In the first place, Dr. Dehn makes a statement that is absolutely untrue and to which I give unhesitating and categorical denial. He says that I devote more than half of my reply to "discussing new physical data not published by him (Baly) when his theory appeared in THIS JOURNAL." These data were published in the *Philosophical Magazine* many months before the paper under discussion.[1] Dr. Dehn's accusation is all the more strange in view of the fact that he includes these two papers in his list of my publications.

In the second place, referring to the changes in absorption with concentration, Dr. Dehn makes the surprising statement that "we must assume not only an infinite series of absorption curves but an infinite series of reactivities. * * * * * These results of course are contrary to fact *as acknowledged by Baly in his reply*." I pointed out in my first reply that Dr. Dehn had got very mixed in his ideas as regards the effect of concentration and by the misuse of the word "band" where "band group" is meant. I said that his criticism therefore falls to the ground and that his statement is absurd. The only notice he takes of this is to add the words which I have italicized above. I am accused of a great sense of humor by Dr. Dehn, but I am sadly afraid that it is not as great as his.

In the third place, the new paragraph added by Dr. Dehn beginning "There can be no quibble that Baly believes, etc.," and indeed also the succeeding paragraphs reveal such a serious number of misconceptions and misconstructions, which I can no longer believe to be withour prejudice, that further discussion has become valueless.

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

THE DROP WEIGHT METHOD FOR THE DETERMINATION OF SURFACE TENSION.[2]

(SURFACE TENSION I.)

BY WILLIAM D. HARKINS AND E. C. HUMPHERY.[3]

Received October 22, 1915.

The two methods in most general use for the determination of the capillary constants of liquids are the capillary tube and the drop weight methods. Of these two, the first is much the more sensitive to the action of impurities, since the surface of the liquid involved in the measurement is made very small, while in the drop weight method the surface is not

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[1] *Phil. Mag.*, **27**, 632 (1914), and **29**, 223 (1915).

[2] Read before the National Academy of Sciences, December 7, 1914.

[3] This series of papers on surface tension has been presented to the University of Chicago by E. C. Humphery as a dissertation in part fulfilment of the requirements for the degree of Doctor of Philosophy.

only made relatively large but it is also renewed much more easily. It is not surprising, therefore, that the most concordant results on the surface tension of a single liquid are obtained by the drop weight method, and that duplicates run by this method, when it is properly applied, show a most remarkable agreement. However, when the results obtained by different workers on different liquids by this method are compared with determinations made by other methods, it is found that they show just as remarkable a disagreement, the deviation in some cases rising to 20%, or even 40%. These very bad results are due however, not to any inherent fault in the method, but to the application of a very faulty theory. Thus many workers have used the equation

$$W = 2\pi r\alpha, \tag{1}$$

where W is the weight of the drop, r the radius of the tip of the dropping tube, and α the surface tension. This equation would be true only when the pendant drop is supported entirely by the surface tension of the surface film at the edge of the tip, and when all of the pendant drop falls, but this is very far from the truth, for the drop which falls is nowhere nearly all of the pendant drop.

The most complete treatment of the mathematical theory of the relation between the forms of drops and surface tension is given in a book published in 1883 by Bashforth and Adams.[1] Much later than this, in 1906, Lohnstein[2] applied the general theory to the special case of the hanging drop just before its fall, and the residue left after the fall, and from the difference he obtained the magnitude of the falling drop itself. By doing this he was able to reduce the problem, which would otherwise be of a kinetic form, to the solution of problems in statics. In solving the problem it was necessary for Lohnstein to make an assumption in regard to a relationship between the form of the drop just before it falls, and that of the residual drop left immediately after the fall. The cross sections of the drop as it increases in size give a family of curves which have different values of a variable parameter. Two values of this parameter give two curves which have the same tangent at the point of contact with the tip. Lohnstein assumed that the drop which remained after the fall had a cross section which gave a curve with the same angle of contact with the tip as the drop just before it fell. In calculating the size of the falling drop, then, he subtracted the volume of the drop with the parameter p from the volume of the drop with the parameter p', where the two curves, due to these different parameters, have the same tangent at the point in which the drop meets the tip. The curve with the parameter p' gives the form of the drop before the fall, and the curve with the parameter p gives the form of the drop remaining after the fall.

