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THE WEIGHT OF A FALLING DROP AND THE LAWS OF TATE. THE DETERMINATION OF THE MOLECULAR WEIGHTS AND CRITICAL TEMPERATURES OF LIQUIDS BY THE AID OF DROP WEIGHTS. II.

BY J. LIVINGSTON R. MORGAN AND ERIC HIGGINS.[1]

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Object of the Investigation.

In a recent paper[2] it was shown that the weight of a drop of liquid falling from a properly constructed tip is proportional, for any one diameter of tip, to the surface tension of the liquid; and, further, that when falling drop weights are substituted for surface tensions in the formula of Eötvös, as modified and presented in two forms by Ramsay and Shields, the molecular weights and critical temperatures of liquids can be calculated with an accuracy equal to that attained by the use of the surface tensions from the capillary rise.

The object of this paper is to present the results obtained with the same beveled tip, as was used in the former work,[3] when attached to a capillary burette of smaller internal diameter than was then obtainable, the drop weights being determined at or near those temperatures at which the surface tensions (from capillary rise) have been measured, thus avoiding the possible errors due to the faulty interpolation of the surface tensions from the smoothed curves, which might have affected the previous comparison. The results of our work, it may be said here, have not only confirmed the conclusions of Morgan and Stevenson in every respect,

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[1] Extract from the Dissertation of Eric Higgins.

[2] Morgan and Stevenson, THIS JOURNAL, **30**, 360–376 (1908).

[3] *Loc. cit.*, page 368.

as far as concerns any one tip, but in addition have shown that for the determination of relative surface tensions, the drop method is more accurate than the one in common use, which depends upon capillary rise. Further, they show that the molecular temperature coefficient of drop weight ($k_{temp.}$) is really a constant, although Ramsay and Shields, for the same liquids, found the corresponding molecular temperature coefficient of surface tension (k), from capillary rise, to vary so much that for the calculation of critical temperatures it was necessary first to find the exact value of k for the liquid in question. This is not necessary when working with drop weights, the one constant value holding for all the non-associated liquids studied, and so, presumably, for all the others. This apparently also makes the drop weight method, at its best, more accurate as a means of determining molecular weight than any other method, with the exception of that for permanent gases, which is based upon the density.

It must be remembered that the method in the form described below is most decidedly not adapted to general laboratory use, in the sense that the Beckmann methods are, for it requires not only considerable experience, but also no small amount of manipulative skill. It may be mentioned here, however, that a simple, and yet very accurate, apparatus for general laboratory purposes is now being tested by one of us, and will be reported upon in the very near future. With this simple form of apparatus, rather than the above, very elaborate one, it is hoped that the exact relationship between falling drop weight and tip diameter can be found, and the behavior of mercury and a large number of associated and non-associated liquids accurately investigated.

Apparatus and Method.

The apparatus for the measurement of the volume of a single falling drop (Fig. 1) in construction was essentially the same as that employed by Morgan and Stevenson, differing only in having a more accurate capillary burette (1 mm. corresponding to 0.000,046 cc.), and in having the tip joined directly to it, without the interposition of a wider tube. Our burette was also of greater length (2.5 meters), thus allowing drops of the liquids having the highest drop volumes to be measured without the use of bulbs, which were found to be a danger when using the more viscous liquids, owing to drainage difficulties. The smaller diameter of the burette enabled us to obtain more accurate readings, the uniformity of the tube removed difficulties as to drainage, and the absence of a constricted "zero-mark" permitted a more deliberate and accurate reading. To obviate the possible loss of a reading due to the meniscus falling in a bend of the burette tube, or at the place where the joining of the two lengths of capillary tubing composing it had distorted the bore, four "zero-marks" at successive distances of 1 cm. from one another were scratched upon the burette tubing just above the tip, and the exact relative volumes of the intervals between them determined. In all other respects the apparatus was exactly the same as that employed by Morgan and Stevenson, and was operated in the same way.

