

4. Attention is called to the inconsistency of the conclusion of Schenck and Ellenberger that acetyl acetone and acetoacetic ethyl ester are composed of tautomeric components. The fluctuations they observe in the Ramsay and Shields temperature coefficient,  $k$ , could well be caused by errors, too slight to be excluded, and hence are meaningless. Their conclusion may be the correct one, but it is quite certain that the surface-tension results cannot be interpreted in the way they attempt.

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[CONTRIBUTIONS FROM THE CHEMICAL LABORATORIES OF COLUMBIA UNIVERSITY,  
No. 221.]

**THE WEIGHT OF A FALLING DROP AND THE LAWS OF TATE,  
XVI. THE DROP WEIGHTS OF CERTAIN ORGANIC  
LIQUIDS AND THE SURFACE TENSIONS AND  
CAPILLARY CONSTANTS CALCULATED FROM THEM.<sup>1</sup>**

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In this investigation the previous work on pure organic liquids is continued, to further test the drop-weight method for surface tension against that based upon the capillary rise, and to further apply the Morgan definition of a normal, non-associated, liquid, *viz.*: that it give at all temperatures of observation the same value of  $t_c$  in the equation

$$t_c = \frac{w(M/d)^{2/3}}{K_B} + t_o + 6,$$

where  $w$  and  $d$  are, respectively, the drop weight and density of the liquid at the temperature of observation,  $t_o$ , and  $K_B$  is a constant, depending only upon the diameter of the tip used. This same formula also holds, of course, for surface tension in dynes per centimeter where  $\gamma$  is substituted for  $w$ , and 2.1148 for  $K_B$ .

The value of  $K_B$  here was found from the drop weight of thiophene-free benzene, and verified by comparison of the surface tension of water, as found by its aid from the drop weight of water, with the value calculated at that temperature from the equation for water found by Morgan and McAfee.<sup>2</sup>

At 30° the average value<sup>3</sup> of a drop of benzene falling from this tip was found to be 29.200 milligrams, which leads to the value

$$K_B = 2.3197.$$

<sup>1</sup> For other papers of this series see reference in preceding article.

<sup>2</sup> THIS JOURNAL, 33, 1275-90 (1911).

<sup>3</sup> Only the average of three or more actual observations are given here to save space.

This value now enables us to find the constants by which the drop weight in milligrams, and the drop volume (weight divided by density), must be multiplied to give surface tensions in dynes per centimeter,  $\gamma$ , and the capillary constant,  $a^2$ . The equations by which these transformations become possible are:

$$\gamma = 0.9117w \text{ and } a^2 = 0.1861w/d.$$

We can now verify our benzene standardization on water. At 30° the average weight of a drop of water was found to be 77.932 milligrams, which, by the above equation gives, as the value of  $\gamma$ , 71.050; while Morgan and McAfee's equation leads to 71.031. This is a difference of but 0.019 milligram or less than 0.03%. The standardization may thus be considered as satisfactory.<sup>1</sup> This standardization either with benzene or water was repeated from time to time to see that nothing had happened to the tip.

All chemicals used in this work were prepared especially for us by the Hoffman and Kropff Chemical Company, and were always further purified to see whether any change in the drop weight would result. As most of the liquids were characterized by very high boiling points, the usual blank to compensate for any possible evaporation was frequently found to be unnecessary. A test was always made, however, and when the blank was unnecessary, the weight of the empty weighing vessel was simply subtracted from that of the vessel plus twenty-five drops. The difference was taken as the weight of that number of drops.

### The Experimental Data.

In the following table will be found the observed *mean* values of the drop weights at the temperatures of observation,  $t_o$ , of the liquids studied. Here, also, are given the densities and the calculated values of the function,  $w(M/d)^{1/3}$ , and of  $t_c$ . In the last column will be found the equations representing the change with the temperature of the *surface tension*,  $\gamma$ , and of the *capillary constant*,  $a^2$  (the height of ascension in a capillary tube of 1 millimeter bore radius). These equations were found from the similar ones for the drop weight,  $w$ , and the drop volume,  $w/d$ , (obtained from our results by aid of least squares when even more than two temperatures were studied), by multiplying each term of the  $w$  equation by the constant to transform drop weight into surface tension, and each term of the  $w/d$  equation by the constant to transform it into a capillary constant. Unless otherwise stated, all densities are from Homfray and Guye.<sup>2</sup>

<sup>1</sup> For further details of the standardization of a tip and the finding of the value of  $K_B$  see THIS JOURNAL, 33, 1317-27 (1911).

