from the liquid. The solid phase between 60° and 95° was found to contain 58.93 per cent. of lead nitrate. The compound $Pb(NO_3)_2.3C_5H_5N$ contains 58.98 per cent. lead nitrate. This is the compound discovered and described by Schmujlow in 1897. Above 95° a compound was found which contained 86.2 per cent. of lead nitrate. This is evidently $3Pb(NO_3)_2.2C_5H_5N$, which contains 86.27 per cent. of lead nitrate.

The transition points may be obtained from the curve. At 51° there is a transition point between $Pb(NO_3)_2.4C_5H_5N$ and $Pb(NO_3)_2.3C_5H_5N$. At 96° there is a transition point between $Pb(NO_3)_2.3C_5H_5N$ and $3Pb(NO_3)_2.2C_5H_5N$.

Summary.

In the foregoing investigation the solubility curve of lead nitrate and pyridine has been established between —19.4 and 110°. The results show that for this range of temperature there are three distinct crystalline compounds of lead nitrate and pyridine in equilibrium with the solution. The three compounds are: $Pb(NO_3)_2.4C_5H_5N$; $Pb(NO_3)_2.3C_5H_5N$; and $3Pb(NO_3)_2.2C_5H_5N$. Of these $Pb(NO_3)_2.4C_5H_5N$ and $3Pb(NO_3)_2.2C_5H_5N$ have hitherto been unknown.

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[CONTRIBUTIONS FROM THE HAVEMEYER LABORATORIES OF COLUMBIA UNIVERSITY. No. 192.]

THE WEIGHT OF A FALLING DROP AND THE LAWS OF TATE VII. THE DROP WEIGHTS OF SOME OF THE LOWER ESTERS, AND THE SURFACE TENSIONS AND MOLECULAR WEIGHTS CALCULATED FROM THEM.

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The object of this research was the further testing of the Morgan drop weight apparatus, for the purpose of (1) applying to additional substances the new definition of normal molecular weight in the liquid state; and (2) the direct comparison of the values of surface tension, as found from drop weight, with those from the capillary rise. The main difficulty encountered thus far in the comparison of drop weight results with those from capilliary rise has been the fact that no one agreeing value in many cases could be found from the work of the various observers of capillary rise, their results varying widely. In order that any such variation might be avoided in the capillary rise results used in this research, those liquids, the lower esters, were selected, eight of which have been carefully studied by Ramsay and Aston,[1] each from observations at three tem-

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[1] *Z. physik. Chem.*, 15, 98 (1894).

peratures, in two capillary tubes of differing bore. One great advantage of this form of comparison is that it enables us at the same time to ascertain the degree of accuracy in agreement that may be expected from the capillary rise method under ideal conditions, *i. e.*, where all is identical except the bore of the capillary used, and that it furnishes us with a criterion as to what variation in capillary rise results may be expected when nothing is identical in the work except the name of the liquid used. Another difficulty previously encountered is also done away with in the use of these uniform results, *viz.*, that due to the employment, in the calculation of a different density or rather difference in density as liquid and as vapor, at the same temperature, for the same liquid, for the value of $\gamma = {}^1/_2$ hr. $(d_l - d_v)$ is very decidedly dependent upon that.

The tip used here was one with a straight, sharp, edge, slightly larger than that used by Morgan and Thomssen, and smaller than that of Morgan and Daghlian, and was very approximately 5.65 millimeters in diameter. Owing to the fact that a number of different weighing vessels were used on this apparatus, the total weights of vessel and drops are different in many cases for the same liquid at different temperatures. It is to be remembered here that in the use of this apparatus no comparison can be made between the weights of the 5-drop blanks, except when they refer to the same liquid, at the same temperature. This is due to the fact that the blank is always held on the apparatus, with a drop hanging, for the same length of time that the 25-drop determinations of that liquid at that temperature are allowed to stand; and consequently it always represents the weight of 5 drops, less the loss by evaporation. Two identical weights, then, for the vessel plus 5 drops, for different liquids, at different temperatures, do not necessitate that the weight of 1 drop be the same in both cases; for that which has the greater drop weight, by its loss from evaporation, due to longer standing or higher vapor pressure, will appear decidedly reduced in total weight. It is only when the blanks are considered in connection with the determinations to which they refer that comparable results, *i. e.*, the weight of 1 drop, are obtained.[1]

In Table I are given the experimental results for benzene at two temperatures, together with the values of $w\left(\frac{M}{d}\right)^{\frac{2}{3}}$ and that of k_B calculated from the relationship $w\left(\frac{M}{d}\right)^{\frac{2}{3}} = k_B\,(288.5 - t - 6)$. This is for the purpose of standardizing the tip, the value of k_B found being then used throughout for the calculation of the t_c of the other liquids, and to prove from its constancy, at various temperatures of observation, in any one

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[1] This is complicated further here by the fact that a cork stopper was used in the weighing vessel in all the cases given with a weight less than 10 grams; and the cork, although constant in weight for each determination, was not the same throughout.

case, that the molecular weight of that liquid is normal, *i. e.*, is the same as a liquid as it is as a gas.

In Table II are given the experimental, as well as the derived values for pyridine, which will serve as a preliminary test of the accuracy of the constant of standardization, k_B, of the tip. As will be observed, this value of k_B leads to a value of $t_c = 346.85°$, in place of 346.6°, as calculated by Morgan from the results of Morgan and Higgins. From this result we may regard the value of k_B as satisfactory.

