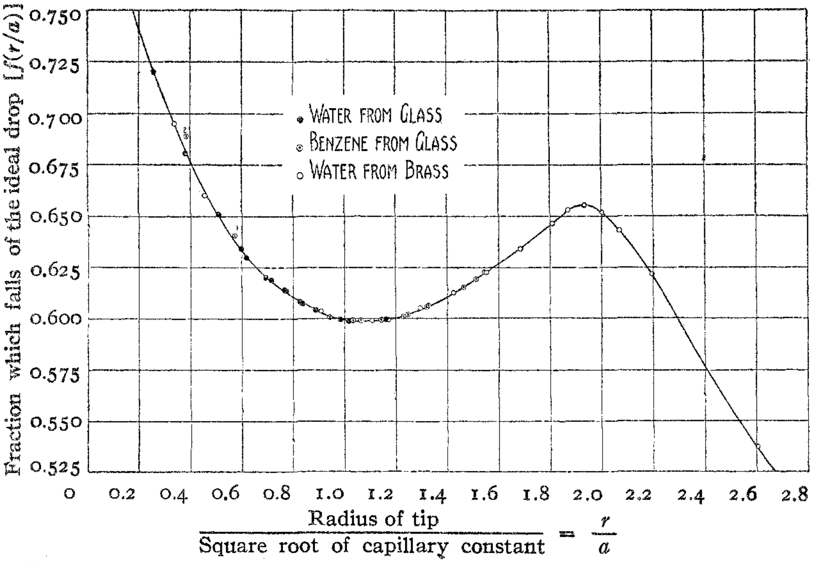

Fig. 3*b*.—Drop-weight correction curve. (Note: Points 1 and 2 do not belong on the curve since the benzene crawled up the side of the tips.)

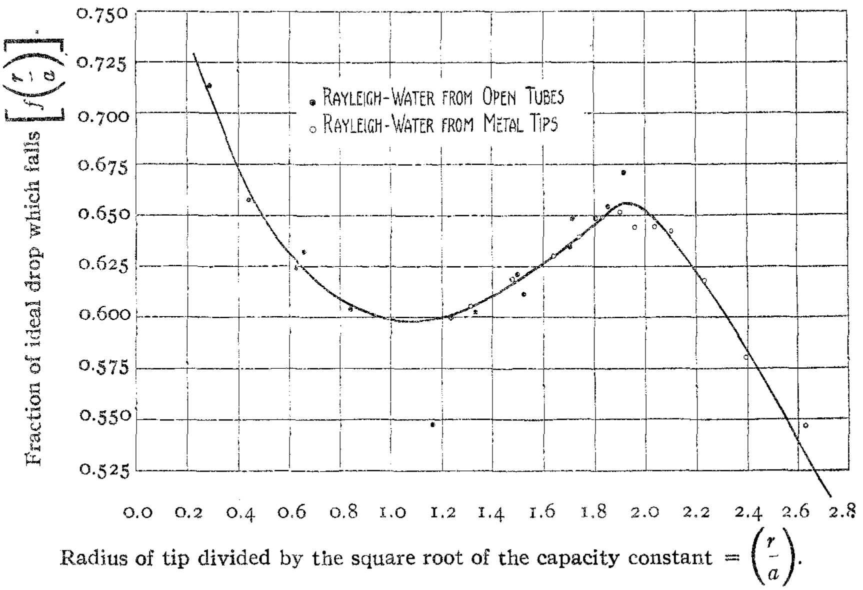

Fig. 4.—Drop-weight correction curve of Harkins and Brown with Rayleigh's data to illustrate the disadvantages in the use of open thin-walled tubes.

