In conclusion, the writers wish to thank Dr. M. L. Hamlin for his aid in developing the classification of reactions presented here.

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[CONTRIBUTIONS FROM THE CHEMICAL LABORATORIES OF COLUMBIA UNIVERSITY, No. 220.]

THE WEIGHT OF A FALLING DROP AND THE LAWS OF TATE, XV. THE DROP WEIGHTS OF CERTAIN ORGANIC LIQUIDS AND THE SURFACE TENSIONS AND CAPILLARY CONSTANTS CALCULATED FROM THEM.[1]

BY J. LIVINGSTON R. MORGAN AND PHILIP M. CHAZAL.

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Six tips were used in the course of this investigation, all of which were standardized against benzene. The mean values of the drop weights of benzene, together with the values calculated for K_B, by aid of the equation

$$K_B = \frac{w(M/d)^{2/3}}{(288.5 - t_0 - 6)},^2$$

are given in Table I. In the last two columns of this table will also be found the constants, k_1, by which the drop weight from the tip must be multiplied in order to give the surface tension, γ, of the liquid in dynes per centimer at the temperature in question; and the constants (k_2) by which the drop volume (drop weight/density) must be multiplied in order to give the capillary constant (a^2 = height of ascension in a capillary tube × the radius of the bore of the tube) of the liquid, also, of course, at the temperature at which the drop weight is found.

TABLE I.—STANDARDIZATION OF THE TIPS.

No.	t_0.	d.	w(mg.).	$w(M/d)^{2/3}$.	K_B.	k_1.	k_2.
1	30.0	0.86824	28.820	578.092	2.2895	0.9237	0.1886
2	30.1	0.86813	28.760	577.100	2.2864	0.9249	0.1888
3	30.0	0.86824	28.415	569.700	2.2573	0.9367	0.1913
4	30.0	0.86824	28.985	581.400	2.3067	0.9168	0.1872
5	30.0	0.86824	29.224	586.240	2.3217	0.9109	0.1860
6	30.0	0.86824	29.352	588.800	2.3319	0.9069	0.1851

The mean diameters of these tips can be calculated, according to Morgan and Cann,[3] from their K_B values. Such a calculation leads to the following results: $D_1 = 5.420$; $D_2 = 5.413$; $D_3 = 5.344$; $D_4 = 5.461$; $D_5 = 5.497$; $D_6 = 5.521$ millimeters.

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[1] For other papers in this series, see THIS JOURNAL, 30, 360, 1055; 33, 349, 643, 657, 672, 1042, 1060, 1275, 1713; 35, 1249, 1505, 1750, 1759. In this paper, as in the other recent ones, only the means of the 30-drop and 5-drop determinations are given, in order to save space.

[2] For details of the calibration in general see THIS JOURNAL, 33, 1713–27.

[3] THIS JOURNAL, 33, 349–62.

During this investigation twenty-five specially purified organic liquids were studied in all, nine of which proved to be non-associated, according to the Morgan definition, which requires that the value of t_c, calculated from

$$t_c = \frac{w(\mathrm{M}/d)^{2/3}}{\mathrm{K_B}} + t_0 + 6,$$

be independent of the temperature of observation, t_0, while the other sixteen are to be regarded as associated.

The method employed here is identical with that in the other papers of this series, so the details must be sought elsewhere. All chemicals were prepared especially for this work, unless it is otherwise stated, by the Hoffman and Kropff Chemical Company, and may be regarded as pure.

The Experimental Data.

In the following table will be found the observed *mean* values of the drop weights at the temperatures of observation, t_0, for the various liquids studied. Here also are given the densities and the calculated values of the function $w(\mathrm{M}/d)^{2/3}$, and of t_c. In the last column will be found the equations representing the change of the *surface tension* γ, and the *capillary constant* a^2 (the height of ascension in a capillary tube of 1 millimeter bore radius) with the temperature. These equations are 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, whenever more than two temperatures are studied), by multiplying each term of the w equation by the proper k_1 value, or each term of the w/d equation by its k_2 value (see Table I).

TABLE II.—THE EXPERIMENTAL DATA.