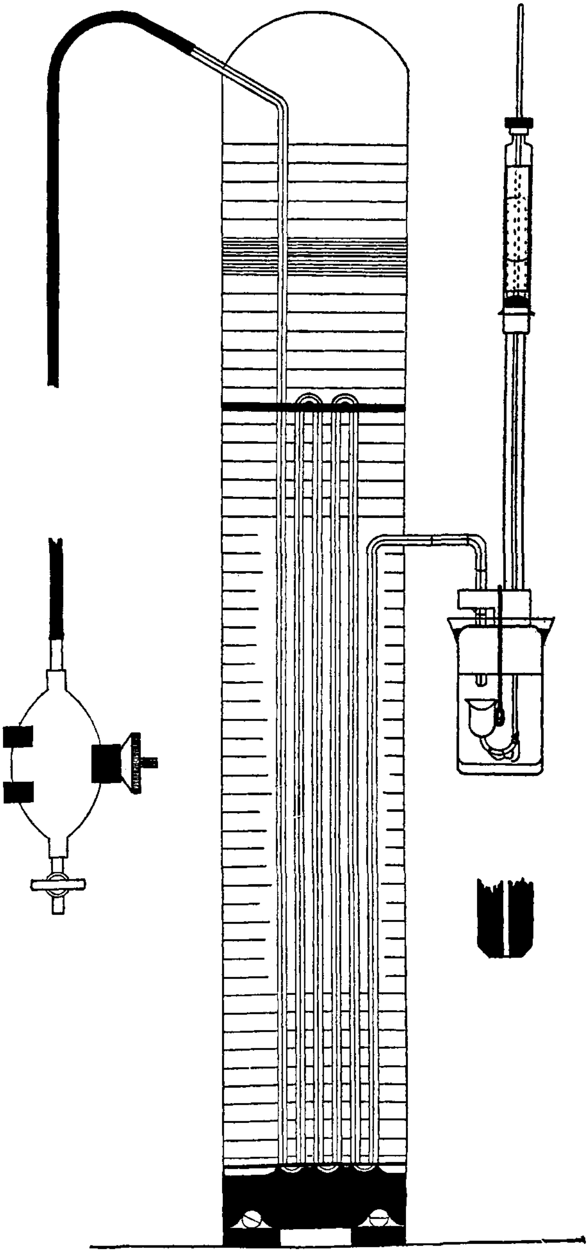

Fig. 1.

The dimensions of the apparatus, 69 by 18 cm., introduced difficulties in maintaining a constant and uniform temperature. The electrically heated thermostat finally adopted for the purpose is shown in Fig. 2, and the electrical connections diagrammatically in Fig. 3. The heating coil and thermo-regulator placed in the outer vessel (a 60 by 30 cm. glass anatomical jar) maintained the inner cylinder (another jar, 60 by 20 cm.) in a bath, the temperature of which varied rapidly within narrow limits. The variation of temperature in the inner vessel was naturally much smaller than this, and it was found easily possible to retain it constant at any temperature from 24° to 76° within 0.02° for any desired length of time. We believe that this "jacket" system yields the most satisfactory results where the conditions limit the disposition of the heating arrangements, and large instruments are to be dealt with. The vibration of mechanical stirrers being fatal to the accurate determination of drop volumes, the water in both the inner and outer cylinders was thoroughly agitated by a current of air passing through block-tin pipes. The trouble which might have been caused by the breaking down of the syphon constant level, owing to the liberation of dissolved air from the cold feed water, was obviated by the air trap shown in the figure.