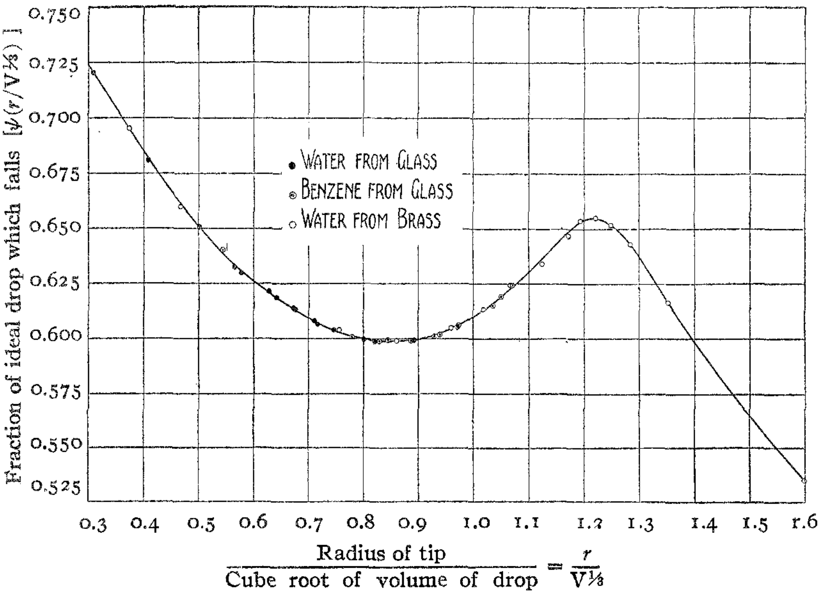

Fig. 5.—Drop-weight corrections. (Note: Point 1 does not belong on the curve since the benzene crawled up the side of the tip.)

TABLE V.—WATER FROM METAL TIPS. (RAYLEIGH.)

Diam. in inches.	Drop wts. G.	r/a.	$f(r/a)$ or $\psi\ (r/V^{1/3})$.	$r/V^{1/3}$.
0.400	0.1446	1.312	0.6054	0.9672
0.450	0.1662	1.476	0.6185	1.039
0.500	0.1882	1.640	0.6304	1.107
0.530	0.2023	1.739	0.6392	1.145
0.550	0.2130	1.804	0.6486	1.169
0.559	0.2167	1.834	0.6492	1.181
0.580	0.2256	1.903	0.6514	1.209
0.597	0.2295	1.959	0.6438	1.238
0.621	0.2389	2.037	0.6443	1.270
0.640	0.2454	2.100	0.6421	1.299
0.680	0.2510	2.231	0.6182	1.368
0.730	0.2531	2.395	0.5806	1.465
0.800	0.2509	2.625	0.5470	1.605

Effects of Density and Viscosity.

To test the effects on the correction curve of differences of density and viscosity the work already carried out on water and benzene was extended to carbon tetrachloride ($d_{20°} = 1.590$) and to ethylene dibromide ($d_{20°} = 2.178$). The data for these liquids are given in Tables VI and VII. When the results for these liquids of high density are plotted they are found to lie on the same curves as those given for water and benzene. The more accurate part of the work on *interfacial tension* also gives points lying on these curves, and the inaccuracies in a part of the interfacial work are found to be due, as was at first suspected, to errors

TABLE VI.—DROPS OF CARBON TETRACHLORIDE FROM GLASS TIPS, 20° C.

Radius of tip. Cm.	Wt. of drop. G.	r/a.	$f(r/a)$ or $\psi(r/V^{1/3})$.	$r/V^{1/3}$.
0.1476	0.015526	0.79733	0.61452	0.68793
0.19724	0.020153	1.0655	0.59709	0.84613
0.23052	0.023735	1.2453	0.60151	0.93642
0.24456	0.025388	1.3211	0.60646	0.97140
0.26802	0.028129	1.4478	0.62313	1.0288
0.29694	0.031898	1.6041	0.62742	1.0930
0.31891	0.034870	1.7228	0.63877	1.1396
0.34188	0.037872	1.8468	0.64730	1.1885
0.34385	0.038036	1.8575	0.64622	1.1936

TABLE VII.—DROPS OF ETHYLENE DIBROMIDE FROM GLASS TIPS, 20° C.

