

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		10.7954			
36.05	10.0868	10.0869	10.7956	10.7955	36.15	29.14
36.35	10.0868					
59.58	10.0472		10.7883			
59.53	10.0474	10.0471	10.7883	10.7883	59.54	25.88
59.53	10.0467					

TABLE II.—ANILINE.

<i>t</i> .	Wt. vessel + 15 drops.	Av.	Wt vessel + 5 drops.	Av.	Av <i>t</i> .	Wt. 1 drop. Mg.
34.3	10.0954					
34.2	10.0960					
34.35	10.0960	10.0956	10.6440 (empty vessel and vapor)		34.3	45.16
34.3	10.0950					

TABLE III.—PYRIDINE.

<i>t</i> .	Wt. vessel + 25 drops.	Av.	Wt vessel + 5 drops.	Av.	Av <i>t</i> .	Wt. 1 drop. Mg.
23.03	11.2548					
22.75	11.2550		10.8484			
23.13	11.2544	11.2549	10.8482	10.8483	22.93	40.66
22.83	11.2553					
58.33	10.6389		10.9346			
58.43	10.6384	10.6386	10.9340	10.9343	58.4	35.215
58.40	10.6385					

TABLE IV.—QUINOLINE.

<i>t</i> .	Wt. vessel + 25 drops.	Av.	Wt vessel + 5 drops.	Av.	Av <i>t</i> .	Wt. 1 drop. Mg.
22.38	10.4846					
22.28	10.4846	10.4846	9.7525 (empty)		22.33	48.807

These results were obtained a year ago, and consequently, as were those given in the previous paper, are not as accurate as those which can be obtained now. The  $k$  values for these liquids from the above results, using the  $t_c$  values actually calculated by Morgan and Higgins from the ratio  $k_{temp.} = \Delta [w(M/d)^{2/3}] / \Delta t$ , are given in Table V, and will serve to show that the values of  $k$  necessary are practically constant. The densities used here are calculated from the formulas already given by Morgan and Thomssen.

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

Liquid.	M.	<i>t</i> .	<i>d</i> .	<i>w</i> .	$w(M/d)^{2/3}$ .	$k$ necessary to give $t_c$ of M & H.
Benzene. . . . .	78	36.15°	0.8617	29.14	587.47	2.3857 } 2.3866 } 288.4°
		59.54	0.8368	25.88	532.06	
Aniline. . . . .	93	34.3°	1.0093	45.16	921.20	2.3898 } 425.8
Pyridine. . . . .	79	22.93	0.9785	40.66	759.31	2.3872 } 347.0
		58.39	0.9430	35.215	674.23	6.3858
Quinoline. . . . .	129	22.33	1.09195	48.807	1175.17	2.3882 } 520.4
						2.3874

Naturally, to transform any result on this tip into one, at the same temperature, on any other tip, we have only to use the proportion

$$w_{M \& D} : w_x :: 2.3866 : k_x,$$

where  $k_x$  is the benzene value of  $k$  of the other, calculated from  $w(M/d)^{2/3} = k(288.5 - t - 6)$ ; and to obtain the surface tension in dynes per centimeter, at the same temperature, we have only to use the relation

$$w_{M \& D} : \gamma :: 2.3866 : k_r$$

where  $k_r$  is the  $k$  value found for benzene as above by the observer whose

results are to be compared; or is the average value found by all observers who have worked with benzene. While, since the volume of a drop is proportional to the capillary constant, we can calculate the capillary constant  $a^2$  by first finding at the same temperature for benzene the ratio  $a^2/w/d$ , and then by multiplying any drop volume (*i. e.*, drop weight divided by density) by it, get the capillary constant at that temperature, of the liquid.

Further, it is to be remembered here that surface tensions as calculated from capillary rise can be compared indirectly with the drop weight at another temperature by finding with the proper  $k_B$  the value of the calculated  $t_c$  for each. An agreement in the values of  $t_c$  here indicates, since the  $M$  is the same, and  $d$  is the same function of the temperature, in each case, that  $K : k :: w : \gamma$ .

### New Liquids.

The experimental results of the 20 new non-associated liquids studied are given in Tables VI to XXV. These results are not as accurate as those which can be obtained, for in many cases only 15 drops were weighed in place of the usual 30, which, with the 5-drop blank, causes an error of 0.1 mg. to become 0.01 in the weight of the single drop. Further, the variation in temperature involves a small error, for it is impossible, when the temperature is changing, to find how much the change in the liquid lags behind that in the thermometer. Notwithstanding these disadvantages, which have been excluded in the papers which are to follow this, it will be observed that the results are very satisfactory. Just as in the last paper, it is to be remembered here also that the results given in the tables throughout are not the only ones which were found, but are representative of a number of results, and are given because the number of drops taken was the same and the temperatures practically identical. In those cases where but one result at each temperature is presented, others were always at hand at a slightly different temperature which checked the value of  $t_c$  resulting within less than one-tenth of one per cent.