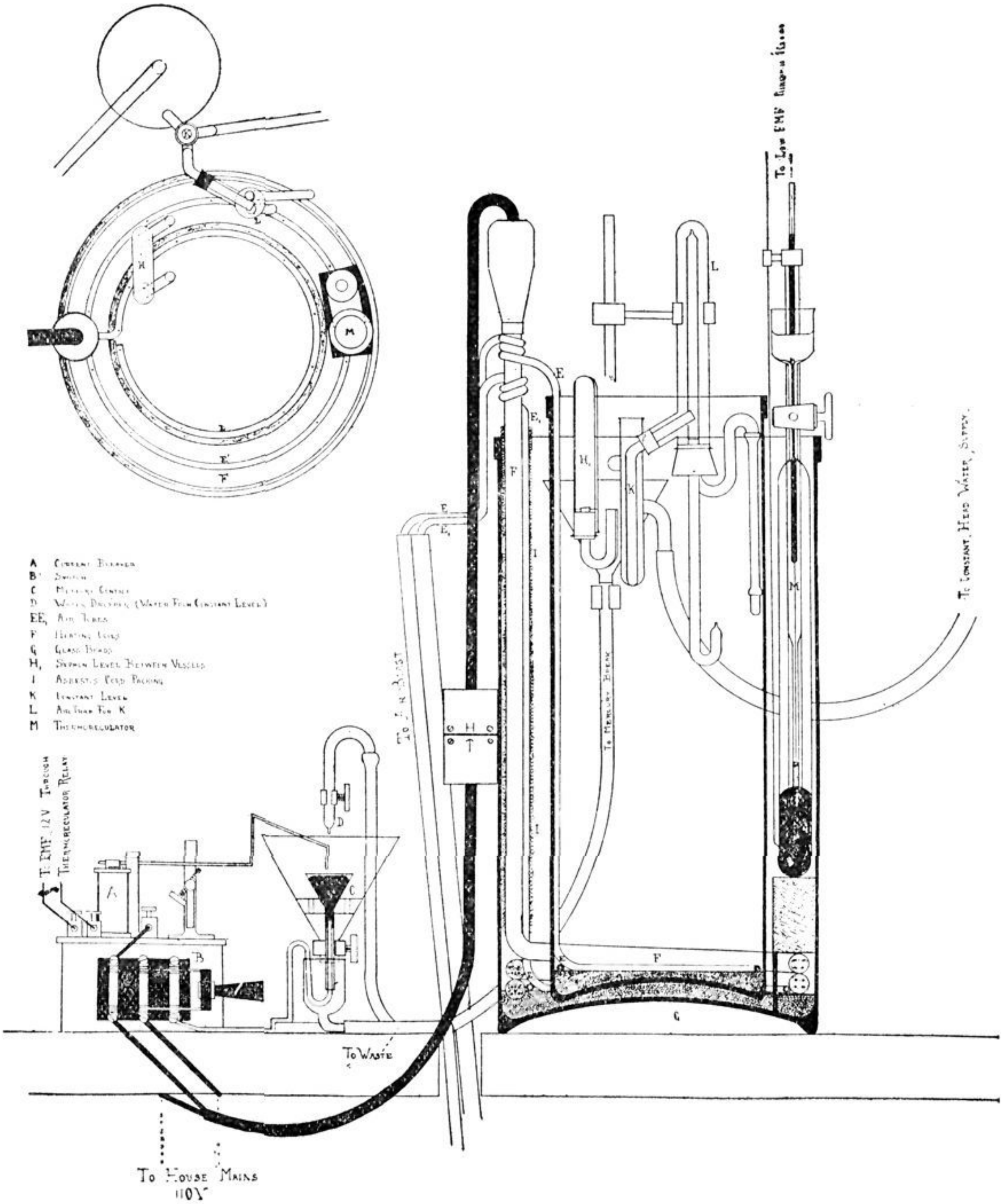

Fig. 2.

The heating current being heavy (10 to 20 amperes at 110 volts) was found to be best broken from a surface of mercury beneath water continually supplied from the overflow of the constant level. The current breaker was operated by twelve "gravity" cells thrown in through a small relay, operated through the toluene thermo-regulator by two of the same cells. By thus breaking a very weak current in the regulator, trouble due to the contamination of its mercury surface was avoided.

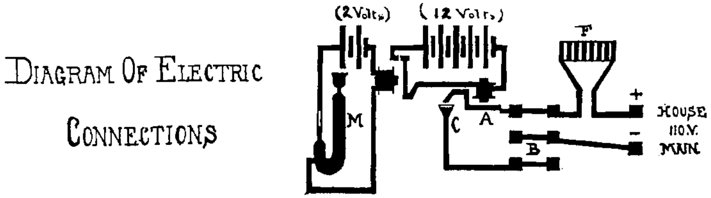

Fig. 3.

The apparatus in this form ran continuously, at various temperatures, and without attention or cleaning for six months and gave perfectly satisfactory results, the only trouble lying in the impossibility of obtaining glass vessels of this size which were sufficiently well annealed to support the higher temperatures for more than six or eight weeks, as is evidenced by the fact that we were forced to replace these three times during the course of our work.

The capillary burette was calibrated with mercury at 20°, successive quantities being blown out and weighed, the operation being repeated four times. The summated volumes calculated from these weights differed from that calculated from the weight of the total content (0.1230 cc.) by only 0.000,003 cc. This calibration was further checked by measuring the length of various threads of mercury in all parts of the tube, thus measuring each centimeter of the burette. These results were plotted on a curve from which volumes could be read to 0.000,005 cc. In the calibration in the air the position of the meniscus was read through an uncorrected lens, taking advantage of its lack of rectilinearity to avoid parallax. In the estimations in the thermostat the same object was attained, when taking an observation of the "zero-marks," by the use of narrow slits in a mask attached to the outer cylinder, centering on similar slits on the opposite side, from which the necessary illumination was obtained from a small electric lamp. The measuring tube itself, when in the thermostat, acted like an uncorrected lens, so that readings of the values on the graduated scale could be made without other aid.