<sup>2</sup> J. chim. Phys., 1, 519.

## THE EXPERIMENTAL DATA.

$t_{\circ}$	$w$	$d$	$w(M/d)^{2/3}$	$t_c$	Change of surface tension and capillary constant with temperature.
1. Dipropyl ketone, $(C_3H_7)_2CO$ . ( $M = 114$ .)					
10	28.294	0.8258	755.76	341.8	$\gamma_t = 26.808 + 0.102t + 0.000145t^2$
30	26.198	0.8105	708.53	341.4	$a_t^2 = 6.563 - 0.0188t + 0.000015t^2$
40	25.182	0.8029	685.36	341.4	
60	23.260	0.7877	641.18	342.4	
2. Diamyl malate, $CH(OH)COOC_5H_{11}$ . ( $M = 274.2$ .)					
$\begin{array}{c}   \\ CH_2COOC_5H_{11} \end{array}$					
30	29.660	1.0047 <sup>2</sup>	1247.95	574.0	$\gamma_t = 28.959 - 0.064t$
40	28.953	0.9961	1225.18	574.2	
60	27.556	0.9789	1179.69	574.5	$a_t^2 = 5.750 - 0.0085t$
3. Amyl formate, $HCOOC_5H_{11}$ . ( $M = 116.14$ .)					
0	28.012	0.9063	711.42	312.7	$\gamma_t = 25.537 - 0.0904t + 0.0000814t^2$
30	25.101	0.8743	652.97	317.5	
40	24.205	0.8636	634.84	319.7	$a_t^2 = 5.745 - 0.0133$
60	22.378	0.8422	596.92	323.3	
4. Iso amyl butyrate, $C_5H_7COOC_5H_{11}$ . ( $M = 158.2$ .)					
0	28.714	0.8880	908.36	397.6	$\gamma_t = 26.179 - 0.0953t + 0.000107t^2$
10	27.689	0.8784	882.29	396.4	
30	25.677	0.8592	830.33	393.9	
40	24.714	0.8496	805.20	393.1	$a_t^2 = 6.014 - 0.0149t$
60	22.876	0.8304	756.76	393.2	
5. Amyl stearate, $C_{17}H_{35}COOC_5H_{11}$ . ( $M = 354$ .)					
30	30.857	0.8448	1719.96	777.5	$\gamma_t = 30.452 - 0.077t$
40	30.038	0.8395	1689.12	774.2	
50	29.176	0.8340	1647.85	766.4	$a_t^2 = 7.228 - 0.0143t$
60	28.332	0.8282	1607.64	759.0	
6. Isobutyl valerate, $C_4H_9COOC_5H_9$ . ( $M = 162$ .)					
0	27.652	0.8775	896.56	392.5	$\gamma_t = 25.212 - 0.0946 + 0.000119t^2$
10	26.628	0.8680	869.64	390.9	
30	24.642	0.8490	816.73	388.1	
40	23.732	0.8395	792.49	387.6	$a_t^2 = 5.864 - 0.0151t$
60	21.890	0.8205	742.23	385.9	
7. Isoamyl trichloracetate, $CCl_3COOC_5H_{11}$ . ( $M = 233$ .)					
0	33.225	1.2533	1082.27	472.6	$\gamma_t = 30.287 - 0.0933t + 0.0000537t^2$
10	32.196	1.2425	1055.39	470.9	
30	30.186	1.2179	1002.22	468.1	
40	29.248	1.2061	977.40	467.4	$a_t^2 = 4.933 - 0.0106t$
60	27.288	1.1825	926.14	465.3	

<sup>1</sup> Perkin, *Trans. Chem. Soc.*, **49**, 323.<sup>2</sup> No densities in the literature, values determined by us.

