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THE WEIGHT OF A FALLING DROP AND THE LAWS OF TATE. IV. THE STANDARDIZATION OF A TIP; AND THE CALCULATION OF THE SURFACE TENSION AND MOLECULAR WEIGHT OF A LIQUID FROM THE WEIGHT OF ITS FALLING DROP.

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After determining, as described in the previous paper,[1] the average weight of a drop of liquid *falling of its own weight alone* from the tip, using for the purpose at least three checking values each, of the 30 drops, and of the 5-drop blank, the next step is to find the constant, of the tip, *i. e.*, the temperature coefficient of the molecular function, $w(M/d)^{2/3}$.

In the previous papers of the series,[2] the method employed to this end was the one first used, for surface tension from capillary rise, by Ramsay and Shields,[3] and since then by all other investigators in that field. This method consists in evaluating k in the equation[4]

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[1] Morgan, THIS JOURNAL, 33, 349–362 (1911).

[2] I. Morgan and Stevenson, THIS JOURNAL, 30, 360 (1908). II. Morgan and Higgins, *Ibid.*, 30, 1055 (1908).

[3] *Z. physik. Chem.*, 12, 431 (1893).

[4] Here γ is the surface tension in dynes per centimeter, d the density, both at the temperature of observation t, M is the molecular weight as a liquid, k for non-associated liquids is a constant which is assumed to be universal and equal to 2.12 ergs, and t_c is the critical temperature.

This law, of course, can also be expressed in the form of a proportion, in which case the arbitrary constant, 6, disappears. We have then for any two non-associated liquids

$$\gamma'(M'/d')^{2/3} : \gamma''(M''/d'')^{2/3} : : (t'_c—t') : (t''_c—t'');$$

in other words, *at temperatures equally removed from the critical temperature (i. e., in corresponding states), the value of the expression* $\gamma(M/d)^{2/3}$ *is identical for all non-associated liquids.*

$$\gamma_1(M/d_1)^{2/3} = k(t_c—t_1—6) \qquad (1)$$

by aid of the second, differential, equation

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

the molecular weight of the substance as a liquid being estimated by the relationship of this value of k to that found in the same way for some other liquid, taken as a standard; or to the average value of k found for several such. The results thus obtained from capillary rise can hardly be considered as satisfactory, for the k values so calculated are found to vary considerably from the mean and to force the conclusion that most substances in the liquid state are either slightly associated (*e. g.*, aniline, k = 2.01–2.053, and pyridine, k = 2.07), or slightly dissociated (quinoline, k = 2.21–2.44), if we can conceive of such a process in a pure liquid.

This value of k, as calculated from (2) for any liquid, was then supposed to be substituted in (1) to obtain the critical temperature of that liquid; but, as Dutoit and Friederich[1] have already observed, the agreement of these values found from capillary rise results with those obtained directly is so unsatisfactory (aniline, quinoline and pyridine, etc.) that the relationship is not of very great value for the calculation of critical temperature.

A glance at equation (2) shows at least one possible cause for much of the variation in the value of k calculated for the various substances from (2), viz., the error induced in k by a known error in one of the experimental results. Thus *when calculated from* (2), *the percentage error in k is equal, not to the original, experimental, error, but to that multiplied by a factor which is the greater, the smaller the temperature interval* $t_2—t_1$, for the actual error in the value of $\gamma(M/d_1)^{2/3}$ is then carried over bodily to the difference $\gamma_1(M/d_1)^{2/3} — \gamma_2(M/d_2)^{2/3}$, which may be but one-tenth or one-twentieth, or even a smaller fraction, of $\gamma_1(M/d_1)^{2/3}$, in which case *the percentage error in the difference, and consequently also in k, will be ten or twenty or even more times that of the original observation.* This error, naturally, will be increased or decreased by an error in $\gamma_2(M/d_2)^{2/3}$, according as that has the opposit or the same sign as the one in $\gamma_1(M/d_1)^{2/3}$; and further will be influenced by the relation of the error in $t_2—t_1$ to that in t_1, or in t_2.