Radius of tip. Cm.	Wt. of drop. G.	r/a.	$f(r/a)$ or $\psi(r/V^{1/3})$.	$r/V^{1/3}$.
0.19724	0.029344	1.0353	0.59930	0.82895
0.23052	0.034369	1.2100	0.60059	0.91909
0.24456	0.036672	1.2831	0.60405	0.95422
0.29694	0.045970	1.5586	0.62363	1.0745
0.31891	0.050128	1.6740	0.63319	1.1215
0.34188	0.054504	1.7945	0.64221	1.1689
0.34385	0.054844	1.8049	0.64151	1.1759

in the capillary height results due to the angle of contact being greater than zero when dense salt solutions were used.

Over this wide range of variation in the liquids and in the methods, the drop-weight method, therefore, gives results independent of changes in the density and viscosity of the liquids employed. We have not tested the method by the use of very viscous liquids, for it is improbable that any method can be found which will give accurate values for liquids of this class, though the drop-weight method may be employed with such liquids when the capillary height method becomes altogether inapplicable.

The apparent variation from the curve of points 1 and 2 for benzene is due to the creeping of liquid up the smooth walls of the tips, and occurs only with very small tips. On this account tips of less than 1.5 mm. radius should not be used for benzene, though smaller tips may be used for water. No one size of tip will give the *most* accurate results in all cases, though a tip of from 5 to 7 mm. diameter gives good results with most liquids alone, while a diameter of 9 to 11 mm. has proved to be useful in much interfacial work. Measurements on interfacial tension require a wider range of tip diameters than work at the surface of a single liquid. *The curves presented in the paper, however, greatly reduce the number of tips necessary for good drop-weight work over a wide range.* For accurate work it is best to have tips of such a size that r/a lies between 0.60 and 1.3, and preferably between 0.9 and 1.2 to give the most accurate results, at least where the surface tension of a single liquid is desired.

Tips for liquids of high density, such as mercury or even ethylene dibromide, should in general be considerably smaller than those for liquids of relatively low density. In interfacial work in special cases the difference between the densities of the two phases may be very small, and this, especially when the interfacial tension is high, makes the use of large tips advisable. Such a case is that of a water phase ($d_{20^\circ} = 0.99715$) and an anisol phase ($d_{20^\circ} = 0.99270$). This gave *13.688* cm. as the volume of *one drop.* Here a tip of 9.5 mm. diameter gave satisfactory results, although a larger one could have been used.

When the values of r/a from Tables I, II, and III were plotted against the corresponding values of $f(r/a)$ it was noticed, as has been stated, that the points so located fall on or near the graph of a cubic equation. When the *differences* between the ordinates of a cubic equation and the ordinates of the corresponding points located by the data from Tables I, II, and III, were plotted against the values of r/a, and a line was drawn through the points so located, a fairly smooth curve resulted. Assuming that the ordinates of this smoothed curve represent the corrections which should be applied to a cubic equation the following values of $f(r/a)$ were calculated for the corresponding values of r/a (Table VIII):

TABLE VIII.—SMOOTHED VALUES RECOMMENDED FOR CORRECTIONS.
[Factors for division = $f(r/a)$.]

Point No.	r/a.	$f(r/a)$.
1	0.0	(1.000)
2	0.025	0.924
3	0.1	0.805
4	0.2	0.741
5	0.30	0.7050
6	0.35	0.6901
7	0.40	0.6762
8	0.45	0.6634
9	0.50	0.6519
10	0.55	0.6417
11	0.60	0.6328
12	0.65	0.6253
13	0.70	0.6198
14	0.75	0.6147
15	0.80	0.6102
16	0.85	0.6065
17	0.90	0.6036
18	0.95	0.6013
19	1.00	0.5997
20	1.05	0.5988
21	1.10	0.5987
22	1.15	0.5992
23	1.20	0.6003
24	1.25	0.6003
25	1.30	0.6048
26	1.35	0.6081
27	1.40	0.6116
28	1.45	0.6156
29	1.50	0.6198
30	1.55	0.6241
31	1.60	0.6281
32	1.65	0.6323
33	1.70	0.6368
34	1.75	0.6412
35	1.80	0.6460
36	1.85	(0.6510)
37	1.90	(0.6550)
38	1.95	(0.6550)
39	2.00	(0.6520)
40	2.05	(0.6470)
41	2.10	(0.6390)
42	2.15	(0.6300)
43	2.20	(0.6220)

