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* *very thorough test has been made of beveled tips, so that it is quite likely that in result they would now be found quite as satisfactory as those with the straight sharp edges.* The use of these latter, however, it must be confessed, is more satisfactory for other reasons, for on them any rise of liquid on the edge can be at once recognized; the diameter can be measured more accurately, and any attempted mathematical treatment is simplified, owing to the fact that the only variable of the tip necessary to be considered is its diameter.

The diameter of the straight-edged tip used in this research was approximately 5.63 millimeters, the bore being about 0.2 millimeter. The experimental results obtained with this tip for the six liquids already investigated by Morgan and Higgins, with the more elaborate form of apparatus, are contained in Tables I–VI.

TABLE I.—BENZENE.

Temp.	Wt. of vessel + 30 drops.	Average.	Wt. of vessel + 5 drops.	Average.	Av. temp.	Wt. 1 drop. Mg.
18	11.2498	11.2498	10.4758	10.4758	18	30.96
18	11.2498		10.4758			
60.3	11.0865	11.0863	10.4587	10.4587	60.3	25.104
60.3	11.0861		10.4587			

TABLE II.—QUINOLINE.

Temp.	Wt. of vessel + 30 drops.	Average.	Wt. of vessel + 5 drops.	Average.	Av. temp.	Wt. 1 drop. Mg.
18	11.7616	11.7615	10.5590	10.5590	18	48.10
18	11.7614		10.5590			
60	11.6091	11.60915	10.5316	10.5318	60.05	43.094
60.1	11.6092		10.5320			

TABLE III.—CARBON TETRACHLORIDE.

Temp.	Wt. of vessel + 30 drops.	Average.	Wt. of vessel + 5 drops.	Average.	Av. temp.	Wt. 1 drop. Mg.
18.7	11.2020	11.20185	10.4805	10.4806	18.7	28.85
18.7	11.2017		10.4807			
59.1	11.0679					
59.25	11.0680		10.4792			
59.4	11.0668	11.0673		10.47845	59.34	23.554
59.5	11.0666		10.4777			
59.45	11.0672					

TABLE IV.—CHLOROBENZENE.

Temp.	Wt. of vessel + 30 drops.	Average.	Wt. of vessel + 5 drops.	Average.	Av. temp.	Wt. 1 drop. Mg.
18.3	11.3892	11.3893	10.4926	10.4926	18.3	35.868
18.3	11.3894		10.4926			
60.5	11.2365	11.2367	10.4748	10.4748	60.5	30.476
60.5	11.2369		10.4748			

TABLE V.—ANILINE.

Temp.	Wt. of vessel + 30 drops.	Average.	Wt. of vessel + 5 drops.	Average.	Av. temp.	Wt. 1 drop. Mg.
22	11.6913	11.69115	10.3167 (empty vessel)		22	45.815
22	11.6910					
60.5	10.5229 (5 drops)		10.3206 (empty vessel and vapor)		60.5	40.475
60.5	10.7255 (10 drops)					

TABLE VI.—PYRIDINE.

Temp.	Wt. of vessel + 30 drops.	Average.	Wt. of vessel + 5 drops.	Average.	Av. temp.	Wt. 1 drop. Mg.
18.2	11.5238	11.52375	10.5145	10.5145	18.25	40.37
18.3	11.5237		10.5145			
60.1	11.3456	11.3458	10.4926	10.4924	60.1	34.136
60.1	11.3460		10.4922			

These results were obtained more than a year ago, before the effect of even the slightest trace of impurity in the liquid was observed (for none but the purest samples were studied by Morgan and Higgins), and before the necessity of washing out the tip and ventilation tubes with ether between determinations of aniline and such liquids was recognized. But although somewhat better results, in the light of our present knowledge, can be obtained for these liquids to-day, these are presented here as the first results obtained with the later form of apparatus. The main object of this test was to show that, using the critical temperatures actually calculated by Morgan and Higgins for these six liquids, from their practically identical value of $k_{\text{temp.}} = \Delta[w(M/d)^{2/3}]/\Delta t$, a k value can be calculated from the results on the later form of apparatus which is also practically identical at all temperatures. For this purpose the k values necessary to give t_c in $w(M/d)^{2/3} = k(t_c - t - 6)$ a value equal in each case to that found for that liquid by Morgan and Higgins have been calculated, and are presented in Table VII. The densities employed here are those calculated by aid of the following formulas, obtained from the values experimentally determined by Morgan and Higgins.

Benzene, $d_t = 0.90022 - 0.001066\ t$.
Quinoline, $d_t = 1.10989 - 0.0008035\ t$.
Chlorobenzene, $d_t = 1.12870 - 0.001092\ t$.
Pyridine, $d_t = 1.00150 - 0.001002\ t$.
Aniline, $d_t = 1.03880 - 0.0008605\ t$.
Carbon tetrachloride, $d_t = 1.62965 - 0.001956\ t$.