TABLE VI.—BROMOBENZENE.

$t$ .	Wt. vessel + 25 drops.	Av.	Wt. vessel. + 5 drops.	Av.	Av. $t$ .	Wt. 1 drop. Mg.
37.9	11.5863		10.8345	10.83485	38.3	37.593
38.4	11.5870	11.5867	10.8352			
38.55	11.5868					
59.63	11.5210		10.8252	10.82495	59.67	34.795
59.70	11.5207	11.52085	10.8247			

TABLE VII.—BROMINE.

	+ 15 drops.					
0	11.4380		10.9141	10.91435	0°	52.368
0	11.4376	10.43803	10.9146			
0	11.4385					

TABLE VIII.—CARBON DISULFIDE.

t.	Wt. vessel + 15 drops.	Av.	Wt. vessel + 5 drops.	Av.	Av. t.	Wt. 1 drop. Mg.
20.15	11.1733		10.8190			
20.35	11.1718	11.17337	10.8190	10.8190	20.13	35.437
19.90	11.1750					

TABLE IX.—CYMENE.

18.95	11.0995		10.7963			
18.75	11.1015	11.1009	10.7968	10.79677	18.7	30.413
18.35	11.1018		10.7972			
59.45	11.0406	11.0407	10.7774	....	59.45	26.33
59.45	11.0408					

TABLE X.—DIPHENYLMETHANE.

59.05	11.2108					
59.0	11.2113	11.2110	10.6440 (empty and vapor)		59.0	37.80
58.9	11.2109					

TABLE XI.—ETHYLBENZENE.

20.9	11.1154	11.11545	10.8022	....	21	31.325
21.1	11.1155					
59.4	11.0528	11.05235	10.7846	....	59.5	26.775
59.6	11.0519					

TABLE XII.—DIMETHYLANILINE.

21.45	11.2381	11.2380	10.8419	10.84185	21.5	39.615
21.55	11.2379		10.8418			
59.50	11.1684					
59.65	11.1673	11.1682	10.8192	....	59.5	34.90
59.45	11.1689					

TABLE XIII.—ETHYLANILINE.

35.8	11.2152		10.8355			
35.8	11.2150	11.2152	10.8355	10.8354	35.8	37.98
35.7	11.2154		10.8352			
58.7	11.1760	11.1760	10.8224	10.8225	58.7	35.35
58.7	11.1760		10.8226			

TABLE XIV.—ETHYLENE CHLORIDE.

34.2	11.1483		10.8166			
34.1	11.1484	11.14843	10.8167	10.81665	34.1	33.178
34.1	11.1486					
	+ 26 drops.		+ 6 drops.			
60.0	11.4258	..	10.8404	....	60.0	29.270

TABLE XV.—ETHYLIDENE CHLORIDE.

	+ 15 drops.		+ 5 drops.			
34.1	10.0427		10.7822			
34.1	10.0422	10.04265	10.7822	10.7822	34.1	26.043
34.0	10.0430					
	+ 25 drops.		+ 10 drops.			
56.9	10.2097	..	10.8683	....	56.9	22.76

TABLE XVI.—TOLUENE.

<i>t.</i>	Wt. vessel + 25 drops.	Av.	Wt. vessel + 10 drops.	Av.	Av. <i>t.</i>	Wt. 1 drop. Mg.
36.05	11.0809	11.08085	10.7916	10.7916	36.05	28.925
36.05	11.0808		10.7916			
59.1	11.0425	11.0423	10.7819	10.78155	59.2	26.075
59.3	11.0421		10.7812			

TABLE XVII.—PHOSPHORUS TRICHLORIDE.

<i>t.</i>	Wt. vessel + 30 drops.	Av.	Wt. vessel + 10 drops.	Av.	Av. <i>t.</i>	Wt. 1 drop. Mg.
35.6	11.5517	11.5514	10.9567	10.9568	35.6	29.73
35.6	11.5515		10.9569			
35.6	11.5510					

TABLE XVIII.—*p*-XYLENE.

