$$\mathrm{Ag} \;\Big|\; \begin{matrix}\mathrm{AgCl,\ KCl} \\ C_1\end{matrix} \;\Big|\; \begin{matrix}\mathrm{KCl,\ AgCl} \\ C_2\end{matrix} \;\Big|\; \mathrm{Ag}$$

With the same solutions in cells of both types, the ratio of the potentials is shown to give accurate values of the transference number of the cation.

The measurements indicate that the "activities" of the ions from potassium chloride are much lower than the concentrations as calculated from conductance measurements. The values of the "activity" and of the concentration, however, apparently approach the same limit for very dilute solutions.

URBANA, ILL.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF COLUMBIA UNIVERSITY, No. 250.]

# THE DROP WEIGHT METHOD FOR THE DETERMINATION OF THE SURFACE TENSION OF A LIQUID.

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This method for the determination of the surface tension is one of the results of the extended, *purely experimental and statistical*, investigation of the relationship between the falling drop weight and the surface tension of a liquid, reports of which have appeared from time to time from this laboratory.[1] As no description of this method, in its present form, has appeared in any one place, however, for it has developed only gradually; and since some misunderstanding appears to exist concerning it; it is thought desirable that a brief résumé of the conditions necessary for its holding, in the light of the searching and conclusive, experimental tests to which it has been subjected in this laboratory, be presented here. This résumé will perhaps be of advantage also, in that it will render the future work published from this laboratory more intelligible; and, further, will make the method available to those other workers who may wish to determine accurate surface-tension values.

The drop weights considered throughout this work are those found by aid of the apparatus already described in some detail in THIS JOURNAL,[2] which enables one to determine with a high degree of precision the weight of any desired number of drops of liquid falling from any sharp-edged capillary dropping tip, at any fixed temperature below 90°; and that, *free from any effect of evaporation*, even when within but a few degrees of the boiling point of the liquid. The drops here are always formed very slowly, at any rate immediately before their fall, so that they drop unaided and of their own weight alone.

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[1] See Morgan and co-workers, "The Weight of a Falling Drop and the Laws of Tate," in a series of eighteen papers, THIS JOURNAL, 30, 33 and 35 (1908–1913).

[2] Morgan, THIS JOURNAL, 33, 349–62 (1911).

As the result of an experimental study of some two hundred especially purified liquids and solutions, for more than one hundred of which the surface tensions (lying between 15.3 and higher than 76 dynes per centimeter), for purposes of comparison, are known from some other method; liquids which include those of every conceivable type, and possessing every property which could possibly and adversely influence the behavior; it has been found that *under certain definite conditions*, the drop weights of liquids from any one dropping tip are proportional to their surface tensions, at the same temperature.

Expressed mathematically, this relationship is

$$\frac{\gamma_{C_6H_6,t}}{w_{C_6H_6,t}} = \frac{\gamma_{H_2O,t'}}{w_{H_2O,t'}} = \frac{\gamma_{l,t''}}{w_{l,t''}} = \text{Constant}, \qquad (1)$$

where, although the surface tension $\gamma$ in the numerator of any one ratio must be at a temperature identical with that for the drop weight value $w$ in its denominator, the $\gamma$ values can be at any desired temperature, $t$, $t'$ or $t''$, and need not be even on the same portion of the scale.

Transforming this equation, we find

$$\gamma_{l,t''} = \left(\frac{\gamma_{C_6H_6,t}}{w_{C_6H_6,t}}\right) w_{l,t''} = \left(\frac{\gamma_{H_2O,t'}}{w_{H_2O,t'}}\right) w_{l,t''} = \text{Constant} \times w_{l,t''}; \qquad (2)$$

the surface tension of any liquid at any temperature is equal to its falling drop weight from any one tip at that temperature, times a constant, the value of which is found once for all for that tip, and is equal to the ratio of the surface tension of some standard liquid to the drop weight of that liquid, both at some one, like, temperature.

This is one of Tate's laws which has been under *experimental* investigation in the series of papers alluded to above, and which has been proven to hold rigidly, under the definite conditions discussed below, for so many liquids. As is apparent, the method is a *relative*, not an absolute one, and consequently it must be standardized by aid of some selected liquid, preferably one which can be readily obtained in the pure state, and which has a comparatively high boiling point. Benzene and water have been employed in general for this purpose, for in addition to fulfilling the above requirements, they differ greatly as far as concerns the magnitude of the surface tension, and thus inspire increased confidence, perhaps, in the range of the method.