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[1] "Capillary Action," Cambridge University Press (1883).

[2] *Ann. Physik*, [4] 20, 237–68, 606–18(1906); *Z. physik. Chem.*, **64**, 686 (1908); **84**, 410 (1913.)

The equation obtained by Lohnstein for the weight of the falling drop is

$$W = 2\pi r \alpha f(r/a), \qquad (2)$$

where r is the radius of the tip and a is the square root of the capillary constant, and $f(r/a)$ represents a function of r/a. The surface tension is given by the equation

$$\alpha = W/2\pi r f(r/a), \qquad (3)$$

and since $f(r/a)$ varies from 1.0 to 0.6, it is evident that results obtained by the older equation (1) may be increased by as much as 65% by the application of this correction. Lohnstein determined the values of the function of r/a for different values of r/a, and his calculation of these corrections from a theoretical standpoint makes it possible to use the drop weight method for the determination of surface tension, and, since, as has been stated, this is the most exact from an experimental standpoint of the methods used in work on capillarity, Lohnstein's work represents a great advance in our knowledge of this fundamental subject.

Unfortunately, however, when it becomes desirable to determine the surface tension by this method, it is found that Lohnstein did not carry his calculations of these corrections to a sufficient degree of accuracy to make this method available for determinations where an accuracy greater than 4% is desired. It is therefore important that this correction, which is a very fundamental one in work on capillarity, should be determined with a greater degree of accuracy. For this purpose the apparatus devised by the writers[1] seemed to make it possible to make determinations of this correction under conditions which are more nearly ideal than is possible by the ordinary methods. Thus the substitution of work on the liquid-liquid interface for the ordinary method in which a liquid-air interface is used makes it possible to compare the drop weight results with those obtained in a capillary tube of large bore (1.4 mm.) when the capillary rise is great enough (78.0 mm.) to give accurate measurements. Not only can the diameter of the large capillary be determined more accurately than that of the smaller tube used for measurements on a single liquid, but in addition it is much easier in the large tube to keep the surface of the meniscus in a pure condition. Then in the drop weight determination itself, the drop falls very much more slowly when it falls into a liquid than when it falls into a gas, so that there is less disturbance in the drop at the time of fall than when it breaks away at a relatively high speed. The corrections determined in this way are given in Table I, and are shown in the form of a curve in Fig. 1. In the figure the ordinates represent the values of the function of r/a, and the abscissae give the values of r/a. The circles which are inked in represent Lohnstein's theoretically determined values, while the circles given in outline give the new

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[1] Described in the paper which follows.