The recognition and attempted elimination of this error, by making $t_2—t_1$ as large as possible, in place of obviating the difficulty, often simply increases it. This is the case with liquids of high viscosity, which, especially when accompanied by low density, makes the measured ascensions a capillary of very small bore probably erroneous at low temperatures, while at the higher ones, that difficulty being partially or wholly eliminated, only the error due to the small height to be measured, which may also be

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[1] *Arch. sci. phys. Genèva*, 9, 128 (1900).

considerable, is present. It is in this respect that the drop weight method has a decided advantage over that of capillary rise as a means of determining surface tension, for with the new form of apparatus the error which may exist can be retained constant (which is the important thing) by weighing a larger number of drops at the higher temperatures, and errors due to changing viscosity are not present. The absence of these errors is also clearly shown in the work of Morgan and Higgins (on the older form of apparatus), who find k values from their extreme values of drop weight, even by aid of (2), for aniline, pyridine and quinoline which are practically identical with those for the other three liquids, benzene, chlorobenzene, and carbon tetrachloride. This is in startling contrast to the results from capillary rise given above.

We can conclude from the above, then, that in calculating k from equation (2) in the customary way, even small irregular, experimental errors (and in capillary rise it must be conceded that these are rarely absent) will become so largely magnified at times as to make the results absolutely meaningless, if not wholly misleading, while in all cases the variation in the calculated value of k from (2) will cause even those experimental results which are exceedingly accurate to appear but mediocre[1].

To avoid this error in the calculation of k from (2) (both for drop weight and capillary rise), so that results on the new form of apparatus can be compared directly with the results obtained from capillary rise, and a new tip standardized as quickly and accurately as possible, another method for the calculation of k has been resorted to with a very satisfactory result. If equation (1) be true, *i. e.*, if the value of the function $\gamma_1(M/d_1)^{2/3}$ is the same for all non-associated liquids at corresponding temperatures; in other words, is simply a function of the reduced temperature $(t_c—t_1—6)$ the value of the molecular temperature coefficient k, calculated from (1), with the known critical temperature, for any one liquid, should lead to the correct critical temperature of any other such liquid when its data (*i. e.*, w, M and d) are substituted with this value of k in (1). From a series of results for any one, standard liquid, then, using the known value of t_c, we would get as many values of k as there are individual results, and could find an average value which when substituted in (1) would give the variation of the value of the function $\gamma(M/d)^{2/3}$, with the temperature, for that liquid, and for all other normal ones, up to 6° below the critical temperature, when its value would become zero.

Naturally, if there were no experimental error, this value of k would be identical with that found by aid of (2). *When any error at all exists,*

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[1] This is shown by the intermediate values of k found in this way by Morgan and Higgins, where the greatest variable experimental error is not greater than a few hundredths of one per cent.

however, here, in contrast to the method based upon (2), *the percentage error in k will be the same as that in the original, experimental, result itself.*

In case this value of k, determined in average for any one standard liquid of known critical temperature, is now substituted in (1) with the data for another non-associated liquid, the value of its calculated t_c should be the same (within the percentage error existing in the experimental work), no matter what the temperature, t, may be; and the mean of these individual values, provided the law (1) is correct, should agree closely with the observed critical temperature of that liquid. Here, when the result at one temperature differs from those at the others, it would point to an unsuspected error, and that value should be scrutinized carefully before including it in the average result.

It is this method which has been selected for the standardization of a tip, benzene (t_c = 288.5°) being employed as the standard liquid. In addition to its use as a means of calculating the molecular temperature coefficient k, it can also serve for the calculation of the factor necessary to transform the drop weight from any tip directly into surface tension; and for the direct comparison of the surface tension results of various observers, even though the determinations were not made at the same temperatures.

In Table I are given the k values which are necessary in equation (1), with capillary rise as well as drop weight results, to give benzene its observed critical temperature of 288.5° C.

TABLE I.

Benzene, t_c = 288.5°; M = 78.

t.	d.	γ.	$\gamma (M/d)^{2/3}$.	k from (1).
		Renard and Guye.[1]		
11.4	0.888	28.83	569.68	2.1014
31.2	0.867	26.68	535.68	2.1316
55.1	0.842	23.53	481.74	2.1185
68.5	0.827	21.70	449.63	2.1011
78.3	0.815	20.51	429.13	2.1015
			Average,	2.1108
		Ramsay and Shields.[2]		
80	...	...	425.1	2.0948
90	...	...	404.5	2.1013
100	...	...	384.0	2.1041
110	...	...	362.9	2.1038
120	...	...	341.6	2.1022
			Average,	2.1012

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[1] *J. chim. phys.*, 5, 81 (1907). Capillary rise in presence of air. Results of $\gamma(M/d)^{2/3}$ recalculated throughout to give uniformity.