TABLE VII.—VALUES OF $w(M/d)^{2/3}$ AND OF k.

Liquid.	M.	t.	w.	d.	$w(M/d)^{2/3}$.	k	necessary to give t_c of M. and H.	
Benzene....	78	18	30.960	0.88103	614.993	2.3260	2.3257	288.4°
		60.3	25.104	0.83594	516.443	2.3253		
Quinoline...	129	18	48.100	1.0943	1156.415	2.3296	2.3286	520.4°
		60.05	43.094	1.0616	1057.230	2.3269		
Chlorobenzene......	112.5	18.3	35.868	1.1087	780.308	2.3279	2.3277	359.5°
		60.5	30.476	1.0626	682.003	2.3276		
Pyridine....	79	18.25	40.370	0.9832	751.707	2.3298	2.3297	347.0°
		60.1	34.136	0.9413	654.353	2.3295		
Aniline.....	93	22	45.815	1.0199	928.164	2.3332	2.3320	425.8°
		60.5	40.475	0.9867	838.273	2.3331		
Carbon tetrachloride...	153.8	18.7	28.850	1.5931	607.140	2.3307	2.3317	285.2°
		59.34	23.554	1.5136	512.895	2.3328		
						Average,	2.3294 ± 0.001 (= 0.05%)	

Here it is quite evident that the tip is too large for the use of carbon tetrachloride, for even the above results, which were only obtained after long practice and after many attempts to control the speed of formation of the drop at the moment of fall, were known to lack perfect control, and consequently are certainly slightly too large. In such cases *it is always observed that the error due to lack of control is about the same at all temperatures, when the best control possible on that piece of apparatus is attained; so that the new definition of normal molecular weight is found to hold also under these conditions, although, of course, the constant t_c calculated is larger than that observed with perfect control.* Experiments undertaken since by other observers in this laboratory have shown that when perfect control certainly exists (for example with a tip of about 4.5 mm. in diameter) the t_c calculated for carbon tetrachloride, from its normal (benzene) value of k (*i. e.*, that necessary to give $t_c = 288.5°$, see the previous paper of this series) is reduced by 0.7 per cent: or to 283.2°, which is not only the value to be found from the capillary rise results of Ramsay and Shields, but is also in perfect agreement with the directly observed critical temperature. The agreement of the value in the Table with that of Morgan and Higgins would indicate, then, that the higher value 285.2° as found by them on the 6.2 mm. tip was also high, due to an unsuspected lack of control, even though the long tail of liquid in the fine capillary buret would tend to slow it up considerably. At any rate, with the new form of apparatus, it is quite certain that if carbon tetrachloride is to be included in the liquids studied with any one piece of apparatus, and the drop perfectly controlled, as are those of all the other liquids, the tip must not be larger than about 4.5 mm., upon which all other liquids also give satisfactory results.[1]

The aniline values here are slightly larger than those which are now being found, taking the necessary precautions, as made clear in No. III of this series, and are due either to the fact that the aniline was not freshly distilled just before the experiment, or to the unrecognized presence of very small threads of liquid which were pushed ahead of the drop. This difficulty is now avoided by washing out the bore with ether between determinations, and then preventing any rise of liquid in the tube until the first drop is sucked over. The results for pyridine are also slightly larger than those now being found, which is probably due to a very slight impurity in the sample used.

The above values for chlorobenzene are not those found by the usual procedure, but only when the drops are formed very rapidly and then checked suddenly at the last moment. In this case there is no question of the drop forming too rapidly, and thus giving too high a result, but rather that any evaporation back to the hanging drop from the liquid which has already fallen, such as was observed by Morgan and Higgins,

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[1] In a later paper will be given the results of an extended study with various liquids on tips varying from 3 to 8 millimeters.

is prevented. That this higher result is not due to rapid formation can be shown by first placing in the weighing vessel a small amount of albolene, containing some chlorobenzene, and, after getting its weight, placing it upon the apparatus, and allowing 30 drops to form in the usual way. Each drop as it falls now sinks below the surface of the albolene, and consequently none of the fallen liquid can evaporate back to the hanging drop. Naturally, a blank of 5 drops must also be treated in the same way. This form of procedure leads to the same results as the above, using t_c = 359.5°[1] The *usual* procedure here, on the new form of apparatus, in contrast to this leads in all cases to the correct k value only when t_c is taken as 357.5°, and it is a question which is the correct value, the one requiring the use of t_c = 357.5°, as obtained by every one using the regular procedure and agreeing with the capillary rise value of Ramsay and Shields; or the 359.5°, which is only obtained under other conditions, and agrees more closely with the observed value of the critical temperature. *It is thought, however, that the 357.5° value is the correct one, as there seems to be no behavior of the liquid which would not be corrected by the 5-drop blank, with the 6th drop hanging long enough to make the elapsed time equal in both cases.*