TABLE I.—BENZENE; M = 78; t_c = 288.5°.

t.	Wt. vessel + 25 drops.	Av.	Wt. vessel + 5 drops.	Av.	Wt. 1 drop. Mg.
10°	7.6515		7.0063		
	7.6516	7.6515	7.0062	7.0063	32.260
	7.6515		7.0064		
	7.6514		7.0063		
40.7	11.0195		10.4610		
	11.0194		10.4612		
	11.0194	11.0194	10.4611	10.4611	27.915
	11.0193		10.4611		

t.	*d*.	*w*.	$w\left(\frac{M}{d}\right)^{\frac{2}{3}}$.	k_B.
10°	0.88956	32.260	636.72	2.3374
40.7	0.85683	27.915	564.90	2.3372

Av. k_B = 2.3373

TABLE II.—PYRIDINE; M = 79; t_c =346.6°.[1]

t.	Wt. vessel + 25 drops.	Av.	Wt. vessel + 5 drops.	Av.	Wt. 1 drop, Mg.
0°	8.5643		7.6986		
	8.5642	8.5643	7.6984	7.69847	43.292
	8.5643		7.6984		
	8.5644		7.6985		
34.25	11.7086		10.9472		
	11.7084		10.9474		
	11.7085	11.7086	10.9475	10.9473	38.065
	11.7087		10.9472		
	11.7088		10.9472		

t.	*d*.	*w*.	$w\left(\frac{M}{d}\right)^{\frac{2}{3}}$.	t_c calc. from k_B.
0.1°	1.0014	43.292	796.31	346.8°
34.25	0.9672	38.065	716.58	346.9°

In Tables III to XIII are given the experimental values of the new liquids studied, *viz.*, methyl formate, ethyl formate, propyl formate,

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[1] See No. IV of this series.

amyl formate, methyl acetate, ethyl acetate, propyl acetate, methyl propionate, ethyl propionate, methyl isobutyrate, and methyl butyrate. These, with the exception of the amyl formate, which was obtained from Eimer & Amend, and though purified before the determination, cannot be considered as satisfactory, were prepared especially for the work by the Hoffman & Kropff Chemical Company, and used as received. It will be noted here that the maximum variation from the mean, *i. e.*, where the "25" determinations differ by 0.4 mg. and the blanks also differ by 0.03, amounts to only about 0.05 per cent., the average variation being much less. This, naturally, is simply the variable error, the absence of a constant error in any one case being shown better perhaps by the results given later:

TABLE III.—METHYL ISOBUTYRATE.

t.	Wt. vessel + 25 drops.	Av.	Wt. vessel + 5 drops.	Av.	Wt. 1 drop. Mg.
10°	9.8776	9.8775	9.3452	9.34512	26.619
	9.8775		9.3450		
	9.8773		9.3451		
	9.8776		9.3452		
33.87	9.8085	9.80845	9.3336	9.33366	23.740
	9.8084		9.3337		
	9.8083		9.3335		
	9.8083		9.3338		
	9.8087		9.3338		
60.1	9.7385	9.73862	9.3260	9.32594	20.634
	9.7386		9.3261		
	9.7387		9.3259		
	9.7387		9.3259		
	....		9.3259		

TABLE IV.—ETHYL PROPIONATE.

t.	Wt. vessel + 25 drops.	Av.	Wt. vessel + 5 drops.	Av.	Wt. 1 drop. Mg.
10°	6.7887	6.78875	6.2480	6.2479	27.043
	6.7888		6.2480		
	6.7888		6.2478		
	6.7887		6.2478		
33.89	9.8185	9.8186	9.3356	9.33557	24.152
	9.8187		9.3356		
	9.8186		9.3355		
	9.8186		9.3356		
59.15	10.7920	10.7920	10.3682	10.36812	21.194
	10.7921		10.3682		
	10.7920		10.3681		
	10.7919		10.3680		

Table V.—Methyl Propionate.

t.	Wt. vessel + 25 drops.	Av.	Wt. vessel + 5 drops.	Av.	Wt. 1 drop Mg.
10°	6.8100		6.2513		
	6.8102	6.81007	6.2513	6.2512	27.944
	6.8100		6.2512		
	6.8101		6.2510		
34.65	10.9364		10.4426		
	10.9362	10.9363	10.4425	10.44257	24.687
	10.9363		10.4425		
	10.9363		10.4427		
59.75°	10.8000		10.3701		
	10.8002		10.3703		
	10.8002	10.8001	10.3702	10.37012	21.499
	10.8001		10.3699		
	10.8000		.....		

Table VI.—Ethyl Formate.

t.	Wt. vessel + 25 drops.	Av.	Wt. vessel + 5 drops.	Av.	Wt. 1 drop. Mg.
0.1°	8.1827		7.6228		
	8.1827	8.18275	7.6230	7.62298	27.989
	8.1828		7.6230		
	8.1828		7.6231		
6.	8.3243		7.7809		
	8.3243	8.3243	7.7810	7.7809	27.170
	8.3242		7.7808		
	8.3244		7.7809		
10	8.3355		7.8028		
	8.3358	8.33567	7.8030	7.80292	26.638
	8.3357		7.8029		
	8.3357		7.8030		
17	8.2888		7.7751		
	8.2886	8.2888	7.7752	7.7752	25.680
	8.2889		7.7753		
	8.2889		7.7752		
33.95°	10.9059		10.4381		
	10.9058	10.9059	10.4382	10.43815	23.388
	10.9059		10.4380		
	10.9060		10.4383		

Table VII.—Methyl Acetate.

t.	Wt. vessel + 25 drops.	Av.	Wt. vessel + 5 drops.	Av.	Wt. 1 drop. Mg.
0.1°	8.2152		7.6292		
	8.2151		7.6291		
	8.2150	8.21512	7.6291	7.6291	29.301
	8.2152		7.6290		

TABLE VII (*Continued*).

t.	Wt. vessel + 25 drops.	Av.	Wt. vessel + 5 drops.	Av.	Wt. 1 drop. Mg.
10	6.8070	6.80687	6.2510	6.25085	27.801
	6.8069		6.2509		
	6.8068		6.2508		
	6.8068		6.2507		
34.2	8.2822	8.28227	7.7990	7.79907	24.160
	8.2823		7.7991		
	8.2822		7.7991		
	8.2824		7.7991		

TABLE VIII.—PROPYL ACETATE.

t.	Wt. vessel + 25 drops.	Av.	Wt. vessel + 5 drops.	Av.	Wt. 1 drop. Mg.
0.1°	8.1884	8.18855	7.6199	7.6199	28.433
	8.1885		7.6198		
	8.1886		7.6199		
	8.1887		7.6200		
34.6	7.4602	7.46022	6.9773	6.97727	24.148
	7.4603		6.9773		
	7.4602		6.9772		
	7.4602		6.9773		
60.1	11.1213	11.12147	10.6972	10.69732	21.208
	11.1216		10.6973		
	11.1215		10.6974		
	11.1215		10.6974		

TABLE IX.—METHYL BUTYRATE.

t.	Wt. vessel + 25 drops.	Av.	Wt. vessel + 5 drops.	Av.	Wt. 1 drop. Mg.
10°	8.3627	8.36262	7.8043	7.80422	27.920
	8.3626		7.8042		
	8.3627		7.8042		
	8.3625		7.8042		
34.8	8.2869	8.2868	7.7885	7.7885	24.915
	8.2867		7.7885		
	8.2868		7.7885		
	8.2868		7.7885		
59.85	8.2217	8.22168	7.7824	7.7824	21.964
	8.2218		7.7824		
	8.2217		7.7824		
	8.2216		7.7824		
	8.2216		....		