[2] *Loc. cit.* Capillary rise, absence of air.

t.	d.	γ.	$\gamma(M/d)^{2/3}$.	k from (1).
		Ramsay and Aston.[1]		
11.2	0.8871	29.21	575.6	2.1216
46.0	0.8500	24.71	502.3	2.1239
78.0	0.8147	20.70	433.1	2.1179
			Average,	2.1211
		Morgan and Higgins.[2]		
11.4	0.888	35.239	696.32	2.5685
30.2	0.868	32.350	649.02	2.5724
53.2	0.844	28.866	590.05	2.5710
68.5	0.827	26.530	549.71	2.5687
			Average,	2.5702

A comparison of these average values of the k necessary to give t_c = 288.5° shows that even though Renard and Guye worked in the presence of air (as did Morgan and Higgins), their results differ less from those in the absence of air of Ramsay and Shields, than do those of Ramsay and Aston, who also excluded air. Except when the liquid dissolves considerable air, then, we should except identical results with and without the presence of air.

These k values at the various temperatures also seem to agree better in the case of drop weight than in that of capillary rise. This is to be expected, however, especially with the new form of apparatus, for the smaller weight of a single drop at the higher temperatures can be compensated by increasing the total number weighed, while with the capillary rise method, even the originally small height of ascension decreases with the increase in temperature, and causes an increase in the percentage error.

In using for any one liquid the equation

$$\gamma(M/d)^{2/3} = k(t_c—t—6)$$

as a means of comparison at any one temperature, since M, t_c, t and d are all taken as the same, it is clear that γ in each case must be proportional to its value of k. We have, then, for the results of different observers, *at the same temperature*,

$$\gamma_1 : \gamma_2 : : k_1 : k_2, \qquad (3)$$

where γ_1 and γ_2 are the surface tensions of benzene that would be found at this temperature by different observers, whose average constants for benzene at other temperatures are k_1 and k_2. This holds, naturally, also for the comparison of drop weights and surface tensions, where we have, *also at the same temperature*,

$$w : \gamma : : K : k, \qquad (4)$$

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[1] *Z. physik. chem.*, 15, 91 (1894). Same conditions as Ramsay and Shields.

[2] *Loc. cit.* Drop weights.

w being the weight in milligrams, and K the constant for drop weight, calculated similarly to k.

Since, further, the ratio of γ for benzene to γ for any other liquid still at the same temperature, as found by one observer must be the same, within the limits of error, as that found under similar conditions by every other observer, it is apparent that

$$\gamma_B/\gamma_x = \gamma'_B/\gamma'_x,$$

where γ_x and γ'_x are the respective values found by two of the observers for the second liquid *still at the same temperature.* Combining this equation with the proportions (3) and (4), remembering that these ratios must also be equal to w_B/w_x under identical conditions of temperature we find

$$\gamma_x : \gamma'_x : : k : k'$$

and

$$w_x : \gamma_x : : K : k,$$

i. e., the surface tensions of the same liquid, x, at the same temperature, as would be found by different investigators, are proportional to the average k values of benzene found by them; and

The drop weight in milligrams of any liquid is related to its surface tension, in dynes per centimeter, at the same temperature, as the K value for that tip is to the k value of surface tension, both being found from benzene by aid of (1), *using t_c = 288.5°.*

The relationship of drop weight to surface tension, *both at the same temperature,* can be found, then, from the equation

$$\gamma_{\text{dynes}} = w_{\text{mg.}} \times k/K, \qquad (5)$$

where, since the constants, k, of the three observers do not agree very satisfactorily, it would be best perhaps to use for K the average of their values. We would have thus for the tip used by Morgan and Higgins, the equation of transformation

$$\gamma_{\text{dynes}} = w_{\text{mg.}}\ 2.1110/2.5702 = 0.82134\ w_{\text{mg.}}$$

In place of calculating by the above relations all the γ and w values to one γ form, to compare the work on other liquids by the various observers (in which case the temperatures would have to be identical), we can more simply attain the desired end in another way, retaining the above average values, $k_{R\,\&\,G}$, $k_{R\,\&\,S}$, $k_{R\,\&\,A}$, and $k_{M\,\&\,H}$.