Even though the results above are not quite as accurate as those which are now being obtained, *and sources of error are undoubtedly found which would correct under proper conditions, with the new form of apparatus, the values of carbon tetrachloride and of chlorobenzene of Morgan and Higgins, it will be seen that they check very satisfactorily those of the latter on the more elaborate apparatus (and this on a smaller tip, which has a straight sharp edge, instead of being beveled) for in both cases the mean error in the k value is about the same.*

This, of course, is not the best way to standardize a tip, and is used here only to show that the results of Morgan and Higgins can be duplicated on the simpler form of apparatus. The best method of testing the k value of a tip as found from benzene by assuming its t_c to have the value 288.5°, the observed critical temperature, is to calculate the value of k necessary to give t_c the values found by Morgan and Higgins from their normal (benzene) value of k, see previous paper of this series. These values, as corrected, are 357.5° for chlorobenzene, 425.7° for aniline, 283.2° (a tip of 4.5 mm.) for carbon tetrachloride, 346.6° for pyridine, and 521.3° for quinoline. These values of k will not disagree, with careful work and pure liquids, by more than one-tenth of one per cent., if by as much.

It is evident here that drop weights from this tip are related, at the same temperature, to those found on that of Morgan and Higgins, as the k

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[1] Miss C. M. Sillcox is now investigating this and another liquid in this way.

value above for benzene (t_c = 288.5°) is to the correspondingly found value of k for their tip, *i. e.*,

$$w_{M\,\&\,T} : w_{M\,\&\,H} :: 2.3257 : 2.5702;$$

and that the surface tension in dynes per centimeter can be calculated from the drop weights in milligrams by aid of the proportion

$$\gamma : w_{M\,\&\,T} :: k : 2.3257,$$

where k would be the value for benzene found by the observer whose work is to be compared with drop weight; or the average value of k found by all those who have worked with the capillary rise method on benzene.

New Liquids.

The new liquids selected to show the application of the method, and of the new definition of normal molecular weight in the liquid state, are the following; ether, ethyl *n*-butyrate, chloroform, phenetole, anisole, benzonitrile, ethylene dibromide, carbon disulfide, and a mixture of equal weights of benzene and carbon tetrachloride.

The experimental results for these are given in Tables VIII to XVI, inclusive.

TABLE VIII.—ETHER.

t.	Wt. vessel + 30 drops.	Av.	Wt. vessel + 10 drops.	Av	Av. *t.*	Wt. 1 drop. Mg.
25.6	8.7111		8.3681			
26.0	8.7089	8.70933	8.3674	8.36775	25.9	17.079
26.1	8.7080					

TABLE IX.—ETHYL *n*-BUTYRATE.

	+ 25 drops.		+ 5 drops.			
26.2	11.0712	11.0707	10.5746	10.5749	26.4	24.74
26.6	11.0702		10.5752			
59.0	10.9722		10.5458			
59.3	10.9708	10.9714	10.5454	10.5456	59.2	21.29
59.3	10.9712					

TABLE X.—CHLOROFORM, b. p. = 61.2°.

22.4	10.7930	10.7926	10.2139	10.2135	22.45	28.955
22.5	10.7922		10.2131			
60.0	11.4155					
60.1	11.4233		10.9512			
60.3	11.4230	11.4221	10.9525	10.9520	60.18	23.505
60.3	11.4266		10.9523			

TABLE XI.—PHENETOLE.

	+ 30 drops.					
22.9	11.7286					
23.1	11.7288	11.7289	10.8665	10.86675	23	34.486
23.0	11.7293		10.8670			
60.0	11.6042					
60.3	11.6031	11.6031	10.8462	10.84675	60.2	30.254
60.3	11.6023		10.8473			

TABLE XII.—BENZONITRILE.

t.	Wt. vessel+ 30 drops.	Av.	Vessel + 5 drops.	Av.	Av. t.	Wt. 1 drop. Mg.
21.8	11.9303					
21.6	11.9301	11.9303	10.8987	10.8987	21.63	41.264
21.5	11.9304					
60.1	11.7868	11.78705	10.8795	10.8794	60.1	36.306
60.1	11.7873		10.8793			

TABLE XIII.—ANISOLE.

22.5	11.8027	11.8029	10.8797	10.87995	22.45	36.918
22.4	11.8031		10.8802			
60.0	11.6663	11.6661	10.8575	10.8574	60.0	32.348
60.0	11.6659		10.8573			

TABLE XIV.—ETHYLENE DIBROMIDE.

24.4	12.0607	12.0606	11.0272	11.0272	24.3	41.336
24.2	12.0605					
60.5	11.9143	11.9140	11.0084	11.0084	60.5	36.224
60.5	11.9137		11.0084			

TABLE XV.—CARBON DISULFIDE.