## THE EXPERIMENTAL DATA (Continued):

Change of surface tension  
and capillary constant  
with temperature.

$t_0$ .	$w$ .	$d$ .	$w(M/d)^{2/3}$ .	$t_0$ .	
8. Butyryl malic acid di-ethyl ester, $C_4H_9COO.CH.COOC_2H_5$ . ( $M = 260$ .)					
$\begin{array}{c}   \\ CH_2COOC_2H_5 \end{array}$					
0	35.808	1.0933	1374.47	598.6	$\gamma_t = 32.653 - 0.0974t + 0.0000797t^2$
10	34.772	1.0831	1343.07	595.0	
30	32.693	1.0626	1278.85	587.3	
40	31.660	1.0523	1246.62	583.4	$a_t^2 = 6.095 - 0.0123t$
60	29.728	1.0319	1185.92	577.3	

9. Ethyl lactate,  $CH_3CH(OH)COOC_2H_5$ . ( $M = 118$ .)

0	33.752	1.0550	783.53	343.8	$\gamma_t = 30.767 - 0.098t + 0.000057t^2$
10	32.681	1.0438	764.09	345.4	
30	30.564	1.0214	725.00	348.5	
40	29.560	1.0102	706.36	350.5	$a_t^2 = 5.955 - 0.0128t$
60	27.525	0.9878	666.62	353.4	

10. Ethyl benzoyl lactate,  $C_6H_5COCH_2CHOHCOOC_2H_5$  ( $M = 222$ .)

30	38.033	1.1099	1307.85	599.8	$\gamma_t = 37.668 - 0.0998t$
40	36.933	1.0915	1277.33	596.7	
50	34.752	1.0727	1215.89	590.2	$a_t^2 = 6.840 - 0.0135t$

11. Oenanthyl malic acid diethyl ester,  $C_9H_{18}COO.CH.COOC_2H_5$ . ( $M = 302$ .)

$\begin{array}{c}   \\ CH_2COOC_2H_5 \end{array}$					
0	34.421	1.0478	1501.89	653.5	
10	33.444	1.0368	1467.89	648.8	$\gamma_t = 31.351 - 0.0824t$
30	31.666	1.0201	1406.60	642.4	
40	30.780	1.0109	1375.51	638.9	$a_t^2 = 6.112 - 0.0113$
60	28.968	0.9923	1310.59	630.9	

12. Caprylyl malic diethyl ester,  $C_7H_{15}COO.CH.COOC_2H_5$ . ( $M = 316$ .)

$\begin{array}{c}   \\ CH_2COOC_2H_5 \end{array}$					
0	34.460	1.0371	1560.55	678.7	
10	33.501	1.0275	1526.38	674.0	$\gamma_t = 31.406 - 0.0856t + 0.0000345t^2$
30	31.660	1.0085	1460.56	665.6	
40	30.772	0.9991	1428.44	661.8	$a_t^2 = 6.184 - 0.0118t + 0.0000064t^2$
60	28.948	0.9805	1360.80	652.8	

13. Pelargonyl malic diethyl ester. ( $M = 330$ .)

0	34.109	1.0246	1602.66	696.9	
10	33.233	1.0156	1577.51	693.0	$\gamma_t = 31.062 - 0.0722t - 0.00013t^2$
30	31.587	0.9993	1510.59	686.6	
40	30.665	0.9906	1472.90	681.0	$a_t^2 = 6.192 - 0.00918t - 0.000036t^2$
60	28.778	0.9721	1400.44	669.7	

## THE EXPERIMENTAL DATA (Continued).

Change of surface tension  
and capillary constant  
with temperature.