Since in comparing the results of the various observers on any one new liquid, at various temperatures, by aid of equation (1) and the normal constant k, the value taken for M would be the same, and d would be the same function of the temperature in all, while in every case, at the same temperature, γ would be proportional to its value of k, it is clear that *when the normal k (i. e., that value found for benzene) is also the real and correct molecular temperature coefficient of the new liquid, the same value* *of t_c (within the experimental error) will be found from all temperatures, not only from the results of one observer, but also independent of the origin of the results. A constant value of the calculated t_c at all temperatures, then, indicates that the normal molecular temperature coefficient k for benzene is also the correct one for this liquid, and that consequently, the liquid is non-associated, notwithstanding the misleading value of k which might be found from equation* (2).

We find then from the above, not only a new definition of normal molecular weight in the liquid state, but also a method of comparing results of surface tension of any liquid, at different temperatures, among themselves, or with drop weights, for the constant t_c calculated in each case for the liquid from the normal specific benzene value of k should always be the same, within the limits of errors, according to the results of all observers.

The above result may also be expressed graphically by plotting the change of the function $w(M/d)^{2/3}$ with the temperature. Here the values of t from 0° up are laid out on the vertical axis, those of $w(M/d)^{2/3}$ being reckoned from 0 up, *to the left*, on the horizontal axis, the temperature axis intersecting that of $w(M/d)^{2/3}$ at the value of $w(M/d)^{2/3} = 0$. The line representing the mean value for benzene begins at 0°, where $w(M/d)^{2/3}$ is large and runs to the right, ending where it intersects the temperature axis at the point t_c—6 (*i. e.*, at 288.5 —6°), where its value becomes zero. Locating the observed point $w(M/d)^{2/3}$ for any new non-associated liquid, at its proper temperature, and drawing through it a line parallel to that for benzene, *i. e.*, of the same slope *k*, we find, where it intersects the temperature axis, its value of t_c—6. Repeating this operation for other points, *i. e.*, at other temperatures for the same liquid, we get a series of parallel lines, each leading to a value of t_c—6. The mean of these values, provided the difference is within the limits of error, is then the correct value of t_c—6; *and the slope k, i. e., the value for benzene which was used is the correct one for that liquid, which must consequently also be non-associated.*

In Tables II–VI are grouped together the values of t_c as calculated in the above way from the drop weights and surface tensions from capillary rise of aniline, carbon tetrachloride, chlorobenzene, pyridine and quinoline, using in each case the value of *k* found above for benzene, where t_c = 288.5°.

TABLE II.—ANILINE, M = 93, t_c = 426.
Renard and Guye, k_B = 2.1108.

t.	*d*.	γ.	$\gamma(M/d)^{2/3}$.	t_c calc. from (1).
10.2	1.026	42.60	859.61	423.4
30.1	1.010	40.71	830.13	429.4
54.5	0.990	37.92	783.61	431.6
66.0	0.979	36.24	754.49	429.4

Average, 428.05

t.	d.	γ.	$\gamma(M/d)^{2/3}$.	t_c calc. from (1).
Dutoit and Friederich,[1] $k_B = 2.1012$.				
19.5	1.018	40.84	827.0	419.1
44.4	0.999	38.36	787.8	425.3
77.7	0.970	35.06	734.6	433.3
			Average,	425.9°
Ramsay and Shields, $k_B = 2.1012$.				
132.1	0.9212	30.23	655.4	450.0
184.5	0.8720	24.36	547.8	451.2
Morgan and Higgins, $k_B = 2.5702$.				
29.0	1.0138	49.362	1004.03	425.7
51.7	0.9944	45.902	945.76	425.7
67.1	0.9810	43.588	906.24	425.7

TABLE III.—CARBON TETRACHLORIDE, M = 153.8, t_c = 283.2.

Ramsay and Shields.				
80	...	...	414.6	283.2
100	...	...	372.3	283.2
Ramsay and Aston, $k_B = 2.1211$.				
11.8	...	...	565.7	284.5
46.0	...	...	492.6	284.2
78.0	...	...	426.3	285.0
			Average,	284.6°
Renard and Guye.				
11.8	1.610	26.93	562.76	284.4
23.8	1.587	25.74	543.08	287.1
33.0	1.569	24.60	522.99	286.8
44.5	1.546	23.21	498.32	286.6
55.3	1.525	21.97	476.01	286.8
68.0	1.500	20.38	446.46	285.5
			Average,	286.2°
Morgan and Higgins.[2]				
24.2	1.5823	30.981	645.946	285.0
54.0	1.5240	26.685	578.397	285.1

TABLE IV.—CHLOROBENZENE, M = 112.5, t_c = 360.