24.5	11.8167	11.81705	10.9819	10.98175	24.4	33.412
24.3	11.8174		10.9816			
3.9	11.9283	11.9290	11.0013	10.00155	3.8°	37.098
3.7	11.9297		11.0018			

TABLE XVI.—BENZENE AND CARBON TETRACHLORIDE; 1 : 1 BY WEIGHT.

23.6	11.6925	11.6926	10.9677	10.9676	23.6	29.00
23.6	11.6927		10.9675			

To show that the new definition of normal molecular weight (see No. IV of the series) may be applied to the above liquids, *i. e.*, to prove that using the normal (benzene) value of k, as found from the relationship $w(\mathrm{M}/d)^{2/3} = k_\mathrm{B}(288.5-t-6)$, in $w(\mathrm{M}/d)^{2/3} = k_\mathrm{B}(t_c-t-6)$, will give a constant value, within the limits of error, of the calculated t_c for each new liquid, independent of the temperature of observation t, the values of the functions $w(\mathrm{M}/d)^{2/3}$, together with the calculated value of t_c at each temperature, are given in Tables XVII to XXV. At the same time the corresponding values of the function, expressed as a surface tension in dynes, as found from capillary rise, and the calculated values of t_c as found from the benzene value, k_B, of the same observer, are given, so far as they are to be found in the literature.

This method of comparing drop weight with surface tension (and the results of the latter among themselves) is used here in preference to the one involving the direct transformation of w into γ, because of the fact that the temperatures of observation are not the same, and it is desired to avoid any interpolation so long as the direct experimental results can be employed. In essence it will be seen that this comparison, by finding the calculated t_c from the work of each observer, *i. e.*, from the equations

$$\gamma(M/d_1)^{2/3} = k_B(t_c—t_1—6)$$

and

$$w(M/d_2)^{2/3} = K_B(t_c—t_2—6),$$

where M is the same in all cases for the same liquid, γ/k_B is equal to w/K_B, and d_1 and d_2 are dependent in the same way upon the temperature t, is the same as transforming the drop weight w in milligrams, into surface tension in dynes, γ, (by multiplying it by the ratio k_B/K_B) and then by the use of the same k_B to show that the $\gamma(M/d)^{2/3}$ is the same function of the temperature, whether calculated from drop weight or capillary rise, and consequently leads to the same calculated t_c. *In other words, when the same t_c is thus found from the results of drop weight, and from those of capillary rise, it means that*

$$\gamma : w : k_B : : K_B,$$

at the same temperature, is the correct relationship for that liquid.

Perhaps the greatest advantage offered by this method of comparison is the saving in the calculation necessary, for if the γ values were calculated from the drop weight, they would all differ slightly, according as the k_B values of the various observers in question differ; and as many values of γ would have to be calculated as there are individual observers, whose results are to be contrasted, before calculating, for the equalization of the temperature, a t_c value from each, with its own proper k_B value. By the method chosen, however, all this is avoided, by simply finding from the work of each observer *the value of t_c resulting from his function value and temperature, by use of his normal (benzene) k value, and then comparing them.*

One thing must be remembered here before drawing any conclusion as to the results of surface tension found by the transformation of w into γ by multiplying it by k_B/K_B, *viz.*: the *value of surface tension in dynes, as calculated from the drop weight is a directly determined weight, multiplied by a ratio, which can be found once for all with practically any desired degree of accuracy. Surface tension when calculated from capillary rise, on the other hand, is a value found by multiplying one-half the radius (assumed to be the same throughout) of a very fine capillary bore, by the density of the liquid, less that of the vapor, by a height of ascension in that tube, which is burdened with a correction for the volume of the meniscus, which may amount to as much as from 6 to 9 per cent.* Further than this, the function value $^1/_2\, h\, r\, (d_l—d_v)(M/d)^{2/3}$ is affected to double the percentage extent that $w(M/d)^{2/3}$ is (neglecting the value of d_v), by a known error in d, as can be shown by a differentiation of the two functions and then dividing them by the original values.

As is also evident here, from the drop weight it is possible to find a number *which is proportional to the so-called capillary constant at that temperature, provided the density is also known at that point.* This can be shown as follows: Since

$$w_t \propto \gamma_t$$

and

$$\gamma_t = {}^1/_2\, h_t\, r\, (d_e - d_v),$$

while for the capillary constant a^2 we have the relationship

$$a_t^2 = h_t r,$$

it follows that

$$w_t/d_t \propto \frac{{}^1/_2\, h_t\, r\, d_t}{d_e - d_v},$$

and

$$v_t = w_t/d_t = \text{constant} \times a_t^2;\ \text{or}\ v_t \propto a_t^2.$$

The capillary constant of any liquid varies directly as the volume of the drop, falling from any one tip, at that temperature.