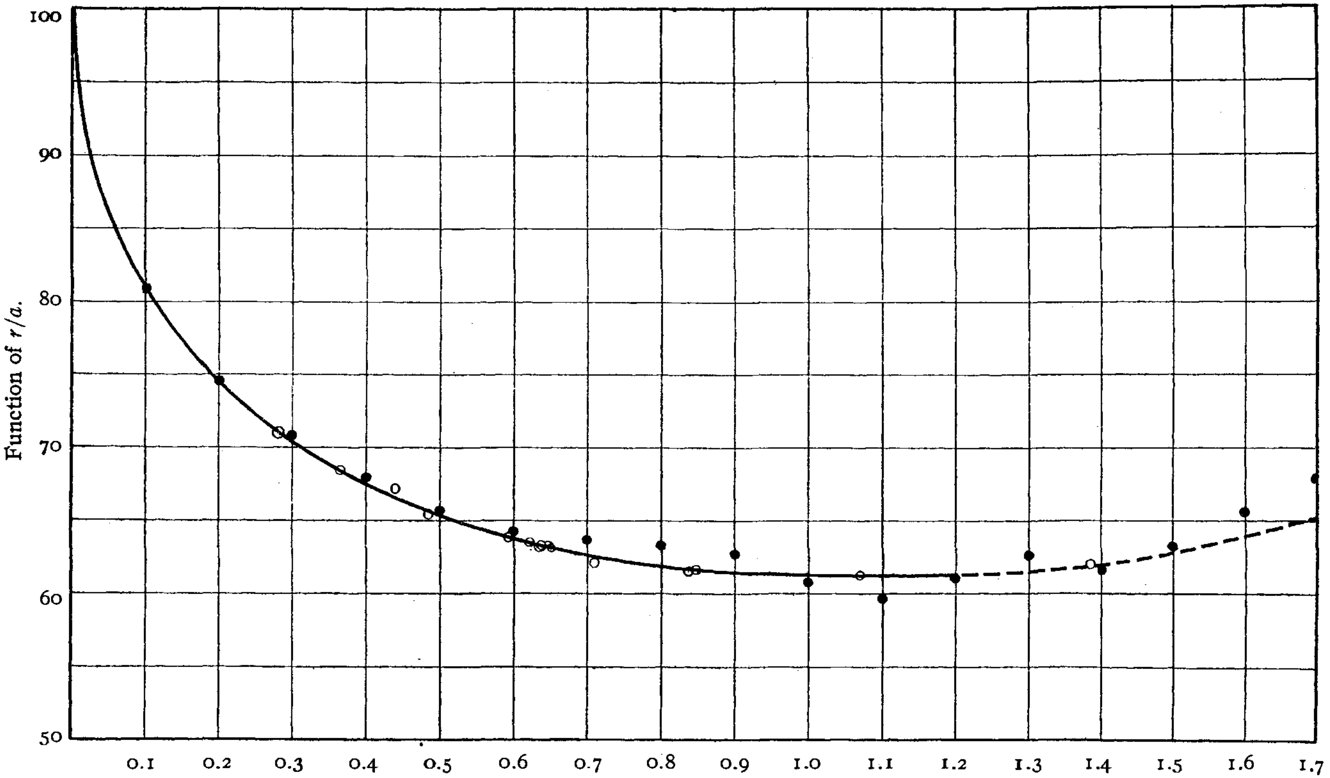

Fig. 1.—Experimental determination of the corrections for the drop-weight method of determining surface tension. Preliminary determination accurate between $r/a = 0.3$ and $r/a = 0.7$. Experimental values = circles in outline. Lohnstein's values = circles inked in.

values determined experimentally. The figure shows that the experimental values give with Lohnstein's first two points for small values of r/a, a much smoother curve than is given by his own theoretical values. The experimental values were determined by the use of a number of different liquids, and measurements were made both upon liquid interfaces, and at the surface of a single liquid. Table II gives a list of the corrections for round values of r/a.

TABLE I.—EXPERIMENTAL CORRECTION FOR DROP WEIGHTS.

Point No.	r/a.	$f(r/a)$.	Interface.	Temperature.
1	0.281	0.709	Water—Ethyl carbonate	(25°)
2	0.366	0.685	Water—Benzene S. T.	(25°)
3	0.441	0.672	Water—Dimethylaniline	(25°)
4	0.484	0.654	Water—$EtCO_3$	(25°)
5	0.592	0.639	Water—Benzene	(10°)
6	0.621	0.636	Water—Benzene	(20°)
7	0.633	0.632	Water—Xylene	(25°)
8	0.636	0.634	Water—Benzene	(25°)
9	0.648	0.634	Water—Benzene	(30°)
10	0.649	0.632	Water—Toluene	(25°)
11	0.709	0.620	Water—Air	(25°)
12	0.837	0.615	Water—Hexane	(25°)
13	0.845	0.616	NaCl Soln.—Benzene	(25°)
14	1.071	0.612	Benzene—Air	(25°)
15	1.387	0.620	$SrBr_2$ Soln.—Hexane	(25°)

TABLE II.—CORRECTIONS FOR DROP WEIGHT—FROM CURVE.