TABLE X.—PROPYL FORMATE.

t.	Wt. vessel + 25 drops.	Av.	Wt. vessel + 5 drops.	Av.	Wt. 1 drop. Mg.
0.1°	7.5616		6.9895		
	7.5615	7.56152	6.9895	6.98945	28.604
	7.5615		6.9894		
	7.5615		6.9894		
5.4	8.3638		7.8050		
	8.3639	8.36382	7.8050	7.8050	27.941
	8.3638		7.8050		
	8.3638		7.8050		
10	8.3492		7.8026		
	8.3494		7.8027		
	8.3494	8.34935	7.8027	7.80262	27.337
	8.3494		7.8025		
17	8.3283		7.7992		
	8.3284	8.32835	7.7992	7.7992	26.458
	8.3284		7.7992		
	8.3283		7.7992		
34.75	7.4595		6.9733		
	7.4593	7.45942	6.9735	6.97347	24.298
	7.4594		6.9736		
	7.4595		6.9735		
60.3	7.3903		6.9620		
	7.3903		6.9619		
	7.3902	7.3903	6.9619	6.96192	21.419
	7.3905		6.9619		
	7.3902		....		

TABLE XI.—METHYL FORMATE.

t.	Wt. vessel + 25 drops.	Av.	Wt. vessel + 5 drops.	Av.	Wt. 1 drop. Mg.
0.1°	8.2323		7.6345		
	8.2323	8.23237	7.6345	7.63452	29.893
	8.2325		7.6345		
	8.2324		7.6346		
6.7	8.3898		7.8125		
	8.3898		7.8126		
	8.3897	8.38975	7.8125	7.81255	28.860
	8.3897		7.8126		
10	7.5554		6.9906		
	7.5553		6.9906		
	7.5554	7.5554	6.9904	6.99055	28.243
	7.5555		6.9906		
16.4	8.3485		7.8013		
	8.3486	8.3485	7.8013	7.8013	27.360
	8.3485		7.8013		
	8.3484		7.8013		
27.82	8.3071		7.7948		
	8.3072	8.30717	7.7949	7.7949	26.614
	8.3071		7.7949		
	8.3073		7.7950		

TABLE XII. AMYL FORMATE.

t.	Wt. vessel + 25 drops.	Av.	Wt. vessel + 5 drops.	Av.	Wt. 1 drop. Mg.
10°	8.3484		7.7993		
	8.3486		7.7992		
	8.3485	8.3485	7.7992	7.79922	27.464
	8.3485		7.7992		
35	8.2813		7.7875		
	8.2813	8.28135	7.7875	7.7875	24.693
	8.2814		7.7875		
	8.2814		7.7875		
60.1	8.2176		7.7796		
	8.2176		7.7796		
	8.2177	8.21767	7.7797	7.7796	21.904
	8.2177		7.7795		
	8.2177		....		

TABLE XIII.—ETHYL ACETATE.

t.	Wt. vessel + 25 drops.	Av.	Wt. vessel + 5 drops.	Av.	Wt. 1 drop. Mg.
0.1°	7.5421		6.9834		
	7.5420	7.5421	6.9834	6.9833	27.940
	7.5421		6.9832		
	7.5422		6.9832		
34.6	7.4442		6.9767		
	7.4443	7.44424	6.9768	6.97674	23.375
	7.4443		6.9767		
	7.4442		6.9769		
60.5	7.4442		6.9766		
	7.3658		6.9646		
	7.3659	7.3659	6.9647	6.96462	20.064
	7.3659		6.9646		
	7.3660		6.9646		

In Tables XIV to XXIV, inclusive, are given the derived values $w\left(\frac{M}{d}\right)^{\frac{2}{3}}$, t_c, and γ (surface tension) calculated from the above experimental results, together with the corresponding quantities from the capillary rise results of Ramsay and Aston and others.

The densities employed here, except those for amyl formate, which were partly extrapolated from those used by Homfray and Guye,[1] were found by plotting the results of Young.[2]

The t_c values from drop weight as given are all calculated by aid of the value of k_B found above for benzene, *viz.* 2.3373, in the equation $w\left(\frac{M}{d}\right)^{\frac{2}{3}} = 2.3373(t_c-t-6)$, while those from capillary rise are obtained by the use of the specific value of k_B found from the work of the investi-

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[1] *J. chim. phys.*, 1, 505–44 (1904).

[2] *J. Chem. Soc.*, 1893, 1191–1262.

gator in question on benzene; or by use of the Ramsay and Shields' constant when the observer calibrated the bore of his capillary by aid of their benzene values. Naturally, here, the comparison of drop weight with surface tension from capillary rise, by aid of 2 equations like the above, is made by the identity in the values of t_c found, for since M is the same in both, while d is the same function of the temperature in each, identity in the t_c shows that *at the same temperature* we would have the relation $\gamma : w :: k_B' : k_B$. When the comparison itself is made at the same temperature, t, the above relationship is, of course, self-evident, since M, d, t and 6 are all alike, so that when *the t_c's are also identical, the drop weight in milligrams is related to the surface tension in dynes per centimeter, as the respective k_B values, i. e.*, at the same temperature $w : \gamma :: k_B : k_B'$.