Tip.	t_0.	w. (mg.).	d.	$w(\mathrm{M}/d)^{2/3}$.	t_c.	Change of surface tension and capillary constant with temperature.
1. Benzonitrile, C_6H_5CN. (M = 103.)						
2	30.0	38.72	0.99684[1]	852.60	408.8	$\gamma_t = 39.469 - 0.1218t$
	40.0	37.41	0.98822	828.53	408.4	$a_t^2 = 7.893 - 0.0180t$
2. *o*-Toluonitrile, *o*-$C_6H_4(CH_3)CN$. (M = 117.1.)						
2	30.0	38.225	0.9863[2]	923.17	439.8	$\gamma_t = 38.527 - 1058t$
	45.0	36.500	0.9737	889.09	439.9	
	59.9	34.805	0.9597	856.04	440.3	$a_t^2 = 7.789 - 0.0157t$
3. *m*-Toluonitrile, *m*-$C_6H_4(CH_3)CN$. (M = 117.1.)						
2	0.0	41.360	1.0478[2]	959.40	425.6	$\gamma_t = 38.243 - 0.1086t$
	30.1	37.774	1.0234	890.08	425.4	
	45.1	36.078	1.0121	856.44	425.7	$a_t^2 = 7.453 - 0.0160t$
4. *p*-Toluonitrile, *p*-$C_6H_4(CH_3)CN$. (M = 117.1.)						
2	49.9	35.940	0.9598[2]	883.87	442.5	$\gamma_t = 38.492 - 0.1051t$
	61.0	34.693	0.9504	858.84	442.6	$a_t^2 = 7.891 - 0.0164t$

[1] Walden, *Z. physik. Chem.*, **65**, 138.

[2] Turner and Merry, *Trans. Chem. Soc.*, **97**, 2075.

TABLE II.—THE EXPERIMENTAL DATA (*Continued*).

Tip.	t_0.	w. (mg.).	d.	$w(M/d)^{2/3}$.	t_c.	Change of surface tension and capillary constant with temperature.
5. Hexane, C_6H_{14}. (M = 86.11.)						
1	0.0	22.404	0.67795[1]	566.14	253.3	$\gamma_t = 20.695 - 0.1001t$
	30.0	19.152	0.65213	496.62	252.9	$a_t^2 = 6.232 - 0.0294t$
6. Ethyl mercaptan, C_6H_5SH. (M = 62.12.)						
1	0.0	27.264	0.8609[2]	472.55	212.4	$\gamma_t = 25.184 - 0.1393t$
	17.0	24.700	0.8425	434.32	212.7	$a_t^2 = 5.972 - 0.0261t$
7. Thiophenol, C_6H_5SH. (M = 110.12.)						
6	10.0	43.310	1.0879[3]	973.72	419.4	$\gamma_t = 40.465 - 0.1188t$
	30.0	40.685	1.0678	894.72	419.7	
	45.0	38.725	1.0528	859.68	419.7	$a_t^2 = 7.531 - 0.016t$
8. Ethyl isothiocyanate, C_2H_5NCS. (M = 87.)						
4	30.0	33.324	0.9888[4]	659.15	322.3	$\gamma_t = 33.724 - 0.106t$
	40.0	32.144	0.9783	640.42	324.1	
	50.0	31.012	0.9768	622.32	326.3	$a_t^2 = 6.770 - 0.0155t$
9. Allyl isothiocyanate, C_3H_5NCS. (M = 99.1.)						
2	0.0	38.555	1.0290[4]	810.06	360.3	$\gamma_t = 35.662 - 0.1175t + 0.0000541t^2$
	31.5	34.613	0.9948	743.83	362.8	
	61.0	31.030	0.9627	681.56	365.1	$a_t^2 = 7.071 - 0.0051t - 0.0000177t^2$
10. Phenyl isothiocyanate, C_6H_5NCS. (M = 135.1.)						
2	30.0	42.518	1.1234[5]	1035.91	489.1	$\gamma_t = 42.492 - 0.1056t$
	40.0	41.368	1.1137	1013.73	489.4	
	50.0	40.233	1.1044	991.39	489.6	$a_t^2 = 7.547 - 0.01337t$
11. Methyl malonate, $CH_2(COOCH_3)_2$. (M = 132.06.)						
5	10.0	40.645	1.1649[6]	951.35	425.8	$\gamma_t = 38.240 - 0.1223t$
	30.0	37.987	1.1465	899.29	423.3	
	50.0	35.320	1.1282	845.20	420.0	$a_t^2 = 6.657 - 0.01665t$
12. Ethyl malonate, $CH_2(COOC_2H_5)_2$. (M = 160.1.)						
5	10.0	35.144	1.0655[6]	993.29	443.8	$\gamma_t = 33.030 - 0.1026t$
	30.0	32.868	1.0441	941.60	441.6	
	50.0	30.640	1.0228	889.94	439.3	$a_t^2 = 6.275 - 0.0141t$
13. Dimethyl acetoacetic ethyl ester, $CH_3COC(CH_3)_2COOC_2H_5$. (M = 158.11.)						
4	30.0	31.136	0.9658[6]	931.77	440.7	$\gamma_t = 31.751 - 0.1068t$
	40.0	29.979	0.9559	903.31	438.3	
	50.0	28.807	0.9460	874.03	435.6	$a_t^2 = 6.537 - 0.0167t$