<i>t.</i>	Wt. vessel + 25 drops.	Av.	Wt. vessel + 5 drops.	Av.	Av. <i>t.</i>	Wt. 1 drop. Mg.
37.9	11.3678	..	10.7921	....	37.9	28.785
59.2	11.3079	10.3081	10.7820	10.78195	59.2	26.308
59.2	11.3083		10.7819			

TABLE XIX.—*o*-XYLENE.

<i>t.</i>	Wt. vessel + 15 drops.	Av.	Wt. vessel + 5 drops.	Av.	Av. <i>t.</i>	Wt. 1 drop. Mg.
23.9	10.2345	10.23455	9.9144	....	23.85	32.015
23.8	10.2346					
23.7	10.2358	..	9.9153	....	23.7	32.05
59.3	10.1756	10.1753	9.8965	....	59.4	27.88
59.5	10.1750					

TABLE XX.—*m*-XYLENE.

<i>t.</i>	Wt. vessel + 15 drops.	Av.	Wt. vessel + 5 drops.	Av.	Av. <i>t.</i>	Wt. 1 drop. Mg.
24.9	10.2095	..	9.9057	....	24.9	30.38
58.9	10.1529	..	9.8888	....	58.9	26.41

TABLE XXI.—METHYLANILINE.

<i>t.</i>	Wt. vessel + 25 drops.	Av.	Wt. vessel + 10 drops.	Av.	Av. <i>t.</i>	Wt. 1 drop. Mg.
24.6	10.8230	10.8231	9.9660	9.9659	24.6	42.86
24.6	10.8232		9.9658			
59.7	11.2219	11.2218	10.8378	10.8380	59.7	38.38
59.7	11.2217		10.8382			

TABLE XXII.—MESITYLENE.

<i>t.</i>	Wt. vessel + 15 drops.	Av.	Wt. vessel + 10 drops.	Av.	Av. <i>t.</i>	Wt. 1 drop. Mg.
23.5	10.0844	10.0844	10.7812	10.7812	23.5	30.32
23.5	10.0844		10.7812			
57.1	10.0452	10.0446	10.7787	10.7786	57.3	26.60
57.4	10.0440		10.7785			

TABLE XXIII.—ISOBUTYL ACETATE.

<i>t.</i>	Wt. vessel + 25 drops.	Av.	Wt. vessel + 10 drops.	Av.	Av. <i>t.</i>	Wt. 1 drop. Mg.
24	10.5146	10.5152	10.0082	....	23.8	25.35
23.6	10.5158					
59.2	10.2991	..	9.8680	....	59.2	21.555
59.3	10.4075 (another vessel)		9.9766	....	59.3	21.545

TABLE XXIV.—IODOBENZENE.

<i>t.</i>	Wt. vessel + 30 drops.	Av.	Wt. vessel + 10 drops.	Av.	Av. <i>t.</i>	Wt. 1 drop. Mg.
23.5	11.9297	..	10.1876	....	23.5	43.55
59.6	10.9270	..	10.1441	....	59.6	39.08

TABLE XXV.—FLUOROBENZENE.

+ 20 drops.		Vessel and vapor.				
9.3	12.8962					
9.3	12.8965	12.89623	12.2747	...	9.3	31.077
9.3	12.8960					
+ 25 drops.						
34.5	12.9630		12.4122			
34.5	12.9631	12.96317	12.4126	12.41243	34.5	27.537
34.5	12.9634		12.4125			

In Tables XXVI to XLV, inclusive, are given the values of the function  $w(M/d)^{2/3}$  and the calculated  $t_c$  resulting from the equation  $w(M/d)^{2/3} = k_B(t_c - t - 6)$ , using the mean value of the  $k$  for benzene, *viz.*, 2.3866. At the same time, wherever it is possible, the surface tension results, as found from capillary rise, together with the calculated value of  $t_c$ , from the proper value of  $k_B$ , are also given, in order that an indirect comparison may be made of the results of surface tension from drop weight and from capillary rise.

TABLE XXVI.—BROMOBENZENE;  $M = 156.96$ ;  $d_t = 1.5203 - 0.001282t$ ;  $t$  obs. =  $397^\circ$ .

$t$ .	$d$ .	$w$ .	$w(M/d)^{2/3}$ .	$t_c$ .
38.3	1.4713	37.593	845.60	398.6 <sup>1</sup>
59.7	1.4438	34.795	792.57	397.8

TABLE XXVII.—BROMINE;  $M_{Br_2} = 159.84$ ;  $t_c$  obs. =  $302.2^\circ$ .

0	3.1872	52.368	712.17	304.4
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Ramsay and Aston,  $k_B = 2.1212$ .