In order that the surface tensions of these liquids, for standardization purposes, may be readily calculated to the temperature at which their drop weights may have been found experimentally, use is made of the following interpolation formulas:

$$\gamma_{C_6H_6,t} = 30.514 - 0.1321t + 0.000082t^2,$$

$$\gamma_{H_2O,t} = 75.872 - 0.1547t - 0.00022t^2,$$

where $\gamma$ is expressed in dynes per centimeter, and $t$ may have any value up to 80°.

The above equation for benzene represents the average of *all* the results of *all* the accurate workers with benzene by the capillary rise method, and was obtained from them by aid of the method of least squares; it thus leads to the most accurate and representative average value of the surface tension of benzene at any temperature up to 80°.[1] The equation for water is that found by Morgan and McAfee[2] after standardizing their tip with benzene, and gives results which are in excellent agreement with the best results on water found by observers using other methods.

### Conditions Necessary for the Holding of $\gamma_{l,t}$ = *Constant* × $w_{l,t}$.

The conditions necessary for the precise holding of the equation, $\gamma_{l,t} =$

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[1] This equation, which is most convenient for laboratory purposes, gives results which are perfectly in accord with those obtained by aid of the *general*, empirical equation found by the author to hold *rigidly* for the average values of $\gamma$, even up to the critical temperature of benzene. This equation is

$$\gamma_{C_6H_6,t} = 2.115\left(\frac{288.5 - t - 6}{(78/d_t)^{2/3}}\right),$$

where $\gamma_t$ and $d_t$ are the surface tension in dynes and density of benzene at the temperature of observation, $t$; 78 is the molecular weight of benzene; 288.5 is its observed critical temperature; and 2.115 and 6 are constants. The density of benzene, for use in this formula, can be found up to 100° by aid of the relation $d_t = 0.9002 - 0.001066t$.

The equation for the work of any *one* observer alone is found to be identical with the above, except as to the value, 2.115, of the constant, which is slightly different for each observer, but *constant* throughout the temperature range studied by him. With a characteristic constant for each observer, in fact, this equation is found to give results which agree with the most remarkable accuracy with the observed values of $\gamma_{C_6H_6}$ of that observer at all temperatures (see Morgan, *Z. physik. Chem.*, **1915**).

The *average* equation to give the *average* result of the surface tension of benzene of *all* observers, then, is the above, in which the *average* value of *all* the individual, slightly differing, constants is used, *i. e.*, 2.115.

Applying this form of equation to the drop weight results of benzene, from any one tip, *under the conditions discussed below*, it is found that the relationship

$$w_{C_6H_6,t} = K\left(\frac{288.5 - t - 6}{(78/d_t)^{2/3}}\right)$$

also represents with very great precision the drop weights in milligrams at various temperatures from that tip, *the value of K being constant and characteristic for any one tip, and independent of the temperature.*

Comparison of these two equations, for $\gamma_{C_6H_6}$ and $w_{C_6H_6}$, at every identical temperature, then, shows that, *independent of the temperature*, since all terms except $\gamma$, $w$, 2.115 and K would be identical

$$\frac{\gamma_{C_6H_6,t}}{w_{C_6H_6,t}} = \frac{2.115}{K} = \text{Constant},$$

for any one tip, $t$ to have any desired value. In other words, Equation 1, as far as concerns the surface tension and drop weight of benzene from any one tip is thus shown to be rigidly true at all temperatures.

[2] THIS JOURNAL, 33, 1275–90 (1911).

constant × $w_{l,t}$ have been most thoroughly investigated from the experimental and comparative point of view. In other words, it has been found experimentally just what conditions are necessary in order that, within the narrow limits of error of the drop weight estimation, the ratios $\frac{\gamma_{C_6H_6,t}}{w_{C_6H_6,t}}$, $\frac{\gamma_{H_2O,t'}}{w_{H_2O,t'}}$, and $\frac{\gamma_{l,t''}}{w_{l,t''}}$, where the sub-letter $l$ represents *any* liquid, may be equal and constant in value, regardless of the values of $t$, $t'$ and $t''$; or, what amounts to the same thing, that the values of $\gamma_{e,t'}$, as calculated from $\gamma_{l,t''} = \left(\frac{\gamma_{C_6H_6,t}}{w_{C_6H_6,t}}\right) w_{l,t''} = \left(\frac{\gamma_{H_2O,t'}}{w_{H_2O,t'}}\right) w_{l,t''} = \text{Constant} \times w_{l,t''}$, may agree with those found at that temperature by some other method. The latter form here, naturally, is the one employed directly in the drop weight method for surface tension, and at the same time leads, perhaps, to a more satisfactory test of the truth of the general relationship; for by aid of the equation giving the change in surface tension with the temperature (which can be readily found from its results at several temperatures), the values of $\gamma_l$ at the various temperatures can be found by interpolation, and then compared with those found directly at those temperatures by the various other observers.