[1] Dutoit and Friderich, *Arch. d. Sci. Phys. et Nat.*, [4] **9**, 122.

[2] Ramsay and Shields, *Z. physik. chem.*, **12**, 466.

[3] Walden and Swinne, *Ibid.*, **79**, 732.

[4] Ramsay and Shields, *l. c.*

[5] Bolle and Guye, *J. chim. phys.*, **3**, 41.

[6] Perkin, *Trans. Chem. Soc.*, **45**, 509.

TABLE II.—THE EXPERIMENTAL DATA (*Continued*).

Tip.	t_0.	w. (mg.).	d.	$w(M/d)^{2/3}$.	t_c.	Change of surface tension and capillary constant with temperature.
14. Diethyl acetoacetic ethyl ester, $CH_3COC(C_2H_5)_2COOC_2H_5$. (M = 186.14.)						
4	30.0	29.700	0.9602[1]	993.93	468.1	$\gamma_t = 30.025 - 0.934t$
	40.0	28.668	0.9513	966.22	465.6	
	50.0	27.663	0.9424	938.19	463.5	$a_t^2 = 6.232 - 0.0148t$
15. Ethyl oxalate, $(COOC_2H_5)_2$. (M = 146.08.)						
6	10.0	35.352	1.0906[1]	925.50	412.9	$\gamma_t = 33.135 - 0.1076t$
	30.0	32.972	1.0671	875.81	411.6	
	50.0	30.604	1.0436	825.06	409.8	$a_t^2 = 6.149 - 0.01432t$
16. Acetonitrile,[2] CH_3CN. (M = 41.)						
6	10.0	32.545	0.7929[3]	451.72	209.7	$\gamma_t = 30.818 - 0.1315t + 0.000105t^2$
	30.0	29.725	0.7714	420.29	216.2	
	40.0	28.385	0.7607	405.01	219.7	$a_t = 7.832 - 0.0233t - 0.0000017t^2$
	50.0	27.015	0.7500	389.12	222.9	
17. Butyronitrile, C_3H_7CN. (M = 69.)						
2	30.0	27.388	0.7842[4]	541.76	272.9	$\gamma_t = 28.350 - 0.1004t$
	40.0	26.310	0.7748	524.68	275.5	$a_t^2 = 7.155 - 0.0187t$
	50.0	25.215	0.7563	508.16	277.7	
18. Valeronitrile, C_4H_9CN. (M = 83.1.)						
6	10.0	28.851	0.8025[5]	630.25	286.3	
	20.0	27.512	0.7935	611.24	288.1	$\gamma_t = 26.909 - 0.101t + 0.000177t^2$
	30.0	26.516	0.7845	593.64	290.6	
	40.0	25.522	0.7757	574.76	292.9	$a_t^2 = 6.772 - 0.0182t + 0.0000302t^2$
	50.0	24.588	0.7666	559.01	295.7	
19. Acetyl acetone, $CH_3COCH_2COCH_3$. (M = 100.06.)						
1	0.00	34.616	0.9990[6]	746.59	332.1	$\gamma_t = 31.976 - 0.101t$
	30.15	31.324	0.9687	689.61	337.4	
	54.00	28.716	0.9452	642.63	340.7	$a_t^2 = 6.537 - 0.0149t$
20. Acetoacetic ethyl ester, $CH_3COCH_2COOC_2H_5$. (M = 139.08.)						
3	30.0	32.448	1.0203[6]	821.92	400.1	$\gamma_t = 33.645 - 0.1082t$
	40.0	31.289	1.0098	789.07	399.6	
	50.0	30.137	0.9993	774.04	398.9	$a_t^2 = 6.554 - 0.0157t$
21. Methyl cinnamate, $C_6H_5CH : CHCOOCH_3$. (M = 162.08.)						
6	40.0	39.272	1.0381[7]	1138.7	534.3	$\gamma_t = 36.690 - 0.102t$
	50.0	38.135	1.0302	1111.3	532.6	
	50.0	37.016	1.0220	1084.6	531.1	$a_t^2 = 7.598 - 0.0149t$