Ramsay and Shields.				
150	...	...	423.2	357.4
180	...	...	360.5	357.6
200	...	...	319.1	357.9
			Average,	357.6°

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[1] *Arch. sci. phys. nat.*, 9, 105 (1900).

[2] Later work with the simple form of apparatus, with a tip of 4.5 mm., where the control is perfect leads to a result for this liquid of 283.1°, which makes it appear that here on this large tip (6.2 mm.), even with long tail of liquid in the buret the drop did not fall of its own weight alone; this will be discussed in a later paper.

t.	d.	γ.	$\gamma(M/d)^{2/3}$.	t_c calc. from (1).
		Ramsay and Aston.		
9.5	1.1182	33.71	729.1	359.2
45.6	1.0795	29.30	648.8	357.5
77.8	1.0444	25.66	581.0	357.7
131.3	0.9836	19.93	469.8	357.8
			Average,	358.1°
		Renard and Guye.		
10.7	1.117	33.47	724.53	359.9
39.0	1.087	29.83	657.06	356.3
50.8	1.073	28.49	633.47	356.9
64.0	1.059	27.02	606.07	357.1
73.8	1.048	25.99	587.04	357.1
86.0	1.034	24.67	562.70	358.6
100.0	1.017	23.16	533.70	358.8
119.3	0.993	21.04	492.62	358.7
126.9	0.985	20.30	477.87	358.3
			Average,	358.2°
		Morgan and Higgins.		
8.2	1.1200	41.082	887.717	359.6
39.2	1.0856	36.628	808.106	359.6
50.8	1.0730	34.990	778.000	359.5
63.9	1.0590	32.200	744.690	359.7
72.2	1.0498	32.054	723.180	359.6

TABLE V.—PYRIDINE, $M = 79$, $t_c = 344.2°$.

		Renard and Guye.		
10.5	0.991	36.67	679.22	338.3
39.2	0.963	33.58	633.99	345.6
58.8	0.943	30.48	583.57	335.0
74.2	0.927	28.32	548.44	340.0
91.1	0.911	26.16	512.52	345.6
108.2	0.894	24.19	479.91	341.6
			Average,	341.0°
		Ramsay and Shields.		
17.0	0.9825	38.40	715.3	362.8
46.2	0.9512	34.17	650.3	360.7
		Dutoit and Friederich.		
17.5	0.985	36.69	682.7	348.4
56.3	0.946	30.86	589.6	342.9
78.6	0.923	28.53	554.0	348.3
91.0	0.911	26.54	521.1	345.0
			Average,	346.2
		Morgan and Higgins.		
10.5	0.991	45.804	848.401	346.6
39.2	0.962	40.980	774.236	346.4
58.8	0.943	38.000	727.546	347.9[1]
74.2	0.927	35.370	684.962	346.7

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[1] Error due to lack of stirring of bath; see original paper.

TABLE VI.—QUINOLINE, M = 129, t_c = $<520°$.

t.	d.	γ.	$\gamma(M/d)^{2/3}$.	t_c calc. from (1).
		Ramsay and Shields.		
15.4	1.098	45.13	1082.0	536.3
78.4	1.044	37.44	928.7	526.4
		Bolle and Guye,[1] k_B = 2.1011.		
10.5	1.1013	41.34	1054.6	518.4
57.6	1.0641	40.10	982.1	531.0
108.2	1.0233	34.36	863.8	525.3
149.8	0.9299	28.24	756.9	515.0
			Average,	522.4°
		Renard and Guye.[2]		
8.2	1.103	44.71	1069.27	520.8
31.0	1.084	41.97	1015.42	517.1
55.0	1.066	39.35	962.96	517.2
65.2	1.058	38.20	939.29	516.0
80.5	1.046	36.50	904.34	514.9
98.0	1.032	34.71	867.75	515.1
			Average,	516.9°
		Morgan and Higgins.		
30.7	1.0852	51.525	1245.68	521.4
55.0	1.0658	48.344	1182.91	521.3
65.0	1.0576	47.053	1157.27	521.3[3]