The conditions found necessary here, in few words, have to do with the *approximate* diameter of the dropping tip, and the drop weight and density, *i. e.*, with the volume of the drop on the tip. Whenever the above law holds, it is observed that the relation of drop volume to tip diameter is such that the drop forms with a "*normal,*" *bag-like profile,* with sides which are parallel for at least a portion of their length. When the drop volume on the tip is so small that the drop runs rapidly to a point, and its sides are nowhere parallel, the law fails to hold; and the same is true when the drop volume for the tip is so large that the drop, at its lower extremity, bulges beyond an imaginary continuation of the walls of the tip.

At first glance it might seem, perhaps, that this imposed condition of "normal" drop profile would limit very materially the number of liquids which could be studied on any one tip; but actual experiment has shown that with *any* tip lying between certain approximate limits of diameter, the liquids excluded, by reason of abnormal drop volume, would be insignificant in number; and would only be those which possess drop volumes that are excessivlely small, *i. e.*, which have average or small surface tensions, accompanied by very high densities.

The purely experimental and comparative study, with various liquids, of a number of tips (17) lying in diameter between 3 and 8 mm. has shown that *for general purposes*, only those between *4.5* and *5.5* mm. leads to satisfactory results. *With any tip lying between these limits of diameter (4.5 and 5.5 mm.), however, it is found that the law holds rigidly, so long as the drop volume on the 4.5 tip is at least equal to 0.0196 cc., and on the 5.5* *to at least 0.0239 cc.,* any intermediate diameter giving a volume which is in simple proportion to the diameter of the tip. These limits include *ether,* with its very small surface tension of *15.3* dynes, and drop volumes of, respectively, *0.0196* and *0.0239* cc., as well as *water* (and probably also considerably higher values), with its almost maximum surface tension, *76* dynes, and very large drop volumes of 0.083 and 0.1 cc.

The study of carbon tetrachloride in this connection, with its average surface tension value of *24.9* dynes, but excessive density, 1.576, giving on the 4.5 tip a volume of but 0.0143 cc. shows that the minimum volume on that tip can be reduced to this value, *i. e.,* considerably below that for ether given above. This volume, 0.0143 cc., is apparently the lowest limit for the 4.5 tip, however, for with a larger tip, carbon tetrachloride, which is very satisfactory in behavior on the 4.5 tip, cannot be considered to lead to very satisfactory results. In the same way we find that 0.0239 cc. is the absolute minimum for satisfactory work on the 5.5 tip, for with ether any increase in diameter above that shows a failure of the law to hold rigidly. When all the possible abnormal liquids of the type of carbon tetrachloride are considered, *i. e.,* liquids of average or small surface tension, accompanied by excessively high densities, we see that the number of liquids excluded from the rigid holding of the law, for any tip lying between 4.5 and 5.5 mm. is indeed a *minimum,* which certainly would not amount to more than a very small fraction of 1% of all liquids. Any such liquid on these tips, giving a volume smaller than those indicated, however, must be excluded from use on these tips; although, naturally, a smaller tip, standardized by aid of a similar liquid, would lead to satisfactory results by the method.

Although actual, average tip diameters, have been given above, it will be noted *that they are not necessary for, or even used in, the calibration of the tip,* that being accomplished simply from the relationship of a $\gamma$ value, as interpolated from observed results, and a $w$ value, found experimentally, both being at some one, like, temperature.[1] To find the approximate diameter of a tip, to ascertain whether or not it lies between the given limits (which were accurately determined by aid of a dividing engine), a micrometer may be held above the tip, and results, usually too high by about 0.1 mm., obtained, or it may be found in millimeters, with an accuracy of about 0.1% by aid of the drop weight diameter of tip relation[2] for benzene at 27.8°, *viz.,* diameter $= \frac{w_{C_6H_6}}{5.37}$.

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[1] It is possible that a misunderstanding on this point was the cause of the unjustified criticism of the method by Lohnstein (*Z. physik. Chem.,* **84,** 410–18 (1913)), and of his "discovery" of a 4% discrepancy in its results. For a reply in detail to that criticism, see Morgan (*Z. physik. Chem.,* **89,** 385 (1915)) in a paper referred to above which was accepted for publication early in 1914, and which although delayed by the war, should certainly appear as of an early date in 1915.