[1] Perkin, *l. c.*

[2] Laboratory sample redistilled.

[3] Dutoit and Friderich, *l. c.*

[4] Turner and Merry, *l. c.*

[5] Densities found by us; no values were given in the literature.

[6] Schenck and Ellenberger, *Ber.*, **37**, 3451.

[7] Walden and Swinne, *l. c.*

TABLE II.—EXPERIMENTAL DATA (*Continued*).

Tip.	t_o.	w. (mg.).	d.	$w(M/d)^{2/3}$.	tc.	Change of surface tension and capillary constant with temperature.
		22. Ethyl cinnamate, $C_6H_5CHCHCOOC_2H_5$.				(M = 176.09.)
5	30.0	38.857	1.0397[1]	1189.4	548.3	$\gamma_t = 38.516 - 0.1042t$
	40.0	37.700	1.0312	1160.4	545.8	
	50.0	36.568	1.0223	1134.7	543.6	$a_t^2 = 7.395 - 0.0149t$
		23. Phenyl hydrazine, $C_6H_5NHNH_2$.				(M = 108.)
6	30.0	46.427	1.0899[2]	994.17	462.3	$\gamma_t = 44.022 - 0.0638t$
	40.0	45.733	1.0817	985.72	468.7	
	50.0	45.020	1.0736	973.77	473.6	$a_t^2 = 8.071 - 0.00614t$
		24. Monoacetin, $CH_2OHCH(OH)CH_2COOCH_3$.				(M = 134.08.)
6	10.0	44.030	1.2209	1007.30	449.0	$\gamma_t = 40.893 - 0.0954t$
	25.0	42.475	1.2063	981.91	452.1	
	37.5	41.145	1.1942	957.58	454.1	$a_t^2 = 6.786 - 0.0108t$
		25. Amyl succinate, $(C_5H_{11}COOCH_2)_2$.				(M = 258.21.)
6	10.0	31.056	0.9698[1]	1285.4	567.2	$\gamma_t = 29.916 - 0.0759t$
	30.0	29.360	0.9528	1229.6	563.3	
	50.0	27.710	0.9358	1174.5	559.7	$a_t^2 = 6.040 - 0.1117t$

Comparison of Results.