This calibration, being performed at 20°, it was necessary to determine the effect of temperature in dilating the tube, and expanding the scale. For this purpose the volume of a thread of mercury, as given by the curve, was observed at every 10° between 5° and 85°, the mercury being subsequently weighed, and its true volume calculated at each of the temperatures. This work showed the effect of dilation to be very small, amounting to but 0.000,000,14 cc. per centimeter of length per degree. All volumes read, however, were corrected in accord with this. The possibility of a residual dilation effect on the capillary tube, after heating to high temperatures, was guarded against by working alternately on an ascending and descending thermometer. A series of estimations at one temperature occupying at least a day, the passage from low to high, and again to low temperature extended over periods of from six to ten days, thus reducing to a minimum the effect of residual dilation.

As a further check on the accuracy of our original calibration, and of our assumption of the absence of residual dilation, the total content of the burette was measured three times during the course of the work, and no appreciable difference observed.

As mentioned by Morgan and Stevenson, all difficulties occasioned by condensation on, or evaporation from, the drop when forming are prevented by the production of a "fog" upon the walls of the dropping cup. This condition we find to be most readily induced by dusting fine graphite powder upon the walls of the cup, above the liquid. By then heating the liquid and cup to a temperature of 100° (or as near that as possible without causing it to boil) for five minutes and plunging the cup in cold water, vapor is deposited upon the various particles, producing a satisfactory and durable fog. The instrument is then placed in the thermostat and a drop allowed to hang from the tip for an hour. At the end of this time the conditions are such that a drop neither gains nor loses in volume. Before each measurement we assured ourselves, by drawing the drop back into the burette several times, that such a condition prevailed, and that the drop neither lost nor gained in volume. When passing from one temperature to another the fog can be maintained by allowing a drop to hang from the tip during the change.

Since a thermometer could not very well be placed in the dropping cup itself, a similar cup, containing a fog, was placed beside the burette, a certified thermometer taking the place of the tip; and no estimation was made until the thermometer within the "blank" had agreed with a similar one in the water of the thermostat for a half hour. Without this somewhat elaborate procedure it was impossible to get agreeing results, drop weight being very sensitive to changes of temperature.

To prove that drainage difficulties were absent, a short thread of liquid was drawn through the tube at various speeds, from 1 cm. to 1 mm. per second, and the length of the thread measured after each passage, but so long as the walls of the capillary tube were wetted, no alteration in volume could be detected with any of the six liquids used.

Morgan and Stevenson measured the volume of a single drop only, for it seemed from the work of other investigators that the successive formation of several drops might introduce complications. Our work has shown, however, that in the presence of a perfect fog and constant temperature, a succession of drops (*i. e.*, where the clinging drop remaining after each fall is not drawn back into the burette, but is increased to the falling point, and simply one final reading made) gives a mean value for one drop that is exactly concordant with that obtained from the measurement of the single drop. Naturally, here, the greatest speed of formation of the drop is somewhat over a minute, owing to the small diameter of the burette.

Results.

Our results, in detail, for the same liquids used by Morgan and Stevenson, and also for carbon tetrachloride are given in Tables 1 to 6. All our densities were carefully redetermined with a 25 cc. Ostwald pycnometer, and agreed in the main with those collected from various sources by Renard and Guye. With quinoline, only, was the deviation worth considering, and even that did not appreciably change the values for surface tension as given by them. The chemicals used were the purest obtainable. The aniline, pyridine, benzene and chlorbenzene were Kahlbaum's "Special K," the carbon tetrachloride, Baker's "Analyzed," and the quinoline Merck's "Pure Synthetical;" and all showed correct and constant boiling points.