$t$ .	$w(M/d)^{2/3}$ .	$t_c$ .
10.6	552.08	276.9
46.0	487.98	282.1
78.1	426.09	285.0

TABLE XXVIII.—CARBON DISULFIDE;  $M = 76.14$ ;  $d_t = 1.29215 - 0.0013025t$ ;  $t_c$  obs. from  $271.8^\circ - 279.6^\circ$ .

$t$ .	$d$ .	$w$ .	$w(M/d)^{2/3}$ .	$t_c$ .
20.13	1.2659	35.437	544.05	254.1

Morgan and Thomsen,  $t_c = 252.1$ ; Ramsay and Shields,  $t_c = 270.2 - 271.7$ ; Ramsay and Aston,  $t_c = 251.1, 257, 257.4$ .

TABLE XXIX.—CYMENE;  $M = 134.112$ ;  $d_t = 0.862 - 0.0008044(t - 11.9^\circ)$ ;  $t_c$  obs. =  $378.6^\circ$ .

18.7	0.8565	30.413	883.52	394.9
59.45	0.8235	26.330	785.20	394.5

<sup>1</sup> Miss C. M. Sillcox, working with a slightly smaller tip, and Miss J. Y. Cann with one larger as well as one smaller, have found since, at all temperatures, that  $t_c = 397.0^\circ$ .

Renard and Guye,  $k_B = 2.1108$ .

$t$ .	$w(M/d)^{2/3}$ .	$t_c$ .	$t$ .	$w(M/d)^{2/3}$ .	$t_c$ .
11.9	809.38	401.3	108.9	591.04	394.9
31.7	767.13	401.1	117.0	571.57	373.7
54.8	711.65	398.0	134.9	532.96	393.4
74.5	667.08	396.5	146.5	505.48	392.0
91.8	627.35	395.0	163.4	469.68	391.9
			172.8	451.50	392.7

Average, 395.5

TABLE XXX.—DIMETHYLANILINE;  $M = 121.1$ ;  $d_t = 0.9589-0.000825 (t-16.7)$ ;  $t_c$  obs. =  $414.45^\circ$ .

$t$ .	$d$ .	$w$ .	$w(M/d)^{2/3}$ .	$t_c$ .
21.5	0.95494	39.615	999.94	446.5
59.53	0.92360	34.900	900.74	442.9

Dutoit and Friederich,  $k_B = 2.1012$ .

$t$ .	$w(M/d)^{2/3}$ .	$t_c$ .	$t$ .	$w(M/d)^{2/3}$ .	$t_c$ .
22.7	891.5	453.0	76.7	762.5	445.6
43.5	838.6	448.6	99.0	708.3	442.1

Renard and Guye,  $k_B = 2.1108$ .

10.9	909.75	447.9	126.7	644.16	437.9
41.0	845.41	447.5	134.8	626.26	437.5
55.0	811.76	445.6	154.0	582.87	436.2
78.9	753.38	441.8	165.0	560.61	436.6
96.0	714.26	440.4	175.5	533.28	435.1
108.8	684.25	438.9			

TABLE XXXI.—DIPHENYLMETHANE;  $M = 168.1$ ;  $d = 1.0126-0.0007914 (t-11)$ ;  $t_c$  obs. =  $497^\circ$ .

$t$ .	$d$ .	$w$ .	$w(M/d)^{2/3}$ .	$t_c$ .
59	0.9746	37.80	1171.26	555.8

Dutoit and Friederich,  $k_B = 2.1012$ .

108.3	..	..	931.4	557.5
210.2	..	..	677.1	538.4

TABLE XXXII.—ETHYLBENZENE;  $M = 106.08$ ;  $d_t = 0.88316-0.0008333t$ ;  $t_c$  obs. =  $463.4^\circ$ .

21.0	0.86566	31.325	772.83	350.8
59.5	0.83358	26.775	681.13	351.3

TABLE XXXIII.—ETHYLANILINE;  $M = 121.098$ ;  $d_t = 0.9796-0.000831t$ ;  $t_c$  obs. =  $425.4^\circ$ .

35.8	0.9499	37.98	962.06	444.9
58.7	0.9310	35.35	907.51	445.0

Dutoit and Friederich,  $k_B = 2.1012$ .

7.4	..	..	927.9	455.0
107.8	..	..	698.4	446.2
210.0	..	..	477.6	443.3

TABLE XXXIV.—ETHYLENE CHLORIDE;  $M = 98.95$ ;  $d_t = 1.28015 - 0.001528t$ ;  
 $t_c$  obs. = 283.3° to 289.3°.