Employing the equations which are given above for each liquid, we can now calculate the values of the surface tension and the capillary constant at any desired temperature, and consequently can compare our results directly with those obtained by other observers according to other methods. In the earlier papers of this series the comparison of results was usually made by aid of the values of t_c, calculated from the value of K_B for the drop weight, and from k_B for the capillary rise method—both being found by the same general equation;[3] the drop weight being used for the former, and the surface tension for the latter. Since it has been shown, however, that the drop-weight method, just like that of capillary rise, is a general and accurate method for the calculation of the surface tension—and much more convenient than that, in many cases, owing to the fact that no knowledge of the density of the liquid is necessary—the comparison is best made directly between the surface-tension values found by the two methods. In this way we can forget all about the drop weight of the liquid and the value of the constant (K_B), which holds for the tip in question, and speak only of the more general factors, the surface tension in dynes, γ, or the capillary constant, a^2. In using this method of comparison, the value of the t_c calculated is of interest only as it is found to be independent of the temperature of observation—in which case the liquid, according to the Morgan definition, is to be regarded as normal or non-associated—or dependent on the temperature,

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[1] Walden and Swinne, *l. c.*

[2] Turner and Merry, *l. c.*

[3] $K_B = w(M/d)^{2/3}/(288.5 - t_o - 6)$ and $k_B = \gamma(w/M)^{2/3}/(288.5 - t_o - 6)$.

TABLE III.—COMPARISON OF RESULTS.

Investigators.	Liquid.	t_o.	γ.	γ(M. & C.).	a^2.	a^2(M. & C.).	t_c.
Turner and Merry	Benzonitrile..............	20.0	38.59	(37.03)	...	....	425.6
		30.0	37.51	35.82	...	....	426.4
		40.0	35.78	34.60	...	....	427.0
		50.0	33.89	(33.38)	...	....	425.6
Turner and Merry	Toluonitrile..............	20.0	37.84	36.41	7.749	7.475	455.3
		30.0	36.70	35.35	7.585	7.317	455.0
		45.0	35.00	33.77	7.330	7.081	454.0
		60.0	33.17	32.18	7.047	6.847	451.7
		75.0	31.46	(30.59)	6.764	(6.611)	449.1
Turner and Merry	*m*-Toluonitrile............	20.0	36.79	36.07	7.269	7.133	433.8
		30.0	35.81	34.99	7.133	6.973	435.0
		45.0	34.34	33.36	6.906	6.733	436.4
		60.0	32.78	(31.73)	6.685	(6.493)	437.0
		75.0	31.22	(30.10)	6.444	(6.250)	438.1
Turner and Merry	*p*-Toluonitrile............	20.0	36.51	(36.39)	7.607	(7.563)	455.0
		45.0	34.80	(33.76)	7.357	(7.153)	454.4
		60.0	33.20	32.19	7.115	6.907	454.3
		70.0	31.54	(31.14)	6.847	6.743	453.1
Dutoit and Friderich	*p*-Toluonitrile............	55.0	31.94	32.71	6.826	6.989	433.8
		126.0	24.93	(25.25)	5.687	(5.925)	435.7
		177.8	20.36	(19.81)	4.906	(4.975)	441.8
Dutoit and Friderich	Hexane..................	8.2	18.54	19.87	5.637	5.991	237.2
		62.5	13.34	(14.44)	4.377	(4.394)	237.3
Ramsay and Shields	Ethyl mercaptan..........	2.0	23.63	24.91	5.611	5.920	201.8
		16.7	21.62	22.86	5.230	5.536	202.2

Walden and Swinne	Thiophenol	16.9	39.19	38.46	7.386	7.261	427.4
		25.5	38.34	37.67	7.270	7.155	426.8
		35.0	36.89	36.31	7.072	6.991	426.1
		58.0	34.10	(33.58)	6.672	(6.603)	424.9
		76.4	32.02	(31.39)	6.373	(6.309)	425.2
		93.5	30.32	(29.36)	6.088	(6.035)	426.0
Ramsay and Shields	Ethyl isothiocyanate	18.4	35.02	31.874	7.124	6.485	349.4
		46.0	31.49	28.848	6.607	6.057	350.0
Ramsay and Shields	Allyl isothiocyanate	18.4	31.53	33.52	6.373	6.787	341.6
		46.0	28.36	30.37	5.904	6.338	343.0
Bolle and Guye	Phenyl isothiocyanate	13.2	41.51	(41.10)	7.425	(7.370)	492.5
		38.8	38.47	38.40	7.034	7.027	490.1
		54.8	36.58	(36.71)	6.777	(6.813)	488.0
		109.2	30.74	(30.96)	5.970	(6.084)	485.7
		152.2	26.35	(26.41)	5.329	(5.508)	484.3
Renard and Guye	Acetonitrile	13.8	29.18	29.02	7.531	7.510	211.8
		31.4	26.81	26.79	7.099	7.102	216.6
		42.8	25.43	25.38	6.840	6.838	220.9
		55.0	23.82	(23.80)	6.527	6.553	224.1
		67.0	22.35	(22.51)	6.233	6.279	227.6
		75.5	21.58	(21.72)	6.078	6.123	230.3
Dutoit and Friderich	Acetonitrile	16.1	29.36	28.73	7.602	7.457	215.6
		56.1	24.06	(23.77)	6.604	(6.530)	227.0
		90.8	19.15	(19.75)	5.704	(5.730)	232.2