<i>t</i> <sub>o</sub> .	<i>w</i> .	<i>d</i> .	$w(M/d)^{2/3}$ .	<i>t</i> <sub>c</sub> .	
14. Caprinyl malic acid diethyl ester. ( <i>M</i> = 344.)					
0	34.476	1.0198	1670.57	726.2	
10	33.541	1.0109	1634.84	720.8	$\gamma_t = 31.434 - 0.0840t - 0.000069t^2$
30	31.776	0.9930	1567.37	713.2	
40	30.906	0.9840	1533.75	707.2	$a_t^2 = 6.290 - 0.01129t + 0.0000038t^2$
60	29.208	0.9662	1467.22	698.5	
15. Diethyl phthalate, $C_6H_4(COOC_2H_5)_2$ . ( <i>M</i> = 222.)					
10	40.531	1.1306 <sup>1</sup>	1369.27	606.3	$\gamma_t = 38.074 - 0.106t + 0.00011t^2$
30	38.421	1.1129	1311.70	601.5	
40	37.314	1.1040	1280.75	598.1	$a_t^2 = 6.804 - 0.0128t$
60	35.208	1.0864	1221.45	592.6	
16. Diamyl phthalate, $C_6H_4(COOC_4H_9)_2$ . ( <i>M</i> = 306.)					
30	32.020	1.0242	1431.02	652.9	$\gamma_t = 31.240 - 0.0683t$
40	31.273	1.0163	1404.86	651.6	
60	29.772	1.0005	1351.49	648.6	$a_t^2 = 6.098 - 0.0093t$
17. Diamyl succinate, $(CH_2COOC_4H_9)_2$ . ( <i>M</i> = 258.)					
30	29.414	0.9527 <sup>1</sup>	1231.21	566.8	$\gamma_t = 28.703 - 0.0738t$
40	28.609	0.9443	1204.60	565.3	
60	26.980	0.9274	1149.77	561.7	$a_t^2 = 6.080 - 0.0111t$
18. Diamyl malonate, $CH_2(COOC_4H_9)_2$ . ( <i>M</i> = 244.)					
30	28.714	0.9571 <sup>1</sup>	1154.48	533.7	$\gamma_t = 28.413 - 0.0746t$
40	27.897	0.9483	1128.54	532.5	
60	26.253	0.9308	1075.31	529.6	$a_t^2 = 5.920 - 0.0112t$
19. Chlorfumalic acid dimethyl ester, $C_6H_7O_4Cl$ . ( <i>M</i> = 178.5.)					
30	40.228	1.2839 <sup>1</sup>	1079.56	501.3	$\gamma_t = 40.104 - 0.1142t$
40	38.985	1.2718	1052.87	499.9	
60	36.469	1.2475	997.69	496.1	$a_t^2 = 6.224 - 0.0131t$
20. Chlorfumalic acid diethyl ester, $C_8H_{11}O_4Cl$ . ( <i>M</i> = 206.6.)					
30	35.313	1.1731 <sup>1</sup>	1109.33	514.2	$\gamma_t = 35.092 - 0.0967t$
40	34.252	1.1593	1084.53	513.5	
60	32.124	1.1317	1033.60	511.6	$a_t^2 = 5.921 - 0.0106t$
21. Chlorfumalic acid diamyl ester, $C_{14}O_4Cl$ . ( <i>M</i> = 290.6.)					
30	31.033	1.0477 <sup>1</sup>	1319.96	605.0	$\gamma_t = 30.527 - 0.0746t$
40	30.210	1.0387	1292.39	603.1	
60	28.576	1.0206	1236.89	599.2	$a_t^2 = 5.814 - 0.0101t$
22. Diethyl sulphite, $(C_2H_5O)_2SO$ . ( <i>M</i> = 138.)					
10	32.380	1.0879 <sup>1</sup>	817.47	368.4	$\gamma_t = 30.505 - 0.0981t$
30	30.236	1.0649	774.29	369.7	
40	29.156	1.0534	752.04	370.2	$a_t^2 = 5.669 - 0.01293t$

<sup>1</sup> Walden and Swinne, *Z. physik. Chem.*, 79, 732.

THE EXPERIMENTAL DATA (*Continued*).