One difficulty with respect to this indirect comparison of drop weight and surface tension is that the densities used may not be the same, or the same function of the temperature; while another is that the t_c found for the liquid in question increases or decreases with the temperature. The simplest way to avoid these difficulties is to make a direct comparison of the surface tensions themselves, at the same temperature. In the second part of each of the following tables will be found the surface tensions as observed directly from the capillary rise, together with those values, interpolated or extrapolated from the surface tensions calculated from the drop weight, at each temperature of observation, by aid of the equation $\gamma = w\frac{k_B}{2.3373}$ dynes, where the value of k_B depends upon the observer of capillary rise. The differing values of γ obtained by use of the various k_B values would best, perhaps ultimately, be made uniform by the use of a value of k_B from capillary rise which is the average of all those which have been observed. This would have a value then of about 2.1111, differing from that of Ramsay and Shields (2.1012) by 0.47 per cent., and from that of Ramsay and Aston (2.1211) by 0.5 per cent., while it is practically identical with that of Renard and Guye (2.1108).

All extrapolated values in the tables are marked with *.

In Table XXV are given the values of t_c for the above liquids, as found from the modified Walden relationship,

$$t_c = \text{constant}\cdot\frac{\alpha' + \alpha''}{\alpha'\alpha''},$$

where α' and α'' are found from the equations

$$w_t = w_0(1 - \alpha' t),$$

$$\text{and } v_t = \frac{w_t}{d_t} = v_0(1 - \alpha'' t),$$

using the values at the extremes of temperature in order that they may be as free from error as possible. The value of the constant here, as in the previous papers, is that which is found necessary to give t_c for benzene the value 288.5°:

TABLE XIV.—METHYL ISOBUTYRATE; M = 102.08; t_c obs. = 267.6°.

t.	d.	w. Mgs.	$w\left(\frac{M}{d}\right)^{\frac{2}{3}}$.	t_c.	$\gamma\left(=w\frac{k_{R\,\&\,A}}{2.3373}\right)$. Dynes.	$\gamma\left(=w\frac{k_{R\&G}}{2.3373}\right)$. Dynes.
10.0°	0.90033	26.619	623.57	*282.8*	24.158	24.040
33.9	0.87328	23.740	567.55	*282.7*	21.545	21.440
60.1	0.84295	20.634	505.06	*282.2*	18.726	18.634

Ramsay and Aston; k_B = 2.1212.

	r = 0.01708 cm.		r = 0.01046 cm.	
t.	$\gamma\left(\frac{M}{d}\right)^{\frac{2}{3}}$.	t_c.	$\gamma\left(\frac{M}{d}\right)^{\frac{2}{3}}$.	t_c.
10.0°	563.6	*281.7*	563.0	*281.4*
46.2	487.3	*281.9*	486.1	*281.4*
78.2	415.0	*279.8*	415.1	*279.9*

Renard and Guye; k_B = 2.1108.

t.	$\gamma\left(\frac{M}{d}\right)^{\frac{2}{3}}$.	t_c.	t.	$\gamma\left(\frac{M}{d}\right)^{\frac{2}{3}}$.	t_c.
10.5°	563	*283.2*	55.0	467	*282.2*
30.5	519	*282.4*	75.0	422	*280.9*
41.0	496	*282.0*	86.6	396	*280.2*

Surface Tensions.

t.	$\gamma_{R\,\&\,A}$.		$\gamma_{M\,\&\,S}$ from $w\frac{2.1212}{3.3373}$.
10.0°	24.11	24.08	24.16
46.2	20.29	20.04	20.22
78.2	16.70	16.64	16.78*

	$\gamma_{R\,\&\,G}$.	$\gamma_{M\,\&\,S}$ from $w\frac{2.1108}{2.3373}$
10.5°	24.06	24.03
30.5	21.82	21.81
41.0	20.63	20.68
55.0	19.18	19.18
75.0	17.02	17.04*
86.6	15.78	15.80*

TABLE XV.—ETHYL PROPIONATE; M = 102.08; t_c obs. = 272.9°.

t.	d.	w.	$w\left(\frac{M}{d}\right)^{\frac{2}{3}}$.	t_c.	$\gamma\left(=w\frac{2.1212}{2.3373}\right)$.
10.0°	0.90106	27.043	633.16	*286.9*	24.543
33.9	0.87435	24.152	576.93	*286.7*	21.919
59.2	0.84502	21.194	517.92	*286.8*	19.234

Table XV (*Continued*).

Ramsay and Aston; $k_B = 2.1212$.

	$r = 0.01708$ cm.		$r = 0.01046$ cm.	
t.	$r\left(\frac{M}{d}\right)^{\frac{2}{3}}$.	t_c.	$r\left(\frac{M}{d}\right)^{\frac{2}{3}}$.	t_c.
10.0°	574.0	*286.6*	576.2	*287.6*
46.2	496.1	*286.1*	496.9	*286.5*
78.2	428.1	*286.0*	427.8	*285.9*

Surface Tensions.

t.	γR & A.		γM & S from $w\frac{2.1212}{2.3373}$.
10.0°	24.57	24.67	24.54
46.2	20.58	20.62	20.60
78.2	17.24	17.22	17.20*

TABLE XVI.—METHYL PROPIONATE; M = 88.06; t_c obs. = 257.4°.

t.	d.	w.	$w\left(\frac{M}{d}\right)^{\frac{2}{3}}$.	t_c.	$\gamma\left(=w\frac{2.1212}{2.3373}\right)$.
10.0°	0.92678	27.944	582.31	*265.1*	25.360°
34.7	0.89758	24.687	525.14	*265.4*	22.405
59.8	0.86692	21.499	468.04	*266.1*	19.511

Ramsay and Aston; $k_B = 2.1212$ cm.