Table III.—Comparison of Results (*Continued*).

Investigators.	Liquid.	t_0.	γ.	γ(M. & C.).	a^2.	a^2(M. & C.).	t_c.
Renard and Guye	Butyronitrile.............	10.2	27.42	(27.33)	6.980	(6.965)	276.3
		44.9	23.83	23.84	6.323	6.317	276.9
		56.8	22.57	(22.65)	6.076	(6.095)	278.9
		69.1	21.36	(21.41)	5.860	(5.866)	282.2
		82.7	20.05	(20.05)	5.583	(5.612)	284.9
		97.8	18.51	(18.53)	5.261	(5.330)	287.7
		112.2	17.11	(17.08)	4.963	(5.061)	290.3
Turner and Merry	Butyronitrile.............	20.0	26.97	(26.34)	6.928	(6.781)	276.3
		30.0	25.88	25.34	6.728	6.594	278.1
		45.0	24.25	23.83	6.422	6.313	280.6
		60.0	22.62	(22.33)	6.107	6.033	282.9
Dutoit and Friderich	Butyronitrile.............	13.0	30.41	(27.05)	7.809	(6.912)	300.2
		34.2	27.97	24.92	7.333	6.517	303.3
		78.1	23.15	(20.51)	6.389	(5.699)	310.0
		96.4	20.85	(18.67)	5.929	(5.356)	309.0
Schenck and Ellenberger	Acetyl acetone............	0.0	32.50	31.98	6.626	6.537	337.3
		17.0	30.59	30.26	6.360	6.284	338.6
		34.0	28.85	28.54	6.097	6.031	340.9
		60.2	26.16	(25.90)	5.676	(5.641)	344.2
		77.7	24.50	(24.13)	5.414	(5.380)	347.2
		109.5	21.58	(20.92)	4.941	(4.907)	353.2
		139.5	18.83	(17.89)	4.454	(4.460)	357.2
Schenck and Ellenberger	Aceto-acetic ethyl ester....	18.0	31.68	(31.70)	6.255	(5.271)	400.2
		34.0	29.98	29.97	6.016	6.020	399.9
		60.2	27.71	(27.13)	5.611	(5.608)	398.8
		78.0	25.41	(25.21)	5.348	(5.328)	398.9