$t$ .	$d$ .	$w$ .	$w(M/d)^{2/3}$ .	$t_c$ .
34.1	1.22805	33.178	618.79	299.5
60.0	1.18850	29.270	558.09	299.8

TABLE XXXV.—ETHYLIDENE CHLORIDE;  $M = 98.95$ ;  $d_t = 1.207 - 0.0016t$ ;  
 $t_c$  obs. = 250, 254.5, 260.0.

$t$ .	$d$ .	$w$ .	$w(M/d)^{2/3}$ .	$t_c$ .
34.1	1.1524	26.043	506.87	252.5
56.9	1.1160	22.760	452.56	252.5

TABLE XXXVI.—TOLUENE;  $M = 92.064$ ;  $d_t = 0.8682 - 0.000953(t - 15.2)$ ;  
 $t_c$  obs. = 320.7°.

$t$ .	$d$ .	$w$ .	$w(M/d)^{2/3}$ .	$t_c$ .
36.0	0.8484	28.925	658.57	318.0
59.2	0.8263	26.075	603.75	318.2

Ramsay and Aston,  $k_B = 2.1212$ .

$t$ .	$w(M/d)^{2/3}$ .	$t_c$ .	$t$ .	$w(M/d)^{2/3}$ .	$t_c$ .
15.2	631.0	318.7	78.4	490.8	315.8
46.6	563.9	318.0	132.5	382.2	319.5

Renard and Guye,  $k_B = 2.1108$ .

$t$ .	$w(M/d)^{2/3}$ .	$t_c$ .	$t$ .	$w(M/d)^{2/3}$ .	$t_c$ .
13.1	630.65	317.9	79.0	490.01	318.1
29.1	596.87	317.9	91.5	464.48	317.5
48.0	555.29	317.1	108.9	431.21	319.2
59.0	532.93	317.5			

TABLE XXXVII.—PHOSPHORUS TRICHLORIDE;  $M = 137.38$ ;  $t_c$  obs. = 285.5°.

$t$ .	$d$ .	$w$ .	$w(M/d)^{2/3}$ .	$t_c$ .
35.6	1.5649	29.73	587.24	287.7

Ramsay and Shields,  $k_B = 2.1012$ 

$t$ .	$d$ .	$w$ .	$w(M/d)^{2/3}$ .	$t_c$ .
16.4	..	..	562.3	288.0
46.2	..	..	499.8	290.0

TABLE XXXVIII.—*p*-XYLENE;  $M = 106.08$ ;  $d_t = 0.8801 - 0.0008468t$ ;  $t_c$  obs. 344.4°.

$t$ .	$d$ .	$w$ .	$w(M/d)^{2/3}$ .	$t_c$ .
37.9	0.8480	28.785	720.0	345.6
59.2	0.8300	26.308	667.51	344.9

TABLE XXXIX.—*o*-XYLENE;  $M = 106.08$ ;  $d = 0.8932 - 0.0008425t$ ;  $t_c$  obs. 358.3°.

$t$ .	$d$ .	$w$ .	$w(M/d)^{2/3}$ .	$t_c$ .
23.85	0.8731	32.015	785.36	358.9
59.4	0.8432	27.880	701.07	359.2

TABLE XL.—*m*-XYLENE;  $M = 106.08$ ;  $d_t = 0.8740 - 0.000944(t - 10)$ ;  $t_c$  obs. = 345.6°.

$t$ .	$d$ .	$w$ .	$w(M/d)^{2/3}$ .	$t_c$ .
24.9	0.8599	30.38	752.86	346.4
58.9	0.8271	26.41	671.67	346.3

Dutoit and Friederich,  $k_B = 2.1012$ .

$t$ .	$d$ .	$w$ .	$w(M/d)^{2/3}$ .	$t_c$ .
15.7	..	..	714.2	361.6
74.9	..	..	583.4	358.5
136.7	..	..	445.8	354.8



Renard and Guye,  $k_B = 2.1108$ .

$t$ .	$w(M/d)^{2/3}$ .	$t_c$ .	$t$ .	$w(M/d)^{2/3}$ .	$t_c$ .
10.0	707.95	351.4	88.0	540.82	350.2
38.0	651.57	352.7	99.4	516.76	350.2
49.8	624.47	351.6	109.0	499.18	351.5
63.9	592.78	350.7	128.3	458.93	351.7
76.8	564.88	350.4	136.5	442.49	352.1

TABLE XLI.—METHYLANILINE;  $M = 107.08$ ;  $d_t = 0.9944 - 0.000801(t-10)$ ;  $t_c$  obs. =  $428.6^\circ$ .