A glance at the t_c values calculated from the capillary rise results for the five additional liquids, using for all the normal change per degree in the value of the function $w(M/d)^{2/3}$, as found for benzene, will serve to show that in general there is either no decided trend in the values for any one case, or that if there is such a trend it is negatived by either an opposit trend, or no trend at all, in the work of one of the other observers; and that throughout the average results from drop weight agree (within a reasonable error) with those of the others. As far as concerns aniline, it is true that the absence of trend is shown only by Renard and Guye, whose results at 66° is the same as that at 30.1°, although the value between them is larger; but this irregularity certainly shows the possibility of an error as high as 0.5 per cent., at any rate. It must be remembered here, however, that aniline, in addition to its high viscosity, is characterized by its extreme stickiness, which is so persistent that the traces of liquid can be removed from a tube only by aid of some solvent; the combination of these two properties, consequently, would make the re-

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[1] *J. Chim. Phys.*, 3, 40 (1905).

[2] The authors here used Kahlbaum's quinoline, without redistilling it. With drop weight the preparation which contains water always gives a result about 1 per cent. too low in value, *i. e.*, about 516° for t_c. It is always to be redistilled just before using.

[3] By an error in the original paper this read 68° in place of 65°.

sults for aniline, more than for any other liquid, open to suspicion in any method depending upon the position assumed by a column in a fine capillary tube when it is drawn above its normal position, and then allowed to settle into it. Even with the drop weight method, the greatest care must be exercized to keep this liquid out of the capillary before the liquid for the first drop is allowed to run over, for otherwise the liquid which adheres will be formed into threads and forced out ahead of the drop; and between determinations the dropping tube must be cleansed out with ether and dried.

The results of Ramsay and Shields for aniline, pyridine, and quinoline are probably incorrect, as they disagree with the results of the other investigators, using the same method. That in the case of aniline the high t_c found by them is not simply the result of the trend is shown by the fact that Renard and Guye at 175°, *i. e.*, a temperature lying between those of Ramsay and Shields find a value of only 436.8° (as against their 450°) which is little more than 1 per cent. larger than the value at 54.5°.

When it is remembered, further, that the results by drop weight are so free from variable error that the k for benzene from (1), as used above, has practically the same value as that found for all the liquids by (2), where the k values from capillary rise as calculated from (2) varies for all irregularly and in a meaningless way, *we must concede that this method of finding k from* (1) *justifies the conclusion that all these liquids not only by drop weight, but also capillary rise, are absolutely non-associated, i. e., have the same molecular temperature coefficient of surface tension, as has benzene which is taken as a standard, notwithstanding the meaningless values of k found (from capillary rise) by equation* (2), *which vary from 1.88 to 2.44 in place of the assumed normal value 2.12.*

It has been shown by Walden[1] that the critical temperature of a liquid can also be found from surface tension by a method which does not necessitate a knowledge of its molecular weight. This method is based upon a knowledge of the temperature coefficient of surface tension and that of the capillary constant. Since the drop weight is proportional to the surface tension and the drop volume ($v = w/d$) to the capillary constant, this method must also be applicable to the drop results above. Walden's values of α' and α'' should then be given by the equations

$$w_t = w_o(1-\alpha' t) \text{ and } v_t = v_o(1-\alpha'' t).$$

The values of α' and α'' should be approximately proportional inversely to the critical temperature in such a way that a variation in one is compensated by the opposit variation in the other, so that the mean leads to the correct critical temperature.

By combining the two relationships

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[1] *Z. physik. Chem.*, 65, 175 (1908).

$$\alpha' \times a = t'_c \text{ and } \alpha'' \times b = t''_c,$$

remembering that $\frac{t_c' + t_c''}{2} = t_c$, where a and b are constants, we find

$$t_c = \text{constant } \frac{\alpha' + \alpha''}{\alpha'\alpha''}. \qquad (6)$$

It will be noted here, of course, that the α' and α'' values are susceptible to the same error that k by (2) is, but notwithstanding this (6) should lead, if the relationship is correct, to practically the same values of t_c found above, when the value of the constant is found for benzene. The values of α' and α'' found for drop weight should, of course, be the same as those calculated for surface tension, for they represent only a percentage change per degree in the property. In Table VII are given these values, as found from the drop weights of Morgan and Higgins, as well as those found by Walden from the mean of all the results of surface tension from capillary rise, together with the values of t_c as calculated for each.