1. The value of a in r/a must be given in terms of the same unit as is used for r, which should be expressed in centimeters. The values for $f(r/a)$ for Points 1, 3 and 4, are those calculated from Lohnstein's theory,[1] while that for Point 2 was calculated from the experimental results of Olliver.[2] The values for Points 5 to 43 have been calculated from our own experimental results. The fact that the experimental values vary from 0.5987 to 0.924 is a sufficient indication that Tate's law is incorrect. While Table VIII makes it possible to determine the surface tension of a liquid using a tip of almost any diameter for which the *tip wets properly*, it is probable that the most accurate results will be obtained where the slope of the curve is not too great, as between the values 0.6 and 1.2. The size of tip to be used for liquids of different densities may be found in Tables I to VII. The values in parentheses are considerably less accurate than the others, and are added only for comparison.

Table IX gives the values of the correction $\psi(r/V^{1/3})$ for values of $r/V^{1/3}$ which differs by 0.05. This table was obtained by the same general method of calculation as was used for Table VIII, except that the smoothing by means of a cubic equation was omitted. While not quite so accurate as Table VIII, it is sufficiently exact for almost all practical purposes, and has the advantage that $V^{1/3}$ may be easily calculated from

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[1] That $f(r/a)$ and $\psi(r/V^{1/3})$ approach 1.000 as a limit when r/a or $r/V^{1/3}$ approaches zero, is a doubtful point in this theory.

[2] *Ann. de chim. phys.*, [8] 11, 229–289 (1907).

the volume of the drop M/D, while a in Table VIII must be obtained by a method of approximation. The equations to be used in calculating by means of this table are either

$$\gamma = Mg/2\pi r\psi(r/V^{1/3})$$

or

$$\gamma = (Mg/2\pi r)\phi.$$

Since $f(r/a)$ is always equal to $\psi(r/V^{1/3})$ for any special drops it is only necessary to know the relation between r/a and $r/V^{1/3}$ in order to shift from the use of Table IX to that of Table VIII, or *vice versa*. This relation is discussed by Professor Lunn in the note which follows this paper, and may be expressed

$$(r/a)^2 = \pi(r/V^{1/3})^3.\psi(r/V^{1/3})$$

so

$$r/V^{1/3} = [(r/a)^2/\pi.\psi(r/V^{1/3})]^{1/3}$$

or

$$r/a = [\pi(r/V^{1/3})^3.\psi(r/V^{1/3})]^{1/2}.$$

TABLE IX.—DROP-WEIGHT SURFACE TENSION CORRECTIONS WHICH MAY BE USED DIRECTLY WITHOUT THE NECESSITY OF EMPLOYING APPROXIMATION METHODS.[1]

[Factors for division = $\psi(r/a^{1/3})$ factors for multiplication = ϕ.]

$r/V^{1/3}$.	$\psi(r/V^{1/3})$.	ϕ.
0.00	(1.0000)	(1.0000)
0.30	0.7256	1.3780
0.35	0.7011	1.4263
0.40	0.6828	1.4645
0.45	0.6669	1.4994
0.50	0.6515	1.5349
0.55	0.6362	1.5718
0.60	0.6250	1.6000
0.65	0.6171	1.6205
0.70	0.6093	1.6412
0.75	0.6032	1.6578
0.80	0.6000	1.6667
0.85	0.5992	1.6688
0.90	0.5998	1.6672
0.95	0.6034	1.6572
1.00	0.6098	1.6398
1.05	0.6179	1.6183
1.10	0.6280	1.5923
1.15	0.6407	1.5608
1.20	0.6535	1.5302
1.225	(0.6555)	(1.5255)
1.25	(0.6521)	(1.5335)
1.30	(0.6401)	(1.5622)
1.35	(0.6230)	(1.6051)
1.40	(0.6033)	(1.6575)
1.45	(0.5847)	(1.7102)
1.50	(0.5673)	(1.7627)
1.55	(0.5511)	(1.8145)
1.60	(0.5352)	(1.8684)

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[1] For single liquids it is usually best to use tips such that $r/V^{1/3}$ lies between 0.759 and 0.95.