$t_o$ .	$w$ .	$d$ .	$w(M/d)^{2/3}$ .	$t_c$ .	Change of surface tension and capillary constant with temperature.	
23. Ethyl formate, $(\text{CHCOOC}_2\text{H}_5)_2$ . ( $M = 172$ .)						
30	33.332	1.0419 <sup>1</sup>	1003.05	468.4	$\gamma_t = 33.250$	$- 0.0945t$
40	32.288	1.0313	978.30	467.7		
60	30.188	1.0101	927.42	465.8	$a_t^2 = 6.346$	$- 0.0131t$
24. Diethyl malate, $\text{CH}(\text{OH})\text{COOC}_2\text{H}_5$ . ( $M = 172$ .) $\text{CH}_2\text{COOC}_2\text{H}_5$						
30	35.536	1.1198 <sup>2</sup>	1089.49	505.7	$\gamma_t = 35.168$	$- 0.0924t$
40	34.520	1.1099	1064.66	505.0		
60	32.488	1.0891	1014.69	503.4	$a_t^2 = 6.261$	$- 0.0118t$

## Comparison of Results.

Just as in the previous paper,<sup>3</sup> in the comparison of our results with those of other investigators, using the other, the capillary rise, method, we shall present here simply our values of the surface tension,  $\gamma$ , and of the capillary constant,  $a^2$ , as calculated from the above equations giving the change in these factors with the temperature. In this way it can be seen at a glance just how our results agree with the others.

The results obtained by other observers, together with ours as calculated for the same temperatures from the exceedingly satisfactory equations given above for each liquid, are collected in the table below. The values enclosed in parentheses are for temperatures beyond the range of our experimental work, *i. e.*, are extrapolated.

## Discussion of Results.

Of the liquids studied in this research, three, *viz.*, dipropyl ketone, diamyl malate, and diethyl malate, have not been studied by other investigators. Of these the first two are normal and non-associated, while the latter is associated. Dipropyl ketone is an especially interesting liquid when considered in the light of the other investigations of this series. Thus Morgan and Owen<sup>4</sup> found methyl-ethyl ketone ( $M = 72.06$ ) and diethyl ketone ( $M = 86.08$ ) plainly associated, as did Morgan and Stone<sup>5</sup> in the case of methyl-propyl ketone ( $M = 86.08$ ), while dipropyl ketone ( $M = 114.1$ ) here and hexyl-methyl ketone ( $M = 128.1$ ), according to Morgan and Owen, are plainly non-associated. This question of association in some series like this seems to be simply a question of the magnitude of the molecular weight—the lower members being as-

<sup>1</sup> Walden and Swinne, *l. c.*

<sup>2</sup> Not being able to find any results for density in the literature, these were determined by us.

<sup>3</sup> Morgan and Chazal, see the preceding article.

<sup>4</sup> THIS JOURNAL, 33, 1317-27.

<sup>5</sup> *Ibid.*, 35, 1505-24.

## COMPARISON OF RESULTS.

Investigators.	Liquid.	$t_b$ .	$\gamma$ .	$\gamma$ (M. & K.).	$a^\circ$ .	$a^\circ$ (M. & K.).
Homfray and Guye	Amyl formate.....	43.8	21.64	21.73	5.134	5.162
		77.8	18.40	(19.00)	4.551	(4.710)
		109.2	15.52	(16.64)	4.009	(4.292)
Homfray and Guye	Isoamyl butyrate.....	48.6	21.46	21.79	5.323	5.290
		78.2	19.33	(19.39)	4.847	(4.850)
		109.3	16.63	(17.05)	4.331	(4.387)
Homfray and Guye	Amyl stearate.....	54.6	26.41	26.25	6.465	6.446
		108.4	22.53	(22.11)	5.772	(5.675)
		150.0	19.63	(18.91)	5.225	(5.079)
Homfray and Guye	Isobutyl valerate.....	14.2	23.87	23.89	5.632	5.650
		57.2	19.91	20.19	4.929	5.003
		106.5	15.74	(16.49)	4.134	(4.260)
Homfray and Guye	Isoamyl trichloracetate.....	57.5	24.90	25.10	4.280	4.322
		108.5	20.50	(20.80)	3.703	(3.781)
		151.5	16.97	(17.39)	3.224	(3.324)
Homfray and Guye	Butyryl malic acid diethyl ester	14.0	31.37	31.31	5.928	5.923
		54.0	27.37	27.63	5.376	5.432
		104.6	22.70	(23.34)	4.693	(4.810)
		145.8	19.35	(20.15)	4.167	(4.304)
Homfray and Guye	Ethyl lactate.....	45.2	26.31	26.45	5.340	5.377
		78.4	22.96	(23.43)	4.839	(4.952)
		108.4	20.08	(20.82)	4.387	(4.568)
Homfray and Guye	Ethyl benzoyl lactate.....	15.4	35.97	36.13	6.580	6.632
		54.4	32.38	32.24	6.030	6.104
		77.6	29.63	(29.92)	5.718	(5.790)
		108.5	26.64	(26.84)	5.287	(5.372)