r/a.	$f(r/a)$.	r/a.	$f(r/a)$.
0.0	1.000	...	...
0.1	0.805	0.9	0.614
0.2	0.741	1.0	0.612
0.3	0.703	1.1	0.612
0.4	0.676	1.2	0.613
0.5	0.655	1.3	0.615
0.6	0.637	1.4	0.620
0.7	0.625	1.5	0.629
0.8	0.618 See note (1)	1.6	0.641

The correspondence between the experimental results and the smooth curve drawn through Lohnstein's first two points, and the additional fact that the experimental curve follows the general trend of Lohnstein's values, shows that the relationship thus developed theoretically by Lohnstein must be, on the whole, the correct one. However, some prominent

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[1] For values of r/a greater than 0.7 the values are only approximate, since enough determinations have not been made in this region to fix these values with certainty. The indications are that if any change is shown by further experiments the change will be such as to *decrease* the values here given. They already represent a considerable *decrease* in comparison with the results obtained by Morgan, when he uses the work of Ramsay and Shields and other investigators in order to obtain the constant in this equation.

workers on surface tension still refuse to accept the validity of Lohnstein's work and prefer to use in place of his relationship the so-called law of Tate. The law of Tate states that the weight of a drop falling from a tube is proportional to the radius of the tube and to the surface tension of the liquid. Thus Morgan, in a paper printed in 1915 and entitled "Das Tatesche Gesetz, Eine Antwort an Herrn Lohnstein," states as the conclusion of one of his sentences

> "Man muss folgern, dass die form des Tateschen Gesetzes $\gamma = Kw$ für die benutzten Mundstücke ein wahres und strenges Gesetz ist."

If Tate's law holds the ratio $\dfrac{\text{Drop weight}}{\text{Tip diameter}} = \text{K}$.

Morgan gives the results of work upon 16 tips varying in diameter from 3.05 to 7.86 mm. in confirmation of this law. In order to see the relation of this work to the experimental correction curve, the corrections have been calculated from Morgan's values (Table III) and plotted in Fig. 2. Morgan has not, in any of these cases, determined the absolute surface tension himself, since his work gives only relative values, so the vertical position of his curves as a whole is dependent upon the value which he chooses as the surface tension of his standard liquid. Now the values of these surface tensions are taken from the work of others, and are usually the result of work by the capillary tube method. It is therefore evident that the curves representing Morgan's work as given in Fig. 2 may be brought down to the same general level as the experimental

Table III.—Calculation of $f(r/a)$ from Morgan's Results.

Benzene.		Quinoline.		Pyridine.		Carbon tetrachloride.		Ether.	
S. T. = 26.92. t = 27.8.		S. T. = 42.66.		S. T. = 35.33.		S. T. = 24.89.		S. T. = 15.33.	
d = 0.87059.		d = 1.08755.		d = 0.97365.		d = 1.57528.		d = 0.7045.	
a = 2.5117.		a = 2.829.		a = 2.708.		a = 1.795.		a = 2.107.	
r/a.	$f(r/a)$.	r/a.	$f(r/a)$.	r/a.	$f(r/a)$.	r/a.	$f(r/a)$.	r/a.	$f(r/a)$.
0.607	0.6595	0.539	0.673	0.5605	0.6573	0.8494	0.6377	0.7238	0.6569
0.782	0.636	0.6946	0.6434	0.7222	0.6425	1.095	0.6273	0.9326	0.636
0.796	0.6356	0.707	0.643	0.7355	0.636	1.114	0.6268	0.9749	0.6359
0.8978	0.6237	0.797	0.624	0.8288	0.623	1.256	0.6237	1.070	0.6234
0.9356	0.6226	0.880	0.624	0.915	0.623	1.309	0.6275	1.182	0.623
0.9913	0.6227	0.972	0.624	1.011	0.6225	1.387	0.631	1.305	0.6227
1.057	0.6227	1.006	0.624	1.022	0.622	1.479	0.6376	1.350	0.626
1.095	0.6223	1.034	0.6213	1.075	0.622	1.532	0.643	1.388	0.6264
1.133	0.622	1.096	0.6215	1.204	0.622	1.585	0.651	1.554	0.642
1.165	0.621	1.158	0.622	1.257	0.6224	1.639	0.658	1.623	0.647
1.234	0.6223	1.209	0.6214	1.352	0.6257	1.727	0.660	1.754	0.6613
1.304	0.6256	1.306	0.6248	1.444	0.630	1.824	0.6636	1.865	0.6757
1.362	0.6297	1.392	0.6294	......	......	1.905	0.671	......	......
1.471	0.639	......	......	......	......	......	......	......	......
1.565	0.6465	......	......	......	......	......	......	......	......