$t$ .	$d$ .	$w$ .	$w(M/d)^{2/3}$ .	$t_c$ .
24.6	0.9827	42.86	977.78	440.3
59.7	0.9546	38.38	892.68	439.7

Dutoit and Friederich,  $k_B = 2.1012$ .

$t$ .	$d$ .	$w$ .	$w(M/d)^{2/3}$ .	$t_c$ .
9.9	..	..	886.5	437.8
108.5	..	..	690.2	443.0
210.8	..	..	477.7	444.1

TABLE XLII.—MESITYLENE;  $M = 120.1$ ;  $d_t = 0.8746 - 0.00081t$ ;  $t_c$  obs. =  $367.7^\circ$ .

$t$ .	$d$ .	$w$ .	$w(M/d)^{2/3}$ .	$t_c$ .
23.5	0.8656	30.32	812.61	370.0
57.3	0.8282	26.60	734.21	370.9

Renard and Guye,  $k_B = 2.1108$ .

$t$ .	$w(M/d)^{2/3}$ .	$t_c$ .	$t$ .	$w(M/d)^{2/3}$ .	$t_c$ .
11.4	758.23	376.6	92.2	582.01	373.9
25.1	722.05	373.2	108.9	544.83	373.0
36.3	703.75	375.7	127.0	509.38	374.3
55.4	661.74	374.9	146.6	465.98	373.4
64.8	646.60	377.1	156.2	445.30	373.2
74.3	619.39	373.8			

TABLE XLIII.—ISOBUTYL ACETATE;  $M = 116.1$ ;  $d = 0.8802 - 0.001055(t-10)$ ;  $t_c$  obs.  $288.3^\circ$ ,  $295.8^\circ$ .

$t$ .	$d$ .	$w$ .	$w(M/d)^{2/3}$ .	$t_c$ .
23.8	0.8656	25.35	664.23	308.1
59.2	0.8282	21.55	581.54	309.0

TABLE XLIV.—IODOBENZENE;  $M = 203.96$ ;  $d_t = 1.8606 - 0.001535t$ ;  $t_c$  obs. =  $448^\circ$ .

$t$ .	$d$ .	$w$ .	$w(M/d)^{2/3}$ .	$t_c$ .
23.5	1.8245	43.55	1010.62	453.0
59.6	1.7691	39.08	925.73	453.5

TABLE XLV.—FLUOROBENZENE;  $M = 96.04$ ;  $d_t = 1.0466 - 0.001208t$ ;  $t_c$  obs. =  $286.6^\circ$ .

$t$ .	$d$ .	$w$ .	$w(M/d)^{2/3}$ .	$t_c$ .
9.3	1.0354	31.077	636.80	282.1
34.5	1.0049	27.537	575.62	281.7

TABLE XLVI.

$t_c = \text{constant} \frac{\alpha' + \alpha''}{\alpha' \alpha''}$	$w_i = w_o (1 - \alpha' t)$	$\frac{w_i}{d_i} = v_i = v_o (1 - \alpha'' t)$	$t_c$	$t_c$ from $k_B$
Liquid.	$\alpha'$	$\alpha''$		
Benzene. ....	0.004078	0.003227	[288.5]	..
	Constant from benzene = 0.51974			
Pyridine. ....	0.003472	0.002678	344.0	..
Bromobenzene. ....	0.003073	0.002423	383.6	398.2
Cymene. ....	0.003103	0.002336	389.6	394.7
Ethylbenzene. ....	0.003496	0.002747	337.9	351.0
Ethylene chloride. ....	0.003934	0.003058	302.0	299.6
Ethylidene chloride. ....	0.004654	0.003737	250.8	252.5
Ethylaniline. ....	0.002729	0.002038	445.5	445.0
Dimethylaniline. ....	0.002935	0.002233	409.8	444.4
Toluene. ....	0.003670	0.002876	322.3	318.1
<i>p</i> -Xylene. ....	0.003504	0.002783	335.1	345.3
<i>o</i> -Xylene. ....	0.003332	0.002590	356.7	359.0
<i>m</i> -Xylene. ....	0.003508	0.002613	347.1	346.4
Methylaniline. ....	0.002775	0.002112	433.5	440.0
Mesitylene. ....	0.003345	0.002307	380.7	370.5
Isobutyl acetate. ....	0.003842	0.002928	312.8	308.5
Fluorobenzene. ....	0.004338	0.003344	275.3	281.9
Iodobenzene. ....	0.002665	0.001969	459.0	453.3