TABLE VII.[1]

	Drop weight.			Surface tension.		
Liquid.	α'.	α''.	t_c.	α'.	α''.	t_c.
Benzene	0.004130	0.003231	[288.5]	0.00416	0.00329	288.5°
Aniline	0.002819	0.002167	426.9	0.00261	0.00208	448
Carbon tetrachloride	0.004182	0.003268	285.1	0.00418	0.00337	279
Chlorobenzene	0.003339	0.002565	360.5	0.00311	0.00266	363
Pyridine	0.003447	0.002661	348.3	...	0.00258	..
Quinoline	0.002347	0.001738	523.8	0.00260[2]	0.00196	..

It is quite clear from the above that this empirical relationship holds better for drop weight than it does for capillary rise, as a means of calculating t_c independently of the molecular weight. If the variation in calculated t_c by equation (1) is large, the value calculated by (6) will depend upon whether the t_c from (1) increases or decreases with the temperature.

It will be noted from the tables that the values calculated for t_c from k_B agree satisfactorily for the liquids considered with the values of critical temperature observed directly. A survey of the literature, however, shows that this is not always the case, although it appears at present as if enough liquids giving the observed value of the critical temperature, with the normal constant k, will be gained, such as pyridine, aniline, and quinoline, to compensate for those which by this method of calculation will give a differing value, but which by a combination of errors gave with the k of (2) the correct value.

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[1] The (benzene) constant for drop weight in (6) is 0.52299, from which the other values of t_c are calculated. The values of Walden are those given by him, using an average constant.

[2] From Ramsay and Shields only.

The great gain by this point of view, however, *is the possibility that by it we may simplify the definition of the normal molecular weight of substances in the liquid state,* which at present is in an extremely unsatisfactory form. It would seem as if the following three important classes of liquids can be distinguished:

I. Those liquids for which the normal (benzene) value of k leads in equation (1) to a value of t_c which agrees closely with the observed value of the critical temperature, at all temperatures.

II. Those liquids for which the normal (benzene) value of k leads in equation (1) to the same calculated value of t_c (within a reasonable error), at all temperatures, but which differs from the observed critical temperature; in some cases, considerably.

III. Those liquids which with the normal (benzene) value of k lead to a calculated value of t_c which is not only lower than that observed, but which increases with an increase in the temperature of observation. This is the typical case of an associated liquid (water, ethyl alcohol, methyl alcohol, and acetic acid) where $w(M/d)^{2/3}$ is not a linear, but a curvilinear, function of the temperature. The true critical temperature can be found in this case by first obtaining the equation of the curve, as has already been done by Morgan.[1]

In cases I and II the liquids are non-associated, *i. e.*, the normal molecular temperature coefficient leads to a satisfactory, constant, value of the term t_c. Case II here would differ from I only that the function does *not become zero at 6 degrees below the observed critical temperature,* but *6 degrees below another, fictitious, temperature*—in other words, the conditions of corresponding states (as judged by the distance from the critical temperature) are fulfilled for those liquids in class I, but for an unknown reason are not fulfilled for those in II.

All these cases, together with the anomalous malic esters, which lead in (2) to a k value greater than 3, as well as water solutions, are now being studied in this laboratory by the drop weight method, and will be discussed as the results are reported.

Of the application of this point of view to the very recent work of Walden[2] on tripalmitin and tristearin, which by (2) give a k value of from 5 to 6, it may be said that using the normal k value of 2.126, as calculated from his results for benzene, it is found that the trend downward in the calculated value of t_c amounts to roughly 7–8 per cent. When we consider here that the difference in the height of ascension between 57.7° and 134.7° is but 0.455 cm. (*i. e.*, from 3.017–3.472) for one, and but 0.4 cm. (*i. e.*, from 3.012–3.412) for the other between 33.7° and 125.1°; and that at 90° the viscosity of tripalmitin is equal to, and that of tri-

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[1] THIS JOURNAL, 31, 309 (1909).