TABLE XVII.—ETHER, M = 74.08: t_c obs. = 194.5°.

t.	w.	d.	$w(\mathrm{M}/d)^{2/3}$.	t_c from k_B = 2.3257.
25.9	17.079	0.7071	379.56	195.1°
	Ramsay and Shields,[1] k_B = 2.1012.			
20	..	..	363.7	199.1
40	..	..	317.4	197.1
70	..	..	251.0	195.5
80	..	..	229.5	195.2
80	..	..	229.5	195.2
90	..	..	208.1	195.0

TABLE XVIII.—CHLOROFORM, M = 119.33, t_c obs. = 260° and 258.8°.

22.45	28.955	1.4840	539.43	260.6
60.18	23.505	1.4107	451.59	260.4[2]

TABLE XIX.—ETHYL *n*-BUTYRATE, M = 116.096; t_c obs. = 292.8° and 304.3°.

26.4	24.79	0.87207	646.33	310.3
59.2	21.29	0.83710	570.41	310.4

TABLE XX.—PHENETOLE, M = 122.08; t_c obs. = 374°.

23.0	34.486	0.9638	869.79	403.0
60.2	30.254	0.9278	782.67	402.7
	Renard and Guye,[3] k_B = 2.1108.			
10.5	33.19	0.976	830.11	406.0
44.0	29.15	0.944	745.42	403.2
52.1	28.31	0.936	728.09	403.0
63.9	27.07	0.925	701.71	401.9
71.7	26.21	0.917	683.07	401.5

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

[2] Boiling point of chloroform is but 1° above this temperature.

[3] *J. Chim. Phys.*, **5**, 81 (1907).

t.	w.	d.	$w(M/d)^{2/3}$.	t_c.
88.9	24.39	0.901	643.42	399.7
99.6	23.20	0.890	617.06	397.9
117.8	21.45	0.873	577.89	397.6
133.1	19.87	0.857	542.05	395.9
150.6	18.28	0.840	505.31	396.0
164.9	16.79	0.825	469.73	393.4

Guye and Baud,[1] k_B = 2.1012.

19.2	32.60	0.9672	819.91	415.7
63.6	27.25	0.9249	706.1	405.6
108.7	22.70	0.8818	607.3	403.7
152.4	18.22	0.8380	504.2	398.4

TABLE XXI.—ANISOLE, M = 108.06; t_c obs. = 368.5°.

22.45	36.918	0.9900	843.19	391.0
60.0	32.348	0.9563	756.07	391.1

Renard and Guye, k_B = 2.1108.

11.1	35.02	1.000	794.5	393.5
33.5	32.51	0.980	747.6	393.7
54.0	30.00	0.962	698.4	390.9
63.1	28.86	0.953	676.1	389.4
76.1	27.47	0.940	649.5	389.8
88.0	26.12	0.929	622.5	388.9
98.6	24.97	0.918	599.7	388.7
109.0	23.74	0.908	574.4	387.1
119.0	22.64	0.897	552.2	386.6
135.9	20.86	0.880	515.4	386.1
147.9	19.59	0.868	488.4	385.3

Guye and Baud, k_B = 2.1012.

9.0	35.48	1.0022	803.5	397.4
54.6	30.36	0.9610	695.9	391.8
98.8	24.80	0.9178	595.5	388.2
152.9	19.28	0.8622	482.6	388.6

TABLE XXII.—BENZONITRILE, M = 103.05; t_c obs. = 426.2°.

21.63	41.264	1.0020	905.8	417.1
60.10	36.306	0.9674	815.8	416.9

Renard and Guye, k_B = 2.1108.

12.3	38.44	1.012	838.2	415.4
21.0	37.43	1.004	820.5	415.7
30.5	36.41	0.995	803.0	416.9
46.8	34.54	0.980	769.5	417.4
59.1	33.24	0.969	746.1	418.6
67.8	32.30	0.963	728.0	418.7
86.8	30.19	0.944	689.6	419.5
99.8	28.83	0.932	664.2	420.4

[1] *Arch. sci. phys. nat.*, 4th series, 11, 449–471, and 537–556 (1901). These authors used Ramsay and Shields' values of γ for benzene to find the radius of their capillary, hence k_B of Ramsay and Shields is employed above.

t.	w.	d.	$w(M/d)^{2/3}$.	t_c.
108.9	27.85	0.924	645.3	420.6
131.3	25.49	0.904	599.3	421.2
150.1	23.66	0.887	563.3	423.0
167.0	22.03	0.872	530.5	424.3
184.1	20.42	0.856	479.9	426.0

Guye and Baud, k_B = 2.1012.

8.0	39.61	1.1016	861.4	424.0
54.9	33.82	0.9726	757.0	421.2
99.1	29.30	0.9388	673.9	425.8
152.4	23.53	0.8848	561.0	425.4

Ramsay and Shields, k_B = 2.1012.