The Calculation of Surface Tension from the Weight of a Drop.

From the mass of the drop and the density of the liquid, the volume is given by the equation $V = M/D$, and from this the value of $r/V^{1/3}$ may easily be calculated, and the corresponding value of $\psi(r/V^{1/3})$ obtained from Table IX. Then

$$\gamma = M'g/2\pi r\psi(r/V^{1/3}). \qquad (1)$$

Here M' is the weight in grams of the drop obtained by weighing in air, or the apparent weight of the drop in air. When the drop is allowed to fall into a gas or vapor other than air, or into a second liquid, the true weights should be used in the equation

$$\gamma = (M - m)g/2\pi r\psi(r/V^{1/3}), \qquad (2)$$

where m is the weight in grams of a volume of the lighter phase equal to the volume of the drop. While the results obtained in this way are sufficiently accurate for almost all practical purposes, the values of $f(r/a)$ in Table VIII have been more carefully smoothed than those given for $\psi(r/V^{1/3})$ in Table IX. If, therefore, the *highest* accuracy is desired, Table VIII may be used if it is remembered that for any special drop $\psi(r/V^{1/3})$ and $f(r/a)$ are equal. This value of $f(r/a)$ may be substituted in Equation (3)

$$a^2 = M'/\pi r D'f(r/a) = (M - m)/\pi r(D - d)f(r/a) = V/\pi r f(r/a) \qquad (3)$$

and from this a may be obtained, the value of r/a calculated,[1] and the corresponding value of $f(r/a)$ found from Table VIII by linear interpolation. When successive values of $f(r/a)$ obtained in this way are identical, the final value of the surface tension may be calculated using in Equation 1 or 2 the value of $f(r/a)$ thus found in place of that for $\psi(r/V^{1/3})$ which was found more directly but is not so exact.[2]

Summary and Conclusions.

1. The two methods most commonly used for determining surface tension are the capillary rise method and the drop weight method. The theory of the former is simple but its technique is difficult, and its use in some cases is the cause of errors as high as 30%, due to its inapplicability

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[1] The value of r/a found should agree with moderate exactness with that found from the relation

$$r/a = [\pi(r/V^{1/3})^3.\psi(r/V^{1/3})]^{1/2}.$$

[2] The following equations are the basis of this calculation:

$$a^2 = hr \qquad (4)$$

$$\gamma = {}^1/_2\, hr\, D'g = {}^1/_2\, hr\, (D - d)\, g \qquad (5)$$

$$= {}^1/_2\, a^2 D'g = a^2/2\, (D - d)\, g \qquad (6)$$

$$a^2 = 2\gamma/D'g \qquad (7)$$

Here contrary to custom, a^2 is to be expressed in sq. cm. The a^2 found in the literature is expressed in sq. mm. Therefore the a^2 used in this paper has $^1/_{100}$ of the numerical value of the a^2 (sq. mm.) usually used, so the a used here has $^1/_{10}$ the value of that usually employed. This is done since the r in the surface tension formula is given in centimeters.

to certain classes of substances. The drop-weight method is applicable to a wide range of liquids and the experimental work is not difficult, but the theory of this method has not been completely worked out, so many of its results as published, are poor while experimentally accurate, on account of the use of an improper theory.

2. In this paper the relation of the experimental results of the drop-weight method to those obtained by the capillary rise method, has been determined by using liquids which give accurate results by either method, and this relation has been plotted in such a way as to show the relation between surface tension and the form of the drop which falls from a circular tip.