[2] See Morgan and Cann, THIS JOURNAL, **33,** 1065 (1911).

In connection with the tip diameter, it will be realized that there must be some one diameter which would give a value of the "Constant" in (1) and (2) equal to unity; in which case the measured drop weight in *milligrams* would also be the surface tension of that liquid, at that temperature, *in dynes.* This diameter can be calculated by first finding $\gamma_{C_6H_6}$ at 27.8° from the $\gamma_{C_6H_6,t}$ relationship, and then substituting that for $w_{C_6H_6}$ in the equation for the "diameter," and solving for that. The value thus found is 5.01 mm. Such a tip would save considerable time in the calculations, but such difficulty would probably be encountered in obtaining it of *just* that diameter, that it is better to do as has been done in the past, and employ a tip possessing a "Constant" which is either somewhat larger or smaller than unity, the actual diameter of which is known only approximately.[1]

The above is a brief sketch of the method for the determination of surface tension from the drop weight which has been developed as the result of the series of investigations mentioned above. *For* SEVENTY *of the* ONE HUNDRED *specially purified liquids, for which the surface tension was known, liquids of every type and giving all possible values of drop volume within the given limits, the above equations, (1) and (2), have been found to hold rigidly, between the tip diameters of 4.5 to 5.5 mm., the calculated surface tensions agreeing with some value as found at the same temperature by the capillary rise method, within a few tenths of 1% at worst. And the same can be said of all the* TEN *solutions, for which surface tension results were at hand.*

In the case of the other thirty liquids for which the surface tensions were known, however, the agreement was not so good; in some few cases being worse than that usually found among the results of different workers on the same liquid by the same (capillary rise) method. These liquids in many cases were those which are difficult to obtain, or then to retain, in the pure state; in which case in *this* work, the liquid was redistilled or purified in some other way immediately before each drop weight measurement was made; *second,* some of these liquids had been studied by only one observer of capillary rise, and in a number of cases the results of this observer for other liquids were consistently either higher or lower

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[1] The values for the "Constant" of the 4.5 tip is found to be 1.109, and that for the 5.5 to be 0.910; and the mean of these would also give constant = 1 for a tip of 5 millimeters.

The values of the "Constant," naturally, can also be employed to calculate the average diameter of the tip with an accuracy of about 0.1%, the value of the "Constant" being inversely proportional to the diameter of the tip. In this way we would have

4.5 : diameter : : "Constant" : 1.109
or 5.5 : diameter : : "Constant" : 0.910

This is indeed the simplest and best method.

than those of other observers by the same method; *third,* none of these liquids showed any variation from the "normal" drop profile, and further, none possessed any property that was not possessed to the same or a greater extent by other liquids which gave satisfactory agreements.

For the above reasons it is considered that the comparison in the case of these thirty liquids *cannot as yet be considered as final,* for until surface tensions, which are known to be *accurate,* are at hand, it must be assumed that it is the fault of the values of this property, that the method which gives such precise results for the *seventy* liquids should suddenly and inexplicably give less precise values for the thirty liquids, which differ from them in no single property that could affect the relationship.

Ferguson,[1] after recognizing the precision of this method, and rightly criticizing the various attempted *theoretical* derivations of a drop-weight—surface tension law (which in all cases have been found to be in disagreement with the experimental results published from this laboratory)[2] brings up the question as to whether or not the drop weight method is affected by the so-called angle of contact, thought to affect the capillary rise method, but not others. The only answer that can be made to this question, as he recognizes, is that based upon experiment. Unfortunately, however, there are not enough data at hand from any method for surface tension other than that of capillary rise, which are sufficiently concordant to standardize and then test with precision any empirical relationship between these surface tensions and the drop weights at the same temperature. Until such data are at hand, and until the effect of the angle of contact is studied sufficiently to show that it *does* have any effect upon capillary rise, upon which at present there is no general agreement, we can only assume, from the seventy cases above, that the angle of contact either exerts a very small influence on the capillary rise results, and the drop weight method is not affected by it; or, that both methods are affected by it in the same way. There is no reason for assuming, as far as can be seen, that the seventy liquids are just those for which the angle of contact is nearly zero, while it has a larger value for the thirty; and that consequently the drop weight not being affected by it, *should* only agree in those cases where the angle is zero.

Until more definite information as to the angle of contact is at hand, the experimental results from this laboratory can only be taken as showing that the drop weight and surface tension, *as found by the capillary rise method,* are proportional.

NEW YORK, N. Y.

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[1] *Science Progress,* No. 35, Jan., 1915.

[2] See Morgan, *Z. physik. Chem., loc. cit.*