### Discussion of Results.

The liquids studied above were of the greatest attainable purity. The bromobenzene and iodobenzene were especially prepared in this laboratory; the diphenylmethane was from Eimer and Amend, redistilled and recrystallized just before the determination was made; the isobutyl acetate, *m*-xylene, *o*-xylene, *p*-xylene, one sample of mesitylene, bromine and phosphorus trichloride were from Kahlbaum, usually redistilled just before using; while the others, including a sample of mesitylene, were especially prepared for this work by the Hoffman and Kropff Chemical Company,<sup>1</sup> and used directly. An idea of the purity of the latter preparations may be gained from the fact that the carbon disulfide possessed only the pleasant ethereal odor which characterizes the pure substance. The two samples of mesitylene, here, from the different sources, seemed to be perfectly interchangeable, no difference in drop weight being observable.

It will be noted that four liquids were studied at but one temperature, *viz.*: bromine, phosphorus trichloride, diphenylmethane, and carbon disulfide. In the case of carbon disulfide it was thought necessary to study only one temperature, to see if this undoubtedly pure sample would give a higher value of  $t_c$  than that found for another sample by Morgan and Thomssen, which might explain the considerably higher value of Ramsay and Shields, that could not be duplicated by Ramsay and Aston. As will be observed the value found, however, is only slightly larger than

<sup>1</sup> 619 Kent Ave., Brooklyn, N. Y.

that of Morgan and Thomssen, showing this smaller value to be correct. With phosphorus trichloride difficulty was experienced at 60°, a yellow substance forming in the ventilation tube, due perhaps to the failure of the drying tubes to exclude water vapor. As the result at the lower temperature agreed with the observed critical temperature, and with that obtained at another temperature from capillary rise, no further determinations were made. The low temperature result for bromine was considered sufficient, since it practically agreed with the observed critical temperature, and the Ramsay and Aston figures by aid of capillary rise, which disagreed with it, were stated by the authors to be probably inaccurate. At low temperatures the diphenylmethane gave trouble, owing to spontaneous crystallization. As the capillary rise value at another temperature agreed with the 60° result; here, also, it was thought unnecessary to make further determinations.

Since the value of  $t_c$  is equal to the observed critical temperature in the case of bromine; and in those of phosphorus trichloride and diphenylmethane practically the same  $t_c$  is to be found from capillary rise at a different temperature of observation, we can conclude that all the above liquids, with the exception of dimethylaniline, are normal in molecular weight, i. e., are non-associated; for all, with this exception, lead to the same calculated value of  $t_c$  (within a very small difference) at both temperatures of observation.

In the case of dimethylaniline, the same trend is shown by drop weight as that observed in the results from capillary rise; but it is quite likely that this discrepancy in  $t_c$  of 0.8 per cent. between 21.5° and 59.5° is due to the decomposition of this very unstable liquid, which darkens very rapidly on exposure to light. Here the low temperature result was obtained first, when the liquid was fresh—possibly a reversed procedure would have shown a trend in the opposite direction. Whatever the cause, however, we cannot say from the results that the molecular weight is normal, although it is quite evident that if it changes with the temperature, the change is not very great.

The agreement of the calculated  $t_c$  with the observed critical temperature is found to be very satisfactory for the following liquids: Bromine, bromobenzene, ethylidene chloride, toluene, phosphorus trichloride, *p*-xylene, *o*-xylene, and *m*-xylene, while for mesitylene, ethylbenzene and iodobenzene the discrepancies are below 1 per cent. for the former, and but slightly above that for the two latter. For all the other liquids the calculated  $t_c$ , i. e., the fictitious critical temperature, viz.: the point 6° below which, by the formula  $w(M/d)^{2/3} = k_B (t_c - t - 6)$ ,  $w(M/d)^{2/3}$  would become zero, is larger than the observed critical value for cymene, dimethylaniline, ethylene chloride, methylaniline, ethylaniline, isobutyl acetate, and diphenylmethane, while it is smaller only for carbon disulfide and fluorobenzene.