	$r = 0.01708$ cm.		$r = 0.01046$ cm..	
t.	$r\left(\frac{M}{d}\right)^{\frac{2}{3}}$.	t_c.	$r\left(\frac{M}{d}\right)^{\frac{2}{3}}$.	t_c.
10.0°	524.3	*263.2*	530.2	*266.0*
46.2	447.3	*263.1*	450.2	*264.4*
78.2	378.8	*262.8*	381.9	*264.2*

Surface Tensions.

t.	γR & A.		γM & S from $w\frac{2.1212}{2.3373}$.
10.0°	25.23	25.51	25.36
46.2	20.85	20.98	21.08
78.2	17.11	17.26	17.30*

TABLE XVII.—ETHYL FORMATE; M = 74.08; t_c = 235.2°.

t.	d.	w.	$w\left(\frac{M}{d}\right)^{\frac{2}{3}}$.	t_c.	$\gamma\left(=w\frac{2.1212}{2.3373}\right)$.
0.1°	0.94697	27.989	511.82	*225.1*	25.401
6.0	0.93958	27.170	499.44	*225.7*	24.658
10.0	0.93458	26.638	491.41	*226.3*	24.175
17.0	0.92618	25.680	476.59	*226.9*	23.306
34.0	0.90418	23.388	441.07	*228.7*	21.226

Ramsay and Aston; $k_B = 2.1212$.

	$r = 0.01843$ cm.		$r = 0.01046$ cm.	
t.	$r\left(\frac{M}{d}\right)^{\frac{2}{3}}$.	t_c.	$r\left(\frac{M}{d}\right)^{\frac{2}{3}}$.	t_c.
10.0°	443.5	*225.1*	446.0	*226.3*
46.5	371.5	*227.6*	375.5	*229.5*
78.5	309.2	*230.3*	309.1	*230.3*

TABLE XVII (*Continued*).

Surface Tensions.

t.	γ R & A.		γ M & S from $w\frac{2.1212}{2.3373}$.
10.0°	24.08	24.22	24.18
46.5	19.50	19.71	19.68*
78.5	15.68	15.68	15.73* (Extrapolated through 44.5°)

TABLE XVIII.—METHYL ACETATE; M = 74.05; t_c obs. = 233.7°.

t.	*d.*	*w.*	$w\left(\frac{M}{d}\right)^{\frac{2}{3}}$.	t_c.	$\gamma\left(=w\frac{2.1212}{2.3373}\right)$.
0.1°	0.95900	29.301	531.23	*233.2*	26.592
10.0	0.94652	27.801	508.54	*233.6*	25.231
34.2	0.91491	24.160	452.19	*233.7*	21.926

Ramsay and Aston; k_B = 2.1212.

	γ = 0.01843 cm.		γ = 0.01046 cm.	
t.	$\gamma\left(\frac{M}{d}\right)^{\frac{2}{3}}$.	t_c.	$\gamma\left(\frac{M}{d}\right)^{\frac{2}{3}}$.	t_c.
10.0°	462.8	*234.2*	459.9	*232.8*
46.2	383.9	*233.2*	387.2	*234.7*
78.3	318.2	*234.2*	319.5	*234.9*

Surface Tensions.

t.	γ R & A.		γ M & S from $w\frac{2.1212}{2.3373}$.
10.0°	25.22	25.06	25.23
46.2	20.32	20.49	20.29*
78.3	16.28	16.35	15.89 (Extrapolated through 44.1°)

TABLE XIX.—PROPYL ACETATE; M = 102.08; t_c obs. = 276.2°.

t.	*d.*	*w.*	$w\left(\frac{M}{d}\right)^{\frac{2}{3}}$.	t_c.	$\gamma\left(=w\frac{2.1212}{2.3373}\right)$.
0.1°	0.91000	28.433	661.20	*289.0*	25.804
34.6	0.87229	24.148	577.63	*287.7*	21.915
60.1	0.84345	21.208	518.81	*288.1*	19.247

Ramsay and Aston; k_B = 2.1212.

	γ = 0.01708 cm.		γ = 0.01046 cm.	
t.	$\gamma\left(\frac{M}{d}\right)^{\frac{2}{3}}$.	t_c.	$\gamma\left(\frac{M}{d}\right)^{\frac{2}{3}}$.	t_c.
10.0°	580.2	*289.5*	582.0	*290.4*
46.2	503.0	*289.3*	502.2	*289.0*
78.2	431.0	*287.4*	432.3	*288.0*

Surface Tensions.

t.	γ R & A.		γ M & S from $w\frac{2.1212}{2.3373}$.
10.0°	24.80	24.88	24.72
46.2	20.86	20.84	20.77
78.2	17.35	17.33	17.27*

TABLE XX.—METHYL BUTYRATE; M = 102.08; t_c obs. = 281.3°.

t.	d.	w.	$w\left(\frac{M}{d}\right)^{\frac{2}{3}}$.	t_c	$\gamma\left(=w\frac{2.1212}{2.3373}\right)$.
10.0°	0.90925	27.920	649.76	*294.0*	25.340
34.8	0.88175	24.915	591.82	*294.0*	22.610
59.9	0.85375	21.964	533.07	*294.0*	19.930

Ramsay and Aston; k_B = 2.1212.

	r = 0.01843 cm.		r = 0.01046 cm.	
t.	$\gamma\left(\frac{M}{d}\right)^{\frac{2}{3}}$.	t_c.	$\gamma\left(\frac{M}{d}\right)^{\frac{2}{3}}$.	t_c.
10.0°	595.0	*296.5*	591.7	*295.0*
46.2	514.5	*294.8*	511.8	*293.5*
78.2	446.9	*294.9*	444.4	*293.7*

Surface Tensions.

t.	γR & A.		γM & S from $w\frac{2.1212}{2.3373}$
10.2°	25.63	25.50	25.34
46.2	21.50	21.39	21.40
78.2	18.15	18.05	17.98*

TABLE XXI.—PROPYL FORMATE; M = 88.06; t_c obs. 264.9°.

t.	d.	w.	$w\left(\frac{M}{d}\right)^{\frac{2}{3}}$.	t_c.	$\gamma\left(=w\frac{2.1212}{2.3373}.\right)$
0.1°	0.92850	28.604	594.88	*260.6*	25.960
5.4	0.92251	27.941	583.60	*261.1*	25.358
10.0	0.91726	27.337	573.16	*261.2*	24.809
17.0	0.90909	26.458	558.05	*261.7*	24.012
34.8	0.88873	24.298	520.29	*263.9*	22.051
60.3	0.85837	21.419	469.39	*267.1*	19.439