3. The surface tension and capillary constant of water and of benzene at 20°, each against air saturated with its own vapor, were very carefully determined by the capillary rise method. The values for water are

$$\gamma = 72.800 \text{ dynes/cm.}; \; a^2 = 14.897 \text{ sq. mm.}$$

for benzene:

$$\gamma = 28.80 \text{ dynes/cm.}; \; a^2 = 6.713 \text{ sq. mm.}$$

One of the features of this work was the steaming out of the tubes with the vapor of the substance. This increased the value of γ for water by about 0.1 dyne.

4. Water, benzene, carbon tetrachloride, and ethylene dibromide were dropped from a large number of tips of glass and of metal with radii varying from 0.09946 cm. to 1.0028 cm. and the weights of the falling drops determined.

5. From these data r/a and the corresponding values of $f(r/a)$ for the Lohnstein equation $Mg = 2\pi r\gamma f(r/a)$ were calculated for values of r/a between 0.25 and 2.60. The value of $f(r/a)$ is not a constant but varies from 0.7256 to 0.5352 in this range, while when r/a falls to 0.025, $f(r/a)$ rises to 0.924.

6. It was assumed that in conjunction with other necessary conditions r/a really determines the shape of a hanging drop and that it is the shape of the drop which determines the fraction of the drop which falls. This shape may also be determined by the ratio of r to the cube root of the volume of the falling drop. Thus a new equation, similar to that of Lohnstein, was derived.

$$Mg = 2\pi r\gamma\psi(r/V^{1/3}).$$

This is more easily applied to the determination of surface tension than Lohnstein's equation since all of the factors except γ are obtained by direct experiment or by reference to a table of values, while the a of Lohnstein's equation cannot be obtained from the direct results of the drop-weight measurements, but must be calculated by methods of approximation.

7. Graphs of results and tables to be used in the calculation for γ by the drop-weight method are given.

8. It was found that variations in density over a wide range and in viscosity over a moderate range, did not appreciably affect the results obtained for the surface tension of liquids by the drop-weight method.

9. The weight of a drop varies rapidly with its time of detachment. In general the natural period of fall of a drop should be 5 minutes or more, if the weight is to be used for the determination of surface tension. If dilute aqueous solutions of long chain organic molecules are used, it is often necessary to let the drop hang at almost full size for a half hour or more in order to obtain the static surface tension of the solution. However, in most cases accurate work takes very little more time than the attempts at measurement made with the ordinary form of stalagmometer.

10. Rayleigh's results show that open, thin walled tubes when used as tips do not give such accurate results as heavy walled capillary tips or perforated discs.

11. The results obtained in this investigation increase the accuracy of the drop-weight method by about 4%, so that now its precision is approximately of the order of one-tenth of one per cent. when used within the range of values of r/a, density, difference of density, and viscosity, where the most accurate determination of the constants has been made, provided the assumption is correct that thoroughly cleaned and steamed capillary tubes of good soft glass give a zero contact angle with water, or with benzene. The fact that water and benzene give exactly the same drop-weight correction curve, is a support to this assumption, since it indicates that the contact angles of water and of benzene are so nearly the same that resulting differences of capillary height could not be detected in this work. It is often assumed that since several experiments on the same liquid by the drop-weight method may be made to agree within a few hundredths of a per cent., that this is an indication that the results calculated from the work give the surface tension with the same accuracy, in spite of the fact that nearly all of such data given in the literature are 3% or more too low. The largest error has crept in by the general adoption of the low values for surface tension obtained by the capillary height method, though in some sets of data the assumption that Tate's law holds causes as large or even a larger deviation from the true values.

12. A source of error which is important in all drop-weight work, and which is a source of even more discrepancy in results obtained by methods involving the pressure volume, or buoyancy of a bubble of gas in the liquid, is that due to a lack of *sharpness*, or to the departure from the circular shape of the tip. It is believed that this source of error has been avoided in this work, since all of the tips used were made under our own