18.1	36.22	1.0070	792.7	401.4
46.3	32.88	0.9806	731.8	400.6
78.3	29.29	0.9526	664.8	400.7

TABLE XXIII.—ETHYLENE DIBROMIDE,[1] M = 187.87; t_c obs. = 309.8°.

24.3	41.336	2.1623	810.88	379.0
60.5	36.224	2.0886	727.22	379.2

Ramsay and Aston, k_B = 2.1211.

12.2	38.91	2.1873	757.7	375.4
44.9	34.57	2.1189	687.7	375.1
77.2	30.37	2.0502	617.6	374.4
131.3	23.74	1.9315	502.2	374.1

TABLE XXIV.—CARBON DISULFIDE; M = 76.14; t_c obs. from 271.8° to 279.6°.

3.8	37.098	1.2865	563.4	252.1
24.4	33.412	1.2556	515.7	252.1

Ramsay and Shields, k_B = 2.1012.

19.4	33.58	1.264	515.4	270.2
46.1	29.41	1.223	461.4	271.7

Ramsay and Aston,[2] k_B = 2.1211.

9.7	32.73	1.2773	499.2	251.1
46.0	27.68	1.2224	434.8	257.0
61.0	25.35	1.1980	403.6	257.4

TABLE XXV.—BENZENE AND CARBON TETRACHLORIDE, 1 : 1 BY WEIGHT.[3]

Av. M = 115.9, Av. t_c = 287.1° $\left(i.e., \frac{288.5 + 285.8}{2}\right)$.

23.6	29.00	1.2293	600.74	287.9

Ramsay and Aston, k_B = 2.1211, t_c calc. = 286.5.[4]

16°	27.70	1.2597	561.9	286.9
46.2	23.50	1.2095	492.0	284.2
78.2	19.71	1.1596	424.5	284.3

[1] This liquid gives a drop volume of the same order as carbon tetrachloride, so this value may be too high, but at any rate its constancy by both methods shows normal molecular weight.

[2] The authors state that it was impossible to duplicate the higher results of Ramsay and Shields.

[3] No special precautions were taken in making this mixture.

[4] Ramsay and Aston find a mean of 284.6° for t_c for carbon tetrachloride from this k_B (see No. IV of this series). The value above is $\frac{288.5 + 284.6}{2}$.

The calculation of t_c by the modified relationship of Walden (see the previous paper) $t_c = \text{constant}\ \frac{\alpha' + \alpha''}{\alpha'\alpha''}$ (where α' and α'' are found from the relations $\gamma_t = \gamma_o(1-\alpha' t)$ and $a_t^2 = a_o^2(1-\alpha'' t)$) using the values found from the drop weight and drop volume relations

$$w_t = w_o\ (1-\alpha' t),$$
$$v_t = v_o\ (1-\alpha'' t),$$

which, as has already been shown, should give the same α' and α'' values as the others, for they are only a percentage change, are given for those liquids studied at two temperatures, in Table XXVI. These values, naturally, are burdened with the same kind of a multiplied error as k is, when it is calculated from the equation $k = \Delta[w(M/d)^{2/3}]/\Delta t$. Thus if the high temperature value is slightly high, while that at the low is slightly low, the temperature coefficient $\Delta w/\Delta t$ from which α' is calculated will be too small, etc. The object here is to show that even with this error, and without the use of a molecular weight, sensibly the same value (within the limits of error of this form of calculation) of t_c is found by this method as by that involving k_B found from

$$w(M/d)^{2/3} = k_B(288.5° - t - 6)$$

for benzene.

TABLE XXVI. $t_c = \text{Constant}\ \frac{\alpha' + \alpha''}{\alpha'\alpha''}$.[1]

Liquid.	α'.	α''.	t_c.	t_c from k_B.
Quinoline	0.0023695	0.0017613	518.6°	...
Pyridine	0.003457	0.0026552	348.9	...
Carbon tetrachloride	0.0041652	0.0032519	287.0	...
Chlorobenzene	0.0033443	0.0025621	361.2	...
Aniline	0.0028384	0.0021484	428.5	...
Ethyl *n*-butyrate	0.0038652	0.0029601	312.6	310.3
Chloroform	0.0044832	0.0035579	264.2	260.5
Phenetole	0.0030662	0.0022613	402.7	402.9
Anisole	0.0030695	0.0023442	394.2	391.0
Benzonitrile	0.0029256	0.0021957	415.9	417.0
Ethylene dibromide	0.0031544	0.0024119	383.4	379.1
Carbon disulfide	0.0047364	0.0036947	252.5	252.1

Discussion of Results.