It is possible to compare with these values of the calculated  $t_c$  the corresponding values found from capillary rise, and consequently to find indirect proof of the relationship, at the same temperature,  $w : \gamma : K_B : k_B$ , for the following liquids only: carbon disulfide, cymene, dimethylaniline, diphenylmethane, ethylaniline, toluene, phosphorus trichloride, *m*-xylene, methylaniline and mesitylene. In the cases of toluene and phosphorus trichloride the agreement is practically perfect between the  $t_c$  values from drop weight and from capillary rise. With diphenylmethane, ethylaniline and cymene and methylaniline, a value of  $t_c$  at some temperature is always found which is equal to the one, constant, figure found at both temperatures from drop weight. In the case of the latter liquid, here, the large change found from capillary rise between  $9.9^\circ$  and  $108.5^\circ$ , when compared with the smaller one between  $108.5^\circ$  and  $210.8^\circ$ , would seem to indicate error somewhere in the capillary rise method. With dimethylaniline the trend is the same in all results, although it can hardly be said that the agreement in the capillary rise results is satisfactory—all this, however, including the trend, may well be due to the decomposition of this very unstable liquid. For cymene it will be noted that the mean of all the values of  $t_c$  from capillary rise  $395.5^\circ$  is in fair agreement with the constant drop weight value of  $394.7^\circ$ . For *m*-xylene the drop weight values are constant, but lower than either set from capillary rise, but as these latter agree only in that they give a higher value, and differ from one another more than the lower one does from that from drop weight, it would seem to indicate a possibility of error in the determination of capillary rise.

In Table XLVI are given the  $t_c$  values calculated by aid of the Walden relationship, which does not require a knowledge of the molecular weight. In 8 cases here the agreement with the values calculated from  $k_B$  is all that could be expected, but in the other 8 the variation is larger than is warranted, it is thought, by the experimental results. This would make it appear as if there are certain cases where this relationship does not hold satisfactorily.

In the next paper of the series a report will be made upon the work on some of the lower esters.

### Conclusions.

The results of this research may be summarized as follows:

I. According to the new definition of normal molecular weight, *i. e.*, that the normal (benzene) constant  $k_B$  give for the liquid a constant value of  $t_c$  independent of the temperature of observation,  $t$ , in the relationship  $w(M/d)^{2/3} = k_B (t_c - t - 6)$ , the following liquids are to be regarded as perfectly non-associated as is benzene itself: bromobenzene, bromine, ethylidene chloride, toluene, phosphorus trichloride, *p*-, *o*-, and *m*-xylene, mesitylene, ethylbenzene, iodobenzene, fluorobenzene, cymene, ethylene chloride,

methylaniline, ethylaniline, isobutyl acetate, carbon disulfide, and diphenylmethane. In the case of dimethylaniline the discrepancy in the values of  $t_c$  is 0.8 per cent., which is much too great for an experimental error, and can show that the molecular weight is only slightly abnormal, which may well be due to the fact that this liquid is very readily decomposed.

II. Of the value of  $t_c$  calculated for the above liquids, those for bromobenzene, bromine, ethylidene chloride, toluene, phosphorus trichloride, *o*-, *m*-, and *p*-xylene agree excellently with the observed values of critical temperature, while the disagreement with this value is below 1 per cent. for mesitylene, and but slightly above that for ethylbenzene and iodobenzene.

III. The agreement between the calculated values of  $t_c$  from drop weight and those from capillary rise, with the 11 liquids which have been studied by that method, is exceedingly good for toluene and phosphorus trichloride. In the other cases the mean of the  $t_c$  value from capillary rise agrees well with that for drop weight; and it is only for mesitylene and *m*-xylene that the values in mean from capillary rise disagree with those from drop weight. In the case of the latter liquid, however, this seems to mean little, as the values by two observers, although higher throughout, do not agree even fairly with one another.

IV. The values of  $t_c$  calculated by aid of the Walden relationship, without the aid of the molecular weight, in 8 cases (out of the 16 to which it could be applied) agree very well with those calculated from  $k_B$ , the variation in the others, however, indicating that probably this relationship is not as general as was at first thought.

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## A MODIFICATION OF THE PERIODIC TABLE.

BY ELLIOT QUINCY ADAMS.

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This article is to set forth and discuss the theoretical basis of an arrangement of the periodic table of the elements.

The principal defect of the earlier forms of the table, those formulated by Mendeléeff, Lothar Meyer and others, was that they placed in the same "family," as entirely homologous, elements as dissimilar as sodium and silver.

The double periods, of sixteen columns, of the more recent tables are a recognition of the fact that the number of elements in the different horizontal rows, or periods, is not constant. In this way the table has been made complete up to xenon (130.2), all known elements of lower atomic weight being accounted for, and only one space in the table, that below manganese, being vacant. Of the elements following xenon, the first two, cesium and barium, are obviously homologous with rubidium