supervision and were very sharp. Though all of the tips which we purchased, about 15 in number, appeared to the eye to be as good as those prepared in our own shops, they were found to show a slightly beveled or somewhat ragged edge. This introduces two serious errors: one in the measurement of the tip, and another even more important, in the fact that the edge is indefinite, and it is not known to what part of the edge the wetting occurs. The indefiniteness of measurement is of import, since a direct measurement of the tip diameter is more precise than testing its diameter by the weight of the drop which falls from it. *Errors due to lack of sharpness*, or to errors in the measurement of the diameter of the tip, *become more important as the tip decreases in radius.* This is the reason they enter so largely into work done by the methods based on pressure in a bubble of gas (Jaeger's method and similar methods), since the tips used for such work have a very small diameter. An error of 0.005 mm. in the radius of a one mm. tip causes a discrepancy in the surface tension of half of one per cent. The "indefiniteness" of wetting is often much greater than this with tips of ordinary grade.

13. Possibly the most common error in the use of the drop-weight method is that expressed in a large number of papers in statements which involve the assumption that while a comparison of the weights of the drops (or of the drop number) obtained in different experiments may not give the correct absolute value of the surface tension, its use in that particular paper is justified since "only the relative values are desired." This, unfortunately, is just what such comparisons of the drop weights do not give, except in such instances as have occurred when the investigator by *accident* has used liquids of such a surface tension and density, and tips of such a size, as to cause all of the values of r/a to be within the narrow limits where the correction curve is practically horizontal. The error introduced in this way is often as high as 10 or 15% in work at the interface between two liquids, it may rise as high as 10% at the liquid-vapor interface when solutions of organic substances are used, but is usually considerably less than this when the surface tension of a pure liquid is measured. When such papers are published, the diameter of the tip used should always be given, since otherwise it is usually impossible to estimate the magnitude of the errors, which may in exceptional cases rise as high as 30%. If the diameter of the tip is not known it may even be measured in a rough way by a micrometer gage, or the drop weight of some well known pure liquid may be given.

14. The drop-weight correction curves found by us have a form represented by a cubic equation; the right hand branch of the curve has thus an entirely different form from that found by Lohnstein. This is one of the most important of the results obtained.

15. While the data of this paper indicate that in the determination of

the surface tension of a single liquid, only the difference in density between the two fluids (liquid and vapor), and not the ratio of the two, appears, the relations might well be different at the interface between two liquids, where the density of the lighter phase becomes relatively more important. All that can now be said in this connection is that the work of Harkins and Humphery indicates that for values of r/a between 0.5 and 0.7, and of $r/V^{1/3}$ between 0.5 and 0.65, the most convenient range for the measurement of the interfacial tension of water and liquids lighter than water, the interfacial correction curve is practically identical with that presented in this paper. Whether further work over a larger range will show that the densities of the liquids enter as two variables instead of as one, is not yet known, but is under investigation in this laboratory. Even with our present knowledge the drop-weight method is undoubtedly the most accurate and the most convenient of those now in use for the determination of interfacial tension, where the principal defect of the capillary height method, the uncertainty as to the angle of contact, becomes more apparent. The corrections presented in this paper should be used in works in interfacial tension, in the place of those given by Harkins and Humphery.

16. It has recently been suggested to one of the writers that by bubbling air upward through a liquid the surface tension might be determined without the use of our factors of correction, but they are involved by a bubble-volume method, the principal difference being that in the application of such a method the diameter of the tip is made small, to prevent the liquid from running down into it, so the value of r/a is small. While this has the apparent advantage that the correction factor $f(r/a)$ or $\psi(r/V^{1/3})$ comes much closer to the value one, it has the much greater disadvantage that the slope of the correction curve becomes at the same time considerable, thus introducing a greater uncertainty as to the exact correction to be applied.

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CHICAGO, ILLINOIS.

THE DETERMINATION OF NITROUS ACID AND NITRITES.

BY J. S. LAIRD AND T. C. SIMPSON.

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In a recent article by Fox[1] entitled "The Chemical Control of Ammonia Oxidation," there is advocated the use of an alkaline solution of hydrogen peroxide as a reagent for the absorption and determination of nitrous gases, the excess of standard peroxide being titrated with potas-

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[1] Fox, *J. Ind. Eng. Chem.*, 9, 737–43 (1917).