In the first column of Tables 1 to 6 is given the temperature, the second contains the actually determined drop volumes, all from the same, beveled, tip, approximately 6.2 mm. in diameter; the third the average drop volume and its mean error, assuming no constant error to exist; the fourth the density; the fifth the drop weight, the product of the average drop value and the density; the sixth the value

$$k_{\text{temp.}} = \frac{w_1\left(\frac{M}{d_1}\right)^{2/3} - w_2\left(\frac{M}{d_2}\right)^{2/3}}{t_1 - t_2},$$

w_1 and w_2 being drop weights in milligrams at the temperatures t_1 and t_2, and d_1 and d_2 the densities, while M is the molecular weight. And, finally, the seventh column, in three of the tables, contains the value

$$k = \frac{\gamma_1\left(\frac{M}{d_1}\right)^{2/3} - \gamma_2\left(\frac{M}{d_2}\right)^{2/3}}{t_1 - t_2},$$

as calculated from Renard and Guye's surface tensions (γ_1 and γ_2) from the capillary rise in saturated air. These are given where four or more temperatures are employed and serve to show the relative variation of the values given by the two methods.

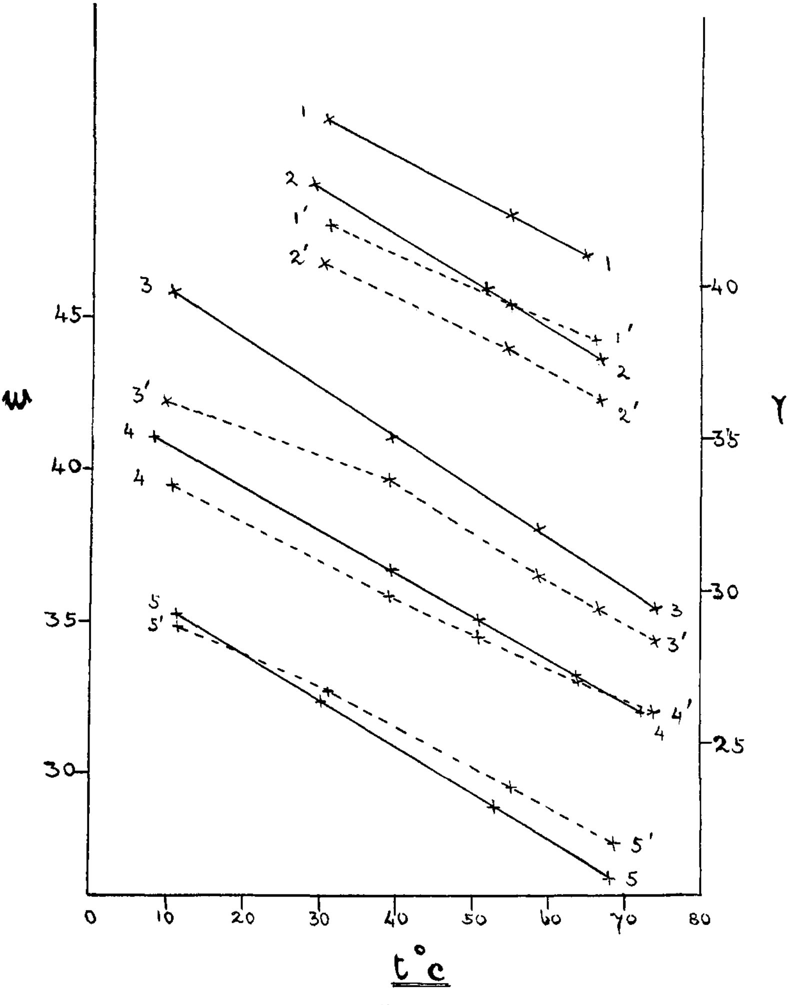

Fig. 4.

	Drop weight in milligrams.	Surface tension in degrees.
Quinoline	1	1'
Aniline	2	2'
Pyridine	3	3'
Chlorbenzene	4	4'
Benzene	5	5'

Table 7 gives a summary of the values of $k_{\text{temp.}}$ and of Renard and Guye's k, as found for the six liquids, together with the critical temperatures as observed, and as calculated from $k_{\text{temp.}}$ and k, by aid of the formulas

$$w\left(\frac{M}{d}\right)^{2/3} = k_{\text{temp.}}\ (t - 6),$$

and

$$\gamma\left(\frac{M}{d}\right)^{2/3} = k(t-6),$$

where t is the difference between the critical temperature and that of

TABLE 1.—BENZENE.