Ramsay and Aston; k_B = 2.1212.

	r = 0.01843 cm.		r = 0.01046 cm.	
t.	$\gamma\left(\frac{M}{d}\right)^{\frac{2}{3}}$.	t_c.	$\gamma\left(\frac{M}{d}\right)^{\frac{2}{3}}$.	t_c.
10.0°	523.6	*262.8*	524.4	*263.2*
46.5	446.3	*262.9*	447.1	*263.3*
78.3	387.0	*266.8*	385.2	*265.9*

Surface Tensions.

t.	γR & A.		γM & S from $w\frac{2.1212}{2.3373}$.
10.0°	25.02	25.06	24.81
46.5	20.67	20.71	20.83
78.3	17.52	17.44	17.61*

TABLE XXII.—METHYL FORMATE; M = 60.03; t_c obs. 214°.

t.	d.	w.	$w\left(\frac{M}{d}\right)^{\frac{2}{3}}$.	t_c	$\gamma\left(w=\frac{2.1012}{2.3373}\right)$.
0.1°	1.00300	29.893	457.39	*201.8*	26.873
6.7	0.99354	28.860	444.38	*202.8*	25.945
10.0	0.98892	28.243	436.23	*202.6*	25.390
16.4	0.97943	27.360	425.32	*204.4*	24.596
27.8	0.96320	25.614	402.64	*206.1*	23.027

Ramsay and Shields; k_B = 2.1012.

t.	$\gamma\left(\frac{M}{d}\right)^{\frac{2}{3}}$.	t_c.	t.	$\gamma\left(\frac{M}{d}\right)^{\frac{2}{3}}$.	t_c.
20°	383.9	*208.7*	50°	322.6	*209.5*
30	363.7	*209.1*	60°	302.5	*210.0*
40	343.2	*209.3*	70°	282.7	*210.5*

Surface Tensions.

t.	γR & S.	γM & S from $w\frac{2.1012}{2.3373}$.
20°	24.64	24.11
30	23.09	22.72*
40	21.56	21.34*
50	20.05	19.95*
60	18.58	18.57*
70	17.15	17.19* (Extrapolated through 43.2°)

TABLE XXIII.—AMYL FORMATE; M = 116.1; t_c obs. = 304.6°.

t.	d.	w.	$w\left(\frac{M}{d}\right)^{\frac{2}{3}}$.	t_c.	$\gamma\left(=w\frac{2.1012}{2.3373}\right)$.
10.0°	0.8882	27.464	706.26	*318.6*	24.686
35.0	0.8682	24.693	645.73	*317.3*	22.199
60.1	0.8420	21.904	584.62	*316.2*	19.691

Homfray and Guye; k_B = 2.1012.[1]

t.	$\gamma\left(\frac{M}{d}\right)^{\frac{2}{3}}$.	t_c.
43.8°	569.5	*320.8*
77.8	497.8	*320.7*
109.2	432.2	*320.9*

Surface Tensions.

t.	γH & G.	γM & S from $w\frac{2.1012}{2.3373}$.
43.8°	21.64	21.51
77.8	18.40	18.12*
109.2	15.52	15.05* (Extrapolated through 49.1°)

TABLE XXIV.—ETHYL ACETATE; M = 88.06; t_c obs. = 250.1°.

t.	d.	w.	$w\left(\frac{M}{d}\right)^{\frac{2}{3}}$.	t_c.	$\gamma\left(=w\frac{2.1061}{2.3373}\right)$.[2]
0.1°	0.92421	27.940	582.86	*255.4*	25.175
34.6	0.88277	23.375	502.77	*255.7*	21.062
60.5	0.85019	20.064	442.51	*255.8*	18.078

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[1] Benzene values not given, but as authors used capillary of Guye and Baud who calibrated the bore from the benzene results of Ramsay and Shields, 2.1012 is assumed as correct.

[2] Average of 2.1108 and 2.1012 used for finding γ for the comparison.

Table XXIV (*Continued*).

Ramsay and Shields; $k_B = 2.1012$.

t.	$\gamma\left(\frac{M}{d}\right)^{\frac{2}{3}}$.	t_c.	t.	$\gamma\left(\frac{M}{d}\right)^{\frac{2}{3}}$.	t_c.
20°	500.7	*264.3*	100°	321.7	*259.1*
80	367.2	*260.8*	110	299.0	*258.3*
90	344.4	*259.9*	120	277.0	*257.9*

Guye and Baud; $k_B = 2.1012$.

t.	$\gamma\left(\frac{M}{d}\right)^{\frac{2}{3}}$.	t_c.	t.	$\gamma\left(\frac{M}{d}\right)^{\frac{2}{3}}$.	t_c.
9.5°	519.6	*262.8*	....	....	....
55.6	413.0	*258.2*	....	....	....
77.0	373.0	*260.5*	....	....	....

Renard and Guye; $k_B = 2.1108$.

t.	$\gamma\left(\frac{M}{d}\right)^{\frac{2}{3}}$.	t_c.	t.	$\gamma\left(\frac{M}{d}\right)^{\frac{2}{3}}$.	t_c.
12.9°	509	*260.0*	55.0°	418.0	*259.0*
31.3	470	*260.0*	65.9	394.0	*258.6*
46.9	437	*259.9*	73.5	381.0	*260.0*

Surface Tensions.

t.	γR & S.	γG & B.	γR & G.	γM & S.
10°	24.81*	24.64	24.50	24.00
20	23.60	23.36	23.27	22.82
30	22.39	22.08	22.04	21.64
40	21.18	20.80	20.89	20.44
50	19.97	19.52	19.71	19.29
70	17.55	17.35	17.39	16.99*
80	16.32	16.32*	16.47*	15.84*

TABLE XXV.