Homfray and Guye	Oenanthyl malic acid diethyl ester.....	13.2 54.0 107.1 147.6	30.49 26.93 22.24 19.14	30.26 26.90 (22.53) (19.19)	6.005 5.501 4.780 4.280	5.963 5.504 (4.906) (4.451)
Homfray and Guye	Caprilyl malic acid diethyl ester.....	17.4 54.2 104.4 146.4	29.84 26.46 22.58 19.44	29.93 26.87 (22.85) (19.61)	5.961 5.471 4.896 4.390	5.980 5.561 (5.015) (4.588)
Homfray and Guye	Pelargonyl malic acid diethyl ester.....	12.3 54.2 105.0 146.5	30.60 <sup>1</sup> 26.75 22.48 19.43	30.15 26.74 (22.04) (19.68)	6.168 5.578 4.916 4.418	6.073 5.587 (4.827) (4.370)
Homfray and Guye	Caprinyll malic acid diethyl ester.....	16.3 55.0 106.6 147.8	30.38 26.90 22.60 19.58	30.08 27.02 (23.26) (19.52)	6.165 5.645 4.990 4.495	6.107 5.681 5.130 4.705
Walden and Swinne	Diethyl phthalate.....	20.0 31.4 54.2 77.8 94.1	36.62 35.43 33.14 30.95 29.49	35.91 34.64 32.01 (28.85) (27.13)	6.653 6.494 6.185 5.890 5.688	6.547 6.401 6.108 (5.805) (5.596)
Walden and Swinne.	Diamyl phthalate.....	20.0 51.5 75.0 100.4	31.12 28.53 26.76 24.97	29.88 27.73 (26.12) (24.39)	6.151 5.770 5.514 5.253	5.912 5.618 (5.399) (5.162)

<sup>1</sup> In the original paper this is incorrectly given at 31.60.



## COMPARISON OF RESULTS (Continued)

Investigators.	Liquid.	$\lambda_D$ .	$\gamma$ .	$\gamma$ (M. & K.).	$\alpha_D^2$ .	$\alpha_D^2$ (M. & K.).
Walden and Swinnc	Diamyl succinate.....	17.0	28.64	(27.45)	6.054	(5.891)
		37.0	26.99	25.97	5.808	5.670
		64.6	24.78	(23.93)	5.466	(5.364)
		100.2	21.98	(21.30)	4.993	(4.970)
Walden and Swinnc	Diamyl malonate	23.0	27.57	(26.70)	5.832	(5.663)
		43.4	25.88	25.18	5.577	5.435
		65.7	24.07	(23.51)	5.297	(5.185)
		79.3	23.00	(22.50)	5.128	(5.033)
		100.4	21.35	(20.92)	4.848	(4.797)
Walden and Swinnc	Chlorfumaric acid dimethyl ester.....	20.6	37.51	(37.75)	5.900	(5.956)
		57.0	33.12	33.60	5.393	5.480
		76.3	30.90	(31.39)	5.128	(5.229)
		99.6	28.31	(28.73)	4.810	(4.925)
Walden and Swinnc	Chlorfumaric acid diethyl ester	15.7	33.67	(33.57)	5.755	(5.755)
		26.9	32.46	32.49	5.610	5.635
		56.7	29.13	29.61	5.225	5.319
Walden and Swinnc	Chlorfumaric acid diamyl ester	27.6	29.22	(28.47)	5.674	(5.536)
		55.0	26.97	26.42	5.360	5.261
		75.0	25.35	(24.93)	5.128	(5.060)
		100.7	23.34	(23.02)	4.834	(4.802)
Walden and Swinnc	Diethyl sulphite.....	21.0	28.28	28.45	5.360	5.398
		40.6	26.23	26.52	5.075	5.145
		62.6	24.00	24.37	4.757	(4.860)
		89.2	21.35	21.76	4.366	(4.516)
Walden and Swinnc	Ethyl fumarate.....	17.6	31.56	(31.59)	6.093	(6.117)
		39.6	29.20	29.51	5.771	5.829
		74.1	25.62	(26.25)	5.244	(5.377)