Temp.	Drop vols. cc.	Mean vol. cc.	Density.	Drop wt. Mg.	$k_{\text{temp.}}$	$k_{\text{R.\&. G.}}$
11.4°	0.039680 0.039692 0.039674 0.039686	0.039683 ±0.000,003 or 0.01%	0.888	35.239		
					2.521	1.717
30.2°	0.037252 0.037285 0.037274 0.037269	0.037270 ±0.000,007 or 0.02%	0.868	32.350		
					2.583	2.230
53.0°	0.034201 0.034210 0.034191 09034202	0.034201 ±0.000,004 or 0.01%	0.844	28.866		
					2.606	2.380
68.5°	0.032076 0.032090 0.032081 0.032074	0.032080 ±0.000,004 or 0.01%	0.827	26.530		

TABLE 2.—CHLORBENZENE.

Temp.	Drop vols. cc.	Mean vol. cc.	Density.	Drop wt. Mg.	$k_{\text{temp.}}$	$k_{\text{R. \& G.}}$
8.2°	0.036656 0.036700 0.036684	0.03668 ±0.000,013 or 0.04%	1.120	41.082		
					2.568	2.332
39.2°	0.033738 0.033729 0.033746 0.033746	0.03374 ±0.000,007 or 0.02%	1.0856	36.628		
					2.590	2.118
50.8°	0.032647 0.032600 0.032588	0.03261 ±0.000,019 or 0.06%	1.0730	34.990		
					2.545	2.045
63.9°	0.031350 0.031300 0.031391 0.031359	0.03135 ±0.000,018 or 0.06%	1.0590	33.200		
					2.577	1.938
72.2°	0.030540 0.030523 0.030540 0.030529	0.03053 ±0.000,004 or 0.01%	1.0498	32.054		

observation. Here we have used in all cases the actually obtained results most separated as to temperature, and not those from the smoothed curve, as is done for the $k_{\text{R. \& G.}}$ values, and has been done by all investigators using the capillary rise method.

In Fig. 4 the comparative accuracy of drop weights and surface tensions by capillary rise for the liquids that were studied at three or more temperatures, is also shown graphically, the surface tensions being the very carefully determined ones of Renard and Guye, against saturated air. It must be noted here that the graphs are only to be compared in relative straightness and uniformity, and not as to slope, for we have as yet made no attempt to express drop weights accurately in terms of surface tension. It will be seen here that our two intermediate results for pyridine lie somewhat off the line joining the low and the high values. These errors are probably due to slight temperature errors, for pyridine was the first

TABLE 3.—CARBON TETRACHLORIDE.

Temp.	Drop vols. cc.	Mean vol. cc.	Density.	Drop wt. Mg.	$k$temp.
24.2°	0.019600 0.019564 0.019577	0.01958 ±0.000,007 or 0.04%	1.5823	30.975	
					2.567
54.0°	0.017516 0.017505 0.017510 0.017511	0.01751 ±0.000,003 or 0.02%	1.5240	26.685	

TABLE 4.—PYRIDINE.

Temp.	Drop vols. cc.	Mean vol. cc.	Density.	Drop wt. Mg.	$k$temp.	$k_{\text{R. \& G.}}$
10.5°	0.046238 0.046194 0.046228	0.04622 ±0.000,014 or 0.04%	0.991	45.804		
					2.589	1.57
39.2°	0.042665 0.042630 0.042585 0.042570 0.042550	0.04260 ±0.000,02 or 0.05%	0.962	40.98		
					2.440	2.54
58.8°	0.040312 0.040343 0.040348 0.040238 0.040234	0.040295 ±0.000,025 or 0.06%	0.943	38.00		
					2.770	2.31
74.2°	0.038180 0.038153 0.038128 0.038154	0.038154 ±0.000,01 or 0.03%	0.927	35.37		

liquid investigated, and our earlier method for the agitation of the water in the inner cylinder was found later to be insufficient. This difficulty was avoided at both the low and the high temperatures, these determinations having been made subsequently.

TABLE 5.—ANILINE.

Temp.	Drop vols. cc.	Mean vol. cc.	Density.	Drop wt. Mg.	$k_{temp.}$
29.0°	0.048720 0.048688 0.048662	0.04869 ±0.000,017 or 0.03%	1.0138	49.362	
					2.5685
51.7°	0.046154 0.046159 0.046170 0.046161	0.04616 ±0.000,004 or 0.01%	0.9944	45.902	
					2.5700
67.1°	0.044436 0.044432 0.044428	0.04443 ±0.000,002 or 0.01%	0.9810	43.588	

TABLE 6.—QUINOLINE.