Liquid.	$t_c = \text{constant}\ \frac{\alpha' \div \alpha''}{\alpha'\alpha''}$.[1]			
	α'.	α''.	t_c.	t_c from k_B.
Pyridine	0.003534	0.002624	348.0	346.9
Methyl isobutyrate	0.004295	0.003321	279.9	282.6
Ethyl propionate	0.004211	0.003231	286.7	286.8
Methyl propionate	0.004426	0.003443	270.7	265.5
Methyl acetate	0.005143	0.003979	233.7	233.5
Propyl acetate	0.004233	0.003244	285.5	288.3
Methyl butyrate	0.004100	0.003148	294.5	294.0
Ethyl acetate	0.004665	0.003630	256.8	255.6
Ethyl formate	0.004847	0.003681	250.6	225.1–228.7
Amyl formate	0.003884	0.003070	305.7	318.6–316.2
Propyl formate	0.004171	0.003060	297.0	260.6–267.1
Methyl formate	0.005165	0.003888	234.4	201.8–206.1

[1] The values for benzene are $\alpha' = 0.004203$ and $\alpha'' = 0.003201$, from which, taking $t_c = 288.5°$, the constant is found to be 0.5243.

Discussion of the Results.

Taking up the liquids in the order they are given in the tables, we find for methyl isobutyrate (XIV) that the calculated value of t_c is constant from drop weight, but has a slight trend downward according to the results from capillary rise, though it must be conceded that the numbers by the latter method are hardly consistent, for Renard and Guye find a sudden break between 55° and 75° of 1.3°, although from 30.5° to 35° there is only one of 0.2°. In other words, it would seem that there is some error in the capillary rise, as judged from the t_c value, which occurs between 55° and 75° for Renard and Guye, and between 46.2° and 78.2° for Ramsay and Aston. This may be very well due to the use of density values which are not quite consistent at the high and the low temperatures. Comparison of the surface tension values as calculated by the two methods, where those from drop weight are free from any effect of density, shows an excellent agreement with the results of Ramsay and Aston, and one that is truly remarkable, even to the extrapolated values, with those of Renard and Guye.

With ethyl propionate the agreement in the values of t_c, which is constant by both methods, is excellent, while the drop weight surface tensions are found to lie between the values found by Ramsay and Aston in two capillaries of differing bore.

The t_c values for methyl propionate by drop weight may be considered as constant, the variation, which is not excessive, being due probably to the density. If a trend is assumed here it is certainly in the opposit direction from that found from the capillary rise. The t_c values in one of Ramsay and Aston's tubes is also practically constant, but is slightly smaller throughout than the drop weight value, while the other shows a higher value even than that, at 10°, and then remains constant at a value midway between that of the other and the drop weight. The comparison of the surface tension values from the two methods shows an agreement which is excellent.

With ethyl formate the t_c values show an increase with the temperature throughout, the values from the two methods being practically identical when with the same density values the t_c's are calculated from the surface tension values of drop weight. These latter, except that extrapolated through 44.5°, lie between the surface tensions from the two tubes of Ramsay and Aston. We shall return to the trend in the t_c values again.

Methyl acetate is the only liquid among those investigated, which leads to a t_c value in agreement with the observed critical temperature, and is found both by drop weight and capillary rise, for the mean of all the Ramsay and Aston values is 234°, as compared with 233.5° by drop weight, and 233.7° observed directly. The surface tensions here also agree in an extremely satisfactory manner, including one of the extrapolated values, although the other, extrapolated through 44.1°, does not. It is to be remembered here that the drop weight surface tension is one that at 78.3° with the constant 2.1212 would still give 233.5°, while the capillary rise value would lead to a higher result.

In the case of propyl acetate, the slight variation in the t_c values is probably due to the density used, and is not thought to indicate a trend. The means of all the Ramsay and Aston values is 288.9°, while that from the drop weight is 288.3°. The surface tensions from drop weight are very slightly smaller throughout than those from capillary rise, but the difference is less than that often noticed between the values from the two tubes of Ramsay and Aston, which should be identical in result.

In the case of methyl butyrate the drop weight t_c is identical at all three temperatures, while a slight variation is shown by the capillary rise method, the results of which differ, when found from the different tubes, by 1°. Considering all this as due to variable error in the capillary rise values, we find the mean t_c to be 294.7°, as compared to the constant 294° from drop weight. The surface tensions here, except for 10°, where the capillary rise values differ considerably among themselves, is very good indeed.

Propyl formate shows an increase in t_c with the temperature by both drop weight and capillary rise, the values from drop weight not agreeing very well, either with respect to t_c or to surface tension, with those from capillary rise. The behavior of this liquid was found to be striking, in that when heated for a few hours at 60°, a reversible reaction appears to take place which increases the drop weight, when it is determined again at 10°. Thus heating for 2 hours, then allowing the liquid to cool naturally, and determining the drop weight at 10°, a value 27.434 is obtained, as against 27.337 for the unheated sample. After standing for 16 hours, this weight is reduced to 27.430, and after 10 days to 27.366. Heating to 60° and cooling suddenly, as in a distillation, leads to a value of 27.337, *i. e.*, one identical with that of an unheated sample. Since nothing else in the behavior of the liquid indicated a reason for this, it is assumed that a definit reaction takes place on raising the temperature, which reverses slowly, unless the cooling is very rapid, when it returns at once to its original state. Using the value at 10° found after heating, the drop weight t_c would be increased to 262.2, which is in better agreement with one of the Ramsay and Aston values. As far as can be found from the paper, Ramsay and Aston always worked at the higher temperatures first, gradually lowering the temperature by reducing the pressure over the boiling liquid which heated the bath. This would account for their higher values at the low temperature—for the actual state at the higher temperature would then persist at the lower one. With the drop weight, on the other hand, the weight at the lower temperature was always determined from a sample, which, if it had been heated, had returned to its original state.

Methyl formate is a liquid which had been investigated by Ramsay and Shields, and was consequently not studied by Ramsay and Aston. Here again a value of t_c increasing with the temperature is observed by both methods. The drop weight surface tensions here at the low temperatures do not agree well with those from the capillary rise, but the agreement becomes better and better as the temperature of observation increases, even though all but one of the drop weight values are extrapolated, until the agreement is perfect. This would indicate a behavior similar to that of propyl formate, the low values of the capillary rise being influenced by the persistence of the high temperature conditions, while the drop weight is unaffected by it. When the possibility of this effect disappears, the two methods lead to identical results. Here the lower values by drop weight, being smaller than they should be, while that at 27.8° is less affected, would produce a curve which when combined would naturally eliminate at the higher temperatures the effect of the heat reaction noticeable at the low temperatures.