sociated. It will be interesting to see how ethyl propyl ketone will behave—with its molecular weight 100.1 lying midway between an associated one, the methyl-propyl,  $M = 86.08$  and the non-associated dipropyl ketone,  $M = 114.1$ .

The values of  $\gamma$  and  $a^2$ , in general, as found from drop weight, are in marvelous agreement, as will be observed, with the values from the capillary rise results of Homfray and Guye; but just as has already been observed by Morgan and Stone, and Morgan and Chazal, the values of Walden and Swinne are usually much higher.

Amyl formate has already been studied in a questionable sample by Morgan and Schwartz.<sup>1</sup> The results given above, however, should be taken in place of these, for the purity of our specimen was undoubted. The agreement of the one *interpolated* value from our results with that observed by Homfray and Guye is excellent; but while our four results show the liquid to be associated, the three of Homfray and Guye show constant values of  $t_c$ , viz.,  $320.8$  at  $43^\circ.8$ ,  $320.7$  at  $77.8^\circ$  and  $320.9$  at  $109.2^\circ$ , which would make it non-associated. It must be said here, however, that the increase in  $t_c$  with the temperature (indicating association), as found by us for this formate, is more consistent with the results on other formates. Thus both Morgan and Schwartz and Ramsay and Aston<sup>2</sup> found them invariably associated. There is no reason why this formate should differ from the methyl, ethyl and propyl formates, for no change with increasing molecular weight, such as is noticed with the ketones, has ever been observed for any of the esters; and without further evidence it cannot be assumed to exist in this case. Our results differ from those of Homfray and Guye in this case only in the change with the temperature; in all the other cases of comparison, the temperature coefficients also are practically identical with those of Homfray and Guye.

Isoamyl butyrate, amyl stearate, isobutyl valerate, isoamyl trichloracetate, butryl malic acid diethyl ester, ethyl lactate, ethyl benzoyl lactate, oenanthyl malic acid diethyl ester, caprylyl malic acid diethyl ester, pelargonyl malic acid diethyl ester, and caprinylyl malic acid diethyl ester are all found to be associated; and the  $\gamma$  and  $a^2$  values are in excellent agreement with those found by Homfray and Guye. In some cases, indeed, even including those of considerable extrapolation, the results are practically interchangeable. If there were any doubt left that the drop-weight method is capable of leading to very accurate values of the surface tension and capillary constant, it would be at once dissipated in the light of this evidence. It may, of course, be that the purity of the substances is higher here than in the case of other comparisons, for these

<sup>1</sup> THIS JOURNAL, 33, 1041-60.

<sup>2</sup> Z. physik. Chem., 15, 98.

liquids are very unusual and must always be specially prepared for the work. Whatever the reason, however, the fact remains that the two sets of results are such that one could regard them simply as members of the same series as determined by one observer, with the same method, and upon the identical liquid specimen. It is certain that no such agreements are to be found in the literature among the results of different observers using the same (capillary rise) method, even for the simple and more common liquids, which presumably could be obtained readily in the pure state.