Temp.	Drop vols. cc.	Mean vol. cc.	Density.	Drop wt. Mg.	$k_{temp.}$
30.7°	0.047456 0.047504	0.04748 ±0.000,024 or 0.05%	1.0852	51.525	
					2.580
55.0°	0.045338 0.045347 0.045405	0.045363 ±0.000,021 or 0.05%	1.0658	48.344	
					2.570
68.0°	0.044474 0.044478 0.044518	0.044490 ±0.000,014 or 0.03%	1.0576	47.053	

TABLE 7.

Showing $k_{temp.}$ k, and critical temperatures. Drop weight results are from the directly observed values at the extreme temperatures, those from capillary rise being from the smoothed curves.

Liquid.	$k_{temp.}$	Crit. Temp.	$k_{R. \& G.}$	Crit. Temp.	Observed Crit. Temp.
Benzene	2.569	288.4	2.12	287.7	ca 288
Chlorbenzene	2.569	359.5	2.10	357.7	ca 360
Carbon tetrachloride	2.567	285.2	2.19	278.0	ca 284
Pyridine	2.567	347.0	2.07	346.2	ca 344
Aniline	2.569	425.8	2.01	448.6	ca 426
Quinoline	2.575	520.4	2.21	496.2	<520
Average	2.5694 ± 0.0013 or 0.05%		2.116 ± 0.0965 or 4.6%		

Mean error of a single observation ±0.0033, or 0.13%.

Discussion of Results.

A glance at Tables 1 to 6 will show that only in one case is our error in the estimation of the volume of a single falling drop, assuming the existence of no constant error, equal to 0.06 per cent., all others being very much less. Drop weights, calculated from these volumes and the carefully redetermined densities, can then, of course, be burdened with no greater error. From the curves in Fig. 4, where drop weight in milligrams and surface tensions from capillary rise in dynes are plotted against temperatures, it will be seen that the results of drop weight are more concordant, among themselves, than are the surface tensions, which allows of but one conclusion—the drop weight method is more accurate than that based on capillary rise, even in the hands of such skilful investigators as Renard and Guye. If there is then any doubt as to the drop weight method giving the *true* relative values of surface tension, rather than the method of capillary rise, it must certainly be dissipated by the consideration of Table 7, in which $k_{\text{temp.}}$, for the six non-associated liquids used, is shown to be 2.5694 ± 0.05 per cent., the mean error of a single determination being 0.14 per cent., while the variation in the corresponding average k value by capillary rise is 4.6 per cent. from Renard and Guye's results, and much larger according to those of Ramsay and Shields. When it is remembered that the Ramsay and Shields formula, from which $k_{\text{temp.}}$ and k are derived, which may be written in the form

$$\frac{x_1\left(\frac{\mathrm{M}}{d_1}\right)^{2/3} - x_2\left(\frac{\mathrm{M}}{d_2}\right)^{2/3}}{t_1 - t_2} = \text{constant},$$

where x is a term proportional to surface tension, was originally designed for capillary rise results, it becomes evident that drop weight is not only also proportional to the true surface tension, *but gives better and more consistent values for it than capillary rise.* The same reasoning holds also with regard to the critical temperatures, and the Ramsay and Shields formula from which they are calculated, except that here the comparison cannot be made quite so satisfactorily, owing to the experimental uncertainty in the determination of critical temperatures. Even here, however, the drop weight method shows to advantage, for the critical temperatures calculated by it for aniline and quinoline agree well with the experimental values, where those by the aid of capillary rise are quite different. *Drop weights, then, satisfy the equations that were designed especially for capillary rise results, better than these themselves do.*

This form of proof of the advantage in accuracy of the drop method over that depending upon capillary rise, is, unfortunately, the only one possible at present, for even a smoothed curve drawn from the capillary rise results is still too much burdened with error to allow any very accurate, direct, comparison of the two methods.

Owing to the unsatisfactory nature of the curve for the surface tensions from capillary rise we have omitted any attempt to calculate the single values of the Morgan and Stevenson term $K_{F.D.}$, for the various liquids and temperatures, but have calculated, for the sake of comparison, for we have made no other use of it, one single value in the following way: Since $k_{\text{temp.}}$ and k, by the above formulas are related to each other as the drop weights are to the surface tensions, the ratio $k_{\text{temp.}}/k$ must give the factor by which drop weights in milligrams must be divided to give true surface tensions in dynes per centimeter. This factor is 1.2143, since $k_{\text{temp.}}$ is equal to 2.5694, and practically invariable, and the mean, and supposedly correct, value of k is 2.116.