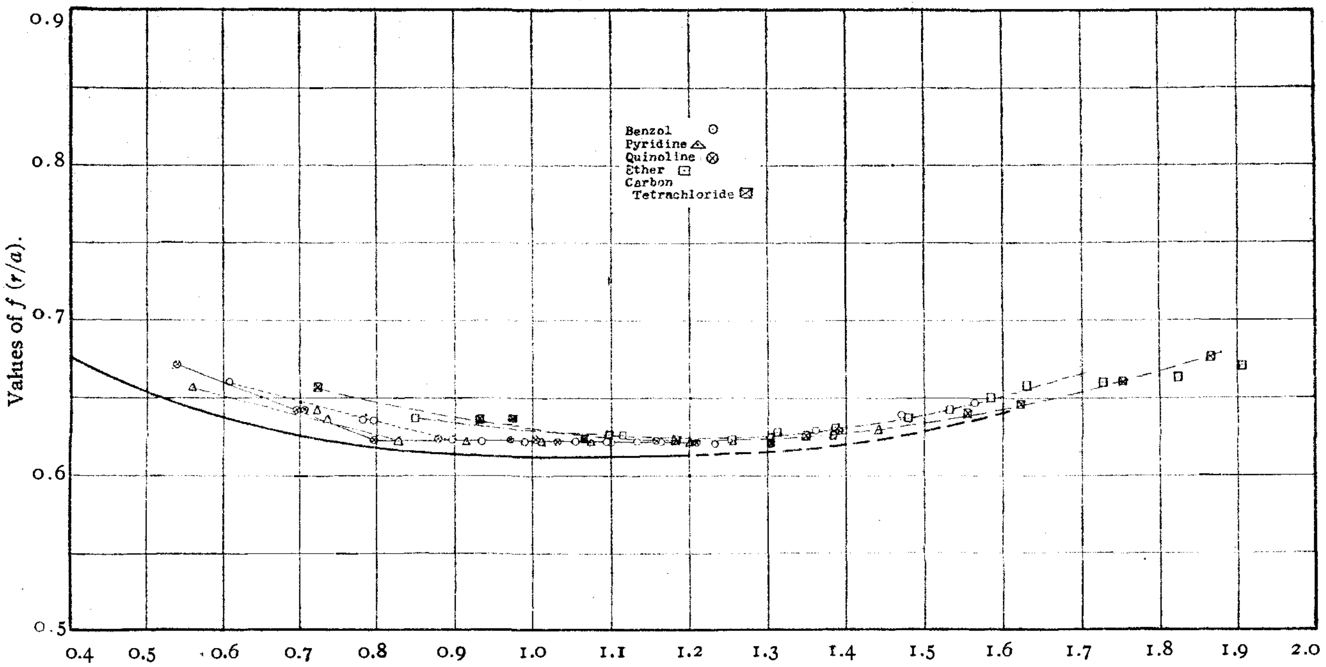

Fig. 2.—Values of the drop-weight correction calculated from Morgan's work with the theoretical curve given below for comparison.

correction curve, but the curves cannot be made coincident. The law of Tate might be said to hold over the region where the correction curve is horizontal, but this is the case only where the curve and its horizontal tangent become the same. This is not strictly the case for any part of the correction curve, but when the corrections are determined from Morgan's work it is seen that a large number of the points do lie on a straight horizontal line; on the other hand a large number of points lie very far from this straight line. In comparing the two results it should be remembered that the lower the correction factor, and therefore the lower the curve, the higher the surface tension, so that values obtained from the correction curve determined by the writers would be higher than those corresponding to Morgan's values.[1]