Quite different is the case of the comparison made with the results of Walden and Swinne. It is true that our results check those of Walden and Swinne closely, for chlorofumaric acid dimethyl ester, chlorofumaric acid diethyl ester, for diethyl sulphite, and for ethyl fumarate; all the liquids being associated; but for diethyl phthalate, diamyl phthalate, diamyl succinate, diamyl malonate and chlorfumaric acid diamyl ester, all of which are associated, there is no question of a comparison; the Walden and Swinne results are always much larger than ours. Why this should be so (and it has been found true also in some of the other investigations of this series) it is impossible to say. Certainly our specimens were as pure as those which were in such remarkable agreement, as to result, with those of Homfray and Guye. Further, there is certainly no peculiarity about the magnitude of the values for surface tension of these liquids, and no changed property inherent to them, which could conceivably cause this drop-weight method to suddenly fail when applied to them. The fact remains, then, that certain of our values here are different from those found by the capillary rise method in the hands of Walden and Swinne.

### Summary.

The results of this investigation may be summarized as follows:

1. The drop weight and drop volumes have been determined, and the surface tensions and capillary constants calculated from them, for twenty-four pure organic liquids at temperatures sufficient to fix the change of these factors with the temperature. Equations giving this change with the temperature have been derived.

2. Of these liquids, but two were found to be non-associated by the Morgan definition of normal molecular weight as a liquid. The other twenty-two show values of  $t_c$  in

$$t_c = \frac{w(M/d)^{2/3}}{K_B} + t_o + 6,$$

which vary with the temperature of observation,  $t_o$ .

3. Exceedingly good agreements in the surface tension and capillary-constant values were found with those observed by Homfray and Guye, and with some of those determined by Walden and Swinne. In cer-

tain other cases, however, the results of Walden and Swinne were found to be from 2 to 4% higher than ours.

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# THE WEIGHT OF A FALLING DROP AND THE LAWS OF TATE, XVII. THE DROP WEIGHTS AND SURFACE TENSIONS OF MOLTEN HYDRATED SALTS, AND THEIR SOLUTIONS.<sup>1</sup>

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In recent papers<sup>2</sup> it has been shown, by the study of the drop weights of more than fifty normal or half-normal solutions, that the law proposed by Valson<sup>3</sup> to the effect that *equivalent solutions of various salts in water exhibit identical values for the surface tension* is not true; for not only do the salts dissolved affect the surface tension of the solvent to a varying extent, but some even depress it. This conclusion has also been drawn by some of the best observers, employing (as did Valson) the capillary rise method; their results agreeing very closely with those calculated from the drop weight, wherever a comparison was possible.

The object of this paper is to present the results obtained by the study, not of many salts at the same concentration, but of many concentrations of a few salts. The molten hydrated salts selected for this purpose, *i. e.*, those salts which melt below 50° in their own water of crystallization being especially satisfactory for this purpose, for the reason that the concentration in some of the cases could even be carried to supersaturation.

Two tips were used in the course of the work, the constants for which were obtained from determinations of the drop weight of water by comparison with the surface tension of water, as found by Morgan and McAfee.<sup>4</sup> At 30°, tip No. 1 gave an average weight of a drop of water of 77.700 milligrams, while tip No. 2 gave 77.472 from which we find  $k_{B_1} = 2.3134$  and  $k_{B_2} = 2.3065$ . To find the surface tension in dynes per centimeter from these tips, then we have the relations<sup>5</sup>

$$\gamma = 0.9143 \times w_1$$

and

$$\gamma = 0.9168 \times w_2$$

*Calcium Chloride Solutions.*—Kahlbaum's purest  $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$  was

<sup>1</sup> For other papers of this series see reference, p. 1821 in preceding article.

<sup>2</sup> Morgan and Bole, *THIS JOURNAL*, 35, 1750; and Morgan and McKirahan, *Ibid.*, 35, 1759.

<sup>3</sup> *Compt. rend.*, 74, 103.

<sup>4</sup> *THIS JOURNAL*, 33, 1275-1290.

<sup>5</sup> For details as to the standardization of a tip, see *THIS JOURNAL* 33, 1713-1727.