[2] *Z. physik. Chem.*, 75, 555 (1910).

stearin, at the same temperature, is 1.18 times, the viscosity of a 40 per cent. sugar solution at 0°, and the density is 0.84–0.89, while the bore of the capillary tube is but 0.0193 cm., it is perhaps more logical to assume that possibly an unrecognized error exists to the extent of from 7 to 8 per cent. in one of the extremes, rather than to conclude that the liquids are dissociated in an unknown way to such an extent that 5 moles are produced from every one originally present. At any rate until the results are carried to higher temperatures, and precautions taken to eliminate the possibility of the above errors, we can hardly consider these liquids as belonging to a new group, as perhaps the liquefied gases, which give low, but constant, values of k, may. It is to be remembered here that no claim is made that all liquids must be included in these classes, although it is quite certain that by this point of view a very large number of liquids, hitherto regarded as anomalous in their behavior, will be proven to be perfectly normal.

It was at first intended to include in this paper a discussion of the relationships existing between drop weight and the various other physical constants of a liquid, but it was thought best to defer that until a larger number of results had been reported upon. It will consequently form the subject of a later paper.

The results of this paper may be summarized as follows:

I. A method is presented for standardizing a tip, *i. e.*, for finding the normal molecular temperature coefficient, k, of all the non-associated liquids falling from it, which is based solely upon the equation $w(M/d)^{2/3} = k(t_c - t - 6)$, and does not make use of the differentiated form of Ramsay and Shields for results from capillary rise, *viz.*: $\Delta[w(M/d)^{2/3}]/\Delta t = k$, with its customary multiplication of the experimental error.

II. It is then shown that the surface tension in dynes of any liquid at any temperature can be calculated from its drop weight in milligrams from any tip at that temperature by multiplying the latter by the ratio of the k value of surface tension, to the k value for that tip, both being found by use of benzene ($t_c = 288.5°$) as the standard.

III. Any liquid which, with this normal (benzene) value of k, gives the same calculated value of t_c, within the limits of error, at all the temperatures of observation, is then to be regarded as a normal non-associated liquid, for this proves that the normal k is also the proper and correct change per degree of its molecular function.

Attention is called here to the fact that this calculated t_c need not always agree with the observed value of the critical temperature, which would indicate that while some liquids are in corresponding states when equally removed from their critical temperatures, others are so only when equally removed from another, fictitious, one.

IV. Aniline, pyridine, and quinoline from this point of view are shown to be perfectly normal in molecular weight, even from the results of capillary rise, although the customary method of calculating k shows the two first to be associated, and the latter dissociated. This confirms the results of drop weight, which being freer from variable error shows the k value for these to be normal, even when calculated in the customary way.

V. It is shown that the application to drop weights of the empirical formula for the calculation of t_c, without a knowledge of the molecular weight, as given by Walden, leads to results which differ but slightly from those calculated by the aid of the normal constant k_B.

LABORATORY OF PHYSICAL CHEMISTRY.

[CONTRIBUTIONS FROM THE HAVEMEYER LABORATORIES OF COLUMBIA UNIVERSITY, No. 187.]

THE WEIGHT OF A FALLING DROP AND THE LAWS OF TATE. V. THE DROP WEIGHTS OF FIFTEEN NON-ASSOCIATED LIQUIDS AS FOUND BY USE OF THE NEW FORM OF APPARATUS, AND THE MOLECULAR WEIGHTS CALCULATED FOR THEM.

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Introduction.

The object of this paper is to present the results of a testing of the Morgan drop weight apparatus, recently described, for the following purposes:

I. To show that the results of Morgan and Higgins can be duplicated with an apparatus of such simplicity that it can be used as a general laboratory method.

II. To apply the new definition of normal molecular weight of a liquid, recently presented by Morgan, and expressed solely in the equation $w(M/d)^{2/3} = k(t_c - t - 6)$, to further liquids; *not only to those cases where the calculated value of* t_c, *constant at all temperatures of observation, agrees with the observed critical temperature, but also, and especially, to those where it does not.*

The Standardization of the Tip.

Several months were spent at the beginning of this research on a study of the best form of tip to be used in the new apparatus, where a number of drops, formed successively, are weighed. The beveled tips which, naturally, were first tried, showed apparently that slight differences in the angle of the bevel caused differing results, although several beveled tips were found to be excellent. It was just at this time, however, that it was found possible by the grinder to produce the straight sharp-edged tips already described, so that no further work was done with beveled ones. It must be conceded, therefore, that *in the light of our present knowledge, when all the possible variables affecting a tip are known, no*