It is quite evident from the above Tables that the new definition of normal molecular weight is perfectly fulfilled, according to the drop weight method, for all the liquids. *Our only conclusion, then, is that the above liquids, since they give a value of t_c from the normal (benzene) value of k_B in the equation $w(M/d)^{2/3} = k_B\ (t_c - t - 6)$, which is constant, independent of the temperature of observation, are perfectly normal in behavior, and consequently are non-associated.*

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[1] The constant is found from benzene for which $\alpha' = 0.0041385$, $\alpha'' = 0.0032373$, and $t_c = 288.5°$; and has the value 0.52404.

It must not be thought that the experimental results given in the Tables were the only ones from which a drop weight of the same value could be calculated. Immediately after each 30-drop determination, a 5-drop blank was made, at nearly the same temperature as possible, so that a series of drop weights at perhaps slightly varying (within 0.2° to 0.5°) temperatures were thus obtained. Within a very slight error these all led to the same value of t_c. The weights given in the tables, beside showing the maximum deviation observed, also lead in all cases to a value giving the same t_c that the average of all, at an average temperature, would give. Granting perfectly constant temperature, there is no reason why the extreme deviation in total weight of the vessel and drops should amount to more than 2 or 3 tenths of a milligram.

It will be observed that only in the cases of ether and chloroform do the calculated t_c values agree with the observed critical temperatures, although the agreement for these two liquids is remarkable. In the other cases, since the t_c is constant (within very small limits), independent of the temperature of observation, it is proof that the normal (benzene) value of k_β is also the correct and proper temperature coefficient of $w(M/d)^{2/3}$ for these liquids; *hence as to molecular weight they are to be considered just as normal and just as much non-associated as benzene itself, although the fictitious critical temperature* t_c, *i. e., the point at 6° below which* $w(M/d)^{2/3}$, *by the equation, becomes zero, does not coincide with the observed critical temperature.* One question arises here which probably must remain open for some time, and which may be stated as follows: Is the observed critical temperature ever influenced by a decomposition of the liquid, due to heat or the presence of mercury, before it reaches that point? It may be said here that ethylene dibromide when heated to a point below the critical in a closed tube, in the presence of mercury, certainly does decompose, as is evidenced by the pressure on opening the tube after cooling. When a gas is thus formed, naturally the observed critical temperature will be lower than it should be, owing to the presence of the gas, with its necessarily low critical temperature; in other words, it will be the mean critical temperature of the mixture that is measured, rather than that of the undecomposed liquid. Such a process might account for the higher fictitious critical temperature t_c calculated for this liquid both by drop weight and by capillary rise. This, of course, would only be true for a limited number of liquids, and would not account in general for the discrepancy existing between the fictitious and the observed critical temperatures.

Although ether was studied here at but one temperature, results by another observer on this tip, at both 0° and 27.8°, lead to the same value of the calculated t_c. Why Ramsay and Shields' value of t_c should have a downward trend is unknown. The drop weight leads to the same t_c at

0° as at other temperatures, while capillary rise gives this value only between 70° and 90°. *We must conclude, then, that either drop weight is not proportional to surface tension at all, in which case we must assume the unlikely thing that the agreement of the value found by the former, at all temperatures, with the value of the latter between 70° and 90° is accidental; or, and it seems that this is the only logical conclusion, they are strictly proportional, but there is a large variable error in the results of capillary rise at times.* This latter seems still more likely when it is recalled that the height of ascension of ether in a capillary tube is very small at all temperatures.

For chloroform and ethyl *n*-butyrate, no surface tensions could be found in the literature, so that a direct comparison is impossible, but the excellent agreement of t_c with the observed value, in the former case, and the not excessive variation in the latter, especially as both show a value of t_c which is independent of the temperature of observation, makes a comparison perhaps unnecessary. The higher chloroform temperature here is out about 1° below the boiling point.

In the case of phenetole, Renard and Guye find a decided trend downward with increasing temperature, but the results of Guye and Baud, although showing a trend, lead to higher values of t_c throughout; so that the former at 40° to 52.1°, and the latter at 108.7° agree with the drop weight at both its temperatures. Assuming the variation in the values of capillary rise to be due to variable error, and then getting the mean t_c of both Renard and Guye (397.7°) and Guye and Baud (405.8°) we find 402.7° as compared to the individual values 402.7° and 403° found from drop weight.

For anisole, we find also a trend downward in the values of t_c of both Renard and Guye and Guye and Baud, the values of Guye and Baud, just as with phenetole, being the larger throughout. Again assuming this to be due to variable error, and getting the mean, we find for the former 389° and for the latter 391.5°, which leads to 390.1°, as compared to the constant value 391° from drop weight. For benzonitrile the results from capillary rise are most confusing. Here the trend of the results of Renard and Guye is upward, agreeing with drop weight at 21.6 and 60°. Guye and Baud, on the other hand, find values varying around 424° at all their temperatures, while Ramsay and Shields find about 401° for their three temperatures. Certainly drop weight here agrees with every value as well as any of the capillary rise values agree with any other, but no comparison can be made because the non-agreement of the results from capillary rise makes it impossible to find any one number to compare the drop weight with.