		109.5	22.81	(21.80)	4.862	(4.833)	398.5
		139.5	19.05	(18.55)	4.402	(4.361)	398.2
		155.1	17.52	(16.86)	4.034	(4.116)	391.6
Ramsay and Shields	Aceto-acetic ethyl ester....	14.8	32.47	32.04	6.427	6.321	407.1
		46.4	29.09	28.62	5.949	5.825	406.1
Walden and Swinne	Methyl cinnamate........	17.6	37.28	(37.89)	7.193	(7.336)	528.5
		32.3	35.77	(36.39)	6.984	(7.118)	526.9
		48.8	34.13	34.71	6.744	6.872	524.9
		62.5	32.73	(33.31)	6.537	(6.669)	522.5
		79.3	31.15	(31.60)	6.305	(6.419)	520.4
		99.7	29.17	(29.52)	6.006	(5.115)	518.7
Walden and Swinne	Ethyl cinnamate..........	19.0	37.08	(36.54)	7.183	(7.112)	558.5
		24.7	36.56	(35.94)	7.135	(7.027)	558.6
		41.4	34.90	34.20	6.904	6.778	555.7
		62.9	32.32	(31.96)	6.513	(6.458)	545.5
Turner and Merry	Phenyl hydrazine.........	20.0	45.55	(42.75)	8.468	7.948	485.0
		30.0	44.31	42.11	8.828	7.887	484.7
		45.0	42.27	41.15	7.996	7.795	482.3
		60.0	40.40	(40.19)	7.731	(7.703)	481.4
Walden and Swinne	Monoacetin..............	17.0	42.12	39.27	7.068	6.602	481.5
		35.0	40.47	37.56	6.884	6.407	485.4
		50.0	39.10	(36.12)	6.730	(6.224)	488.9
		70.0	37.41	(34.22)	6.527	(6.028)	494.0
Walden and Swinne	Amyl succinate...........	17.0	28.64	27.92	6.054	5.850	585.8
		37.0	26.99	26.01	5.808	5.627	579.7
		64.6	24.78	(23.84)	5.466	(5.318)	571.7
		100.2	21.98	(21.04)	4.993	(4.921)	564.5

in which case it is to be considered as abnormal or associated. In calculating the value of t_c from the results of surface tension, whether found by aid of drop weight or from the capillary rise, the value of k_B taken is the mean value found from the capillary rise results of the best observers for benzene, *viz.*, 2.1148.[1] The results, as far as the values derived from the drop-weight method are concerned, are identical with those found from the drop weights themselves and the specific constant for the tip—for it is by aid of that value, 2.1148, that the surface tension itself is found from the drop weight.[2]

In Table III the directly observed values of the surface tension and of the capillary constant (as given by other investigators employing the capillary rise method) are collected together with the values we find from the exceedingly satisfactory equations giving the change in the factors with the temperature. The values of t_c calculated from their results are presented simply that a conclusion as to the state of polymerization of the liquid may be drawn, and a separate comparison made with our conclusion. The numbers enclosed in parentheses are extrapolated for temperatures beyond those employed in our experiments.

Discussion of the Results.

The agreement of the values of surface tension and of capillary constant, as calculated from drop weight, with those calculated from the capillary rise is exceedingly poor in the case of many of the liquids studied in this paper. This is probably due, in the main, to the fact that the liquids studied are those which are not only difficult to obtain in the pure state, but are still more difficult to retain in that state. For this reason we have always purified the liquid immediately before working on it, if any sign of change on standing could be noted in it.

Of the twenty-five liquids studied, we find nine, *viz.*, benzonitrile, ortho-, meta-, and paratoluonitrils, hexane, ethyl mercaptan, thiophenol, phenyl iso-thiocyanate and acetoacetic ethyl ester, to be non-associated according to the Morgan definition; in other words, in the case of these nine the value of t_c calculated is independent of the temperature of observation, t_0.

Perhaps more work has been done on benzonitrile than on any other similar liquid. In a previous paper[3] these results have been collected, so it is unnecessary to repeat them here. Morgan and Thomssen (with a sample of doubtful purity) found somewhat higher results than ours—but the sample reported upon above was certainly pure. The variation in the results found by the various observers can perhaps be presented most briefly by giving the values of t_c calculated from them. For example, Ramsay and Shields find 398.9, 398.3 and 398.7; Morgan and

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[1] See THIS JOURNAL, **33**, 1275–90.

[2] See *Ibid.*, **33**, 1713–27.

[3] Morgan and Thomssen, THIS JOURNAL, **33**, 666.

Chazal, 408.8 and 408.4; Renard and Guye, 414.7, 415.0, 416.1, 416.7, 417.9, 418.0, 418.9, 419.9; Guye and Baud, 421.4, 418.9, 423.8 and 423.7; and Turner and Merry, 425.6, 426.4, 427.0 and 425.6. It will be seen from this that the values of surface tension, calculated from the drop weight, agree as well with the capillary rise values as they do among themselves. In general, it is observed that the results by Turner and Merry are somewhat higher than those by any other observer, just as they are for benzonitrile. Why this should be so is unknown. According to all observers, benzonitrile is non-associated.