Amyl formate has been investigated only by Homfray and Guye. The sample used here was probably not pure, and certainly the densities employed were not satisfactory, as the three values given by Homfray and Guye did not allow an accurate extrapolation. As will be observed, the t_c values from capillary rise are very constant, while those from drop weight decrease slightly, and are smaller throughout. This may, of course, be due either to the effect of density or to an impurity. The surface tensions differ as do the values of t_c; this would seem to indicate that the purity of the liquid used for the drop weight is questionable. It can be concluded there that through no fault of the drop weight method, the results from capillary rise are probably the more correct.

For ethyl acetate a constant t_c is found both from drop weight and from capillary rise as found by Guye and Baud and Renard and Guye, although the values differ considerably. Ramsay and Shields find a downward trend. The difference in the three values of surface tension from capillary rise is best shown perhaps when all are calculated to the same temperature. It will be observed here that it is at the low temperatures especially that the results of the 3 observers of capillary rise differ, differences of 1 per cent. and more being common. It is unfortunate that this liquid was not investigated by Ramsay and Aston in their two tubes. As it is, there is no apparent reason why drop weight and capillary rise should differ as they do, especially in view of the other excellent agreements. One thing is certain from the constant t_c, both from drop weight and from capillary rise, *viz.*, ethyl acetate is to be regarded as normal in molecular weight, *i. e.*, it is non-associated.

It will be seen from the above that *according to the new definition of normal molecular weight the following liquids are to be regarded as normal and non-associated: methyl isobutyrate, ethyl propionate, methyl propionate, methyl acetate, propyl acetate, methyl butyrate, amyl formate (from capillary rise values of t_c), and ethyl acetate.* Ethyl formate, methyl formate, and propyl formate do not satisfy this definition and consequently are not to be considered as normal; but their behavior may in all cases be due to such a reversible reaction as is indicated above in the case of propyl formate when heated.

A sample of amyl formate was heated to 230° in the presence of mercury in a closed tube for 4 hours, *i. e.*, submitted to somewhat the same conditions that would hold during an observation of the critical temperature. On opening the tube considerable pressure was observed, while the liquid, which had a somewhat different odor, showed a drop weight at 10° of 27.309, as compared to the value 27.464, obtained before heating. This, of course, is not to be considered as the opposit behavior to that of propyl formate when heated to 60°, for here an actual decomposition takes place. If this decomposition always takes place in the determination of the critical temperature, it would account for the differences between the 304° observed and the fictitious critical temperature, t_c, found above, *viz.*, 321°.

Table XXV gives the results of t_c calculated by aid of the Walden relationship $t_c = \text{constant}\ \frac{\alpha' + \alpha''}{\alpha'\alpha''}$, where the values of α' and α'' are found from the equations $w_t = w_0(1 - \alpha' t)$ and $v_t = \frac{w_t}{d_t} = v_0(1 - \alpha'' t)$. It will be observed here that the agreement is as good as can be expected (remembering the multiplication of error in finding α' and α''), *i. e.*, in all cases where the t_c found from k_B is constant.

Conclusions.

The results of this investigation may be summarized as follows:

1. It is shown by aid of the new definition of normal molecular weight in the liquid state, *i. e.*, the finding of a calculated value of t_c from the equation $w\left(\frac{M}{d}\right)^{\frac{2}{3}} = k_B(t_c - t - 6)$, which does not vary with the temperature of observation, using in all cases the value of k_B found for benzene and taking $t_c = 288.5°$, that methyl acetate, ethyl acetate, propyl acetate, methyl butyrate, methyl isobutyrate, methyl propionate, ethyl propionate, and amyl formate are normal in molecular weight, *i. e.*, are non-associated.

2. It is found that only in the case of methyl acetate does the calculated t_c agree with the observed critical temperature, the fictitious critical temperatures, t_c, being the higher in all the others except ethyl, methyl

and propyl formates, where it approaches the observed value with increased temperature.

3. Methyl, ethyl and propyl formates show varying values of t_c with the temperature. In one of these (it is probably true for all) it is shown that apparently a reaction which is reversible is caused by increased temperature, which can be reversed by sudden cooling, but which persists on slow cooling, leading at the lower temperatures to a higher drop weight (and also t_c) than the unheated sample. It is only after some days that this heated sample again returns to its original, unheated value. This reaction is probably what causes the drop to be heavier than it should be at the higher temperature, and to lead to the value of t_c which is larger at 60° than at 0° by 6° in the maximum. We cannot say then that these three formates are either associated or normal; but simply that increased temperature causes a reaction of an unknown nature to take place.

4. Surface tensions in dynes per centimeter, calculated from the drop weight by multiplication by the ratio of the benzene constant for capillary rise to that for drop weight, are found to agree exceedingly well with those of Ramsay and Aston. The agreement of methyl formate with the figures of Ramsay and Shields is not so good, nor that of amyl formate with those of Homfray and Guye (although this is probably due to the impurity of the sample used with drop weight), while the values for ethyl acetate vary considerably from those of the workers on capillary rise, although these do not agree well among themselves.

5. The values of t_c calculated from the modified Walden relationship agree as well with those from the k_B formula as can be expected, except for ethyl, methyl and propyl formates, where since the k_B values are variable, no agreement can be expected.

LABORATORY OF PHYSICAL CHEMISTRY.

[CONTRIBUTIONS FROM THE HAVEMEYER LABORATORIES OF COLUMBIA UNIVERSITY, No. 194.]

THE WEIGHT OF A FALLING DROP AND THE LAWS OF TATE. VIII. THE RELATIONSHIP EXISTING BETWEEN THE WEIGHT OF THE DROP, THE DIAMETER OF THE TIP FROM WHICH IT FALLS, AND THE SURFACE TENSION OF THE LIQUID.

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It has been shown in previous papers that *for any one tip the laws of Tate, viz.: the weight of a falling drop is proportional to the surface tension of the liquid; and the weight of the drop decreases with increased temperature*, are true. The object of this paper is to present the results of a study