In the case of ethylene dibromide, the drop weight result may well be a trifle high (as is the case with the similar liquid carbon tetrachloride), for this drop has a very small volume, and lack of control, even though slight, would cause an error, owing to the very great density. At any rate, here the calculated values of t_c are constant, as they also are, although of a slightly different value, when calculated from the capillary rise. The Ramsay and Shields result for carbon disulfide could not be confirmed by Ramsay and Aston, who spent considerable time in the attempt, especially at low temperatures. The specimen used for the drop weight, though called pure, and redistilled several times, still had an unpleasant odor. Later, a report will be made upon the work on a specimen so pure that it has its supposedly characteristic pleasant ethereal odor. For the mixture of benzene and carbon tetrachloride a t_c is found which differs but slightly from the mean of those found for the components. The value of Ramsay and Aston, at the lower temperature, also agrees well with the mean of their observed values, but the others do not seem to be very constant, which may be due to changes in the mixture on heating.

By the above treatment drop weight and surface tension from capillary rise are shown to be proportional, at least in those cases where it is possible to find from the work of observers with the latter method any one approximate value upon which they can agree, and with which the drop weight result can be compared. *One thing at least is clear with respect to capillary rise, viz.: that a variable error exists. Allowing for this error, it will be seen that surface tension from capillary rise also shows by the new definition of normal molecular weight that the above liquids are normal and non-associated. Further, wherever the results of capillary rise can be confirmed by other observers, it will be noticed that the fictitious critical temperatures t_c are the same when found from capillary rise, as when found from drop weight.*

In the next paper of this series will be considered the results of 20 other non-associated liquids, together with the corresponding values found by capillary rise.

Summary.

The results of this investigation may be summarized as follows:

I. From drop weight results it is shown that, using the new criterion of normal molecular weight, *viz.:* the finding of a value of t_c, using the normal (benzene) value of k_B, in the equation $w(M/d)^{2/3} = k_B\,(t_c—t—6)$, which is constant, independent of the temperatrue of observation, is fulfilled for ether, ethyl *n*-butyrate, anisole, phenetole, ethylene dibromide, chloroform, benzonitrile and carbon disulfide, which consequently are non-associated. This same conclusion can be reached from the results of capillary rise (when they are given), provided we assume in that method the presence of a not excessive variable error.

II. Only in the cases of ether and chloroform do the values of t_c as calculated agree closely with the observed critical temperatures, but the fictitious values of the critical temperature found for the others agree with those that are calculated from the capillary rise.

III. The values of t_c both true and fictitious, found by aid of the modified Walden method, applied to drop weight, without the use of the molecular weight, agree as closely as could be expected, remembering the possibilities of error inherent in the method.

IV. It is shown that the calculated t_c for a mixture of benzene and carbon tetrachloride, 1 : 1 by weight, is practically the mean of the values found for these two liquids alone.

LABORATORY OF PHYSICAL CHEMISTRY.

[CONTRIBUTIONS FROM THE HAVEMEYER LABORATORIES OF COLUMBIA UNIVERSITY, No. 188.]

THE WEIGHT OF A FALLING DROP AND THE LAWS OF TATE. VI. THE DROP WEIGHTS OF TWENTY NEW NON-ASSOCIATED LIQUIDS, AND THE MOLECULAR WEIGHTS CALCULATED FOR THEM.

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The object of this paper is to present the results of a further testing of the Morgan drop weight apparatus, similar to that carried out by Morgan and Thomssen, for the purpose of testing the new definition of normal molecular weight, and comparing the results with those found from the capillary rise, wherever that is possible; studying those liquids which lead to a calculated value of t_c in $w(M/d)^{2/3} = k\,(t_c - t - 6)$, which agrees with the observed critical temperature, as well as those which do not.

The tip used in this research was one with a sharp, straight edge, having a diameter of about 5.7 mm., with a bore of 0.2 mm. It was at once recognized here that it would be impossible on this tip to use any liquid of such a great density and small surface tension as carbon tetrachloride, as it would produce a drop too small in volume to be controlled, so that liquid was not studied. All the other liquids gave drops of such a volume that their speed of formation at the moment of fall could be perfectly controlled.

The experimental results for the standardization of this tip, using benzene, aniline, pyridine, and quinoline, are given in Table I to IV inclusive:

TABLE I.—BENZENE.

t.	Wt. vessel + 15 drops.	Av.	Wt. vessel + 5 drops.	Av.	Av. t.	Wt. 1 drop. Mg.
36.05	10.0871					
36.05	10.0868	10.0869	10.7954 10.7956	10.7955	36.15	29.14
36.35	10.0868					
59.58	10.0472					
59.53	10.0474	10.0471	10.7883 10.7883	10.7883	59.54	25.88
59.53	10.0467					