With the exception of aniline and quinoline, drop weights interpolated (or extrapolated) from our curves agree with those found with the same tip by Morgan and Stevenson within a few tenths of 1 per cent. With aniline and quinoline the difference is slightly larger, but all are well within the limits of error mentioned in their paper. These slight errors, unavoidable at that time, with the densities they used, are sufficient, however, to account for the slightly higher value of $k_{\text{temp.}}$ and its variation which they observed, *i. e.*, the value 2.598 ± 1.56 per cent., as compared to 2.5694 ± 0.05 per cent., and also for the difference in $K_{F.D.}$, which in average they found to be 1.226, as against our value of 1.2143. And the same is true for their critical temperatures.

Certainly the most striking and important fact brought out by our work is the practically absolute constancy for all the liquids, at all the temperatures, of the molecular temperature coefficient of drop weight, $k_{\text{temp.}}$, for it apparently makes the drop weight method, for large temperature intervals, where slight errors in temperature have little effect, the most accurate known method for the determination of molecular weight, with the exception of that for permanent gases which is based upon the density. The truth of this can be shown by assuming as correct either the maximum, the minimum, or the average value of $k_{\text{temp.}}$ in Table 7, and calculating from it, by aid of the specific drop weights and densities, the molecular weight of any of the liquids given. The maximum error for any of the six liquids is less than 0.5 per cent. when M for the liquid giving the smallest value of $k_{\text{temp.}}$ is calculated from the largest value found for $k_{\text{temp.}}$, and is very much less when the M for any liquid is calculated from the average $k_{\text{temp.}}$. That this must be true is evident, for it can be readily shown that the percentage variation in M is equal to 2/3 of the percentage variation in the value of the $k_{\text{temp.}}$ from which it is calculated.

Another advantage of the constant value of $k_{\text{temp.}}$ is that it is not necessary in calculating the critical temperature from drop weight as Ramsay and Shields found it in using the capillary rise values to first find the exact value of the molecular temperature coefficient for the specific liquid in question, for we can simply use the value of $k_{\text{temp.}}$ as found for any other non-associated liquid.

Summary.

(1) An apparatus is described, by which, using the same tip employed by Morgan and Stevenson, the error (assuming the existence of no constant error) in the estimation of the volume (and consequently of the weight) of a single falling drop is reduced to a few hundredths of 1 per cent.

(2) The elimination of their known error, and a redetermination of the densities, confirm all the conclusions of Morgan and Stevenson, as regard any one, beveled, tip, the more accurate work simply accentuating them and proving the method to be even better than they claimed it to be.

(3) Drop weights calculated from the experimentally observed volumes, by the aid of redetermined densities, for benzene, chlorbenzene, carbon tetrachloride, pyridine, aniline, and quinoline, at the same, or nearly the same, temperatures at which the surface tensions from capillary rise have been measured, show that drop weights are proportional to the temperature, and that the singly determined values lie upon a straight line, whereas the values from capillary rise vary considerably and irregularly on the one side or the other of such a line. In other words, drop weight leads more accurately to true surface tensions than does the capillary rise.

(4) The molecular temperature coefficient of drop weight, calculated by aid of the Ramsay and Shields formula

$$\frac{x_1\left(\frac{M}{d_1}\right)^{2/3} - x_2\left(\frac{M}{d_2}\right)^{2/3}}{t_1 - t_2} = \text{constant},$$

where x is a term proportional to surface tension, which was designed especially for results from capillary rise, is found for drop weight to be practically invariable for all the six non-associated liquids, while the use of capillary rise results leads to a variation of 6.4 per cent. from the average, according to the results of Renard and Guye, and to a still larger one according to those of Ramsay and Shields. The consequence of this is that the drop weight method, when used for such a temperature interval as we have employed, is the most accurate method for the determination of molecular weight known, except for permanent gases as based upon the density. And critical temperatures can be more readily and accurately calculated from drop weight than from capillary rise, as is shown for aniline and quinoline by the agreement with experiment when calculated from drop weight, and the wide divergence when calculated from capillary rise.

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