Such great care has been taken by Morgan in his work that it would seem worth while to endeavor to find a cause for the fact that the correction curve determined by us is so closely in accord with Lohnstein's theoretical work, and that the values given by Morgan for small values of r/a deviate so widely from the general form of the correction curve. This work is now being done by Mr. E. D. Wilson in this laboratory. He is beginning the work with the aim of making more complete calculations than those of Lohnstein, and at the same time to introduce into the equations such factors as viscosity, in order to see what would be the result of variations in these properties. The deviations in Morgan's work do not follow the order which would be given them by a variation of any one of the following properties of the liquids: viscosity, vapor pressure, density; but it is of course possible that more than one of these may be effective at the same time. The effect of differences of vapor pressure in changing the volatility of the liquid should not enter into the equations, since such effects should be eliminated by the experimental methods.

The use of very small tips makes the value of the function of r/a approach the value one, but the slope of the curve for these very small values of r/a is so great that it is difficult to tell exactly what correction to apply. This is illustrated by the irregularity in the corrected results of Antonow

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[1] That our *lower* values for the correction factor, that is, the *higher* values for surface tension are more apt to be the better, is confirmed by the recent work of Richards and Coombs, THIS JOURNAL, July, 1915, who obtain surface-tension values for benzene which are considerably higher than those found by the capillary-tube method by Ramsay and Shields, Renard and Guye, and Walden and Swinne. The deviation is of the order of 3%. The fact that Morgan's results give a higher correction factor than ours does not mean, therefore, that his drop weights are as a whole too low, but it indicates that the capillary-height method has in the past given results which are in general too low, for Morgan has not used any capillary-height measurements of his own, but seems to have determined the constant of his equation from the average capillary height determinations of other investigators. The discrepancy is therefore due, in all probability, to errors in the capillary-height methods and, not to deviations in the weights of the drops themselves.

on the surface tension at the interface water-benzene, as given in Table IV, where the variation amounts to 8% of the maximum value.

TABLE IV.—ANTONOW'S DETERMINATIONS OF THE SURFACE TENSION AT THE BENZENE-WATER INTERFACE BY THE USE OF EXTREMELY SMALL TIPS.

Radius in mm..........	0.13	0.175	0.350	0.630
$\alpha_{18°}$ corrected..........	34.93	36.04	37.97	35.40

The value obtained by the writers with larger tips is 34.18 dynes.

The correction curve is now most accurately known between the values of r/a from 0.3 to 0.8, since that is the more common range for the tips which have been available for work on the liquid-liquid interface. Seven new tips are now available for use and the corrections from 0.8 to larger values of r/a will be made more accurate by further work.

The writers wish to express their indebtedness to the American Academy of Sciences, Arts, and Letters for a grant of three hundred dollars from the C. M. Warren Fund. The grant will be used in a continuation of this research. The work described in papers II, III, and IV of this series has been accomplished by the use of this fund.

CHICAGO, ILL.

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

APPARATUS FOR THE DETERMINATION OF THE SURFACE TENSION AT THE INTERFACE BETWEEN TWO LIQUIDS.

(SURFACE TENSION II.)

BY WILLIAM D. HARKINS AND E. C. HUMPHERY.

Received October 22, 1915.

The surface tension at the interface between two liquids has been determined by a number of different methods,[1] but of these only two, the method of the falling drop, and the capillary-tube method, seem well adapted for general use. The importance of the interfacial tension in work in colloidal chemistry and in biological research, makes it essential that the apparatus for the determination of the surface tension should be of better design than that which has been used in most of the research work on this subject.

The Drop-Weight Apparatus.

The most essential features of a drop-weight apparatus are that the tip shall be ground almost perfectly round, with very sharp edges, and that the diameter of the tip shall be of the proper magnitude to give a ratio between the radius of the tip (r) and (a) the square root of the capillary constant, such that the Lohnstein correction[2] for the particular value

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[1] For a critical account of twenty methods see "A critical paper by Ferguson," *Science Progress*, Jan., 1915, p. 428.

[2] For an explanation of the Lohnstein correction see the paper which precedes this one.