The three toluonitriles are shown to be non-associated by the Morgan definition, but the γ and a^2 values are lower than those found by Turner and Merry. Only in the case of paratoluonitrile can a comparison be made with another investigator, and then the values of γ and a^2 from drop weight are found to lie practically midway between those of Turner and Merry and those of Dutoit and Friderich. There is a considerable discrepancy between the results of these two investigators, those of Turner and Merry being the larger. In the case of these three modifications, the rule formulated by Feustel[1] does not seem to hold as it does in the case of the cresols, toluidines and xylenes. Here the ortho derivative gives the greatest surface tension, and the para the lowest. Although the ortho has the greatest surface tension in the case of the toluonitriles, the para is next to it and the meta is the lowest in value. And this same relationship is also shown by the work of Turner and Merry.

Our values for γ and a^2 for hexane do not agree at all with those of Dutoit and Friderich, although both sets of results show the liquid to be non-associated. Schiff finds $a_0{}^2 = 6.226$, as compared to our value of 6.232; and $a^2_{68.1} = 4.514$, as compared to our (4.230).

The specimen of ethyl mercaptan, used here, was an especially pure preparation, while that of Ramsay and Shields was not redistilled. This may account for the discrepancy in result. Both sets of values, however, prove the liquid to be non-associated.

Just as the results of Turner and Merry are found to be higher than ours, so, also, are those given by Walden and Swinne. For example, we find their results nearly 2% higher than ours for thiophenol, although both sets of values point to a non-associated state. So far we have not studied any liquid which was studied by another investigator as well as by Walden and Swinne. We cannot say, therefore, that this is always observed; but it usually is, as far as the surface tensions from drop weight are concerned.

Ethyl and allyl iso-thiocyanate give results according to the drop-weight method, which show them to be associated; but the values do not agree at all with those found by Ramsay and Shields. On standing, the

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[1] *Trans. Chem. Soc.*, **97**, 2074.

allyl iso-thiocyanate was observed to change color, so a fresh sample was distilled just before each drop-weight determination. Ramsay and Shields' results would seem to indicate that the ethyl compound is non-associated, while the allyl compound is associated. This is, however, absolutely contrary to all experience, for, while we very frequently find that the lower members of a series may be associated, and the higher ones are non-associated; in no case has the reverse been observed. This general rule, indeed, is also found to hold for the isothiocyanates, so soon as we consider phenyl iso-thiocyanate, which we find to be non-associated. This reminds one of the ketones, where also the lower members are associated and the higher ones non-associated. This relationship, however, does not seem to hold for either the acids or the alcohols, where all members are associated.

No results of capillary rise could be found in the literature for methyl malonate, ethyl malonate, dimethyl acetoacetic ethyl ester, diethyl acetoacetic ethyl ester, or ethyl oxalate. According to our observations, however, all of these are associated.

Acetonitrile, butyronitrile and valeronitrile are all shown to be associated, whereas the higher members, benzonitrile and the toluonitriles, are non-associated. The agreement of our γ and a^2 values with those of Renard and Guye is very remarkable. The results of Dutoit and Friderich for both acetonitrile and butyronitrile, and those of Turner and Merry for butyronitrile, are considerably higher than Renard and Guye's and ours. No results for surface tension could be found in the literature for valeronitrile, but apparently its molecular weight is not sufficient to cause it to be non-associated.

Acetyl acetone and acetoacetic ethyl ester have both been studied by Schenck and Ellenberger. They conclude that both these liquids are non-associated and made up of tautomers which possess different critical temperatures. Below a certain temperature, the one with the lower critical temperature, is supposed to exist alone; above another temperature, the one with the higher critical temperature, is supposed to exist alone. At all temperatures between these two, mixtures of the two tautomers are assumed to exist. The entire basis for this hypothesis is the fact, which their work showed, that the Ramsay and Shields temperature coefficient of the molecular surface tension,

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

seems to decrease and then to increase. The values of k they found for acetyl acetone are 1.95, 1.83, 1.85, 1.64, 1.64, 1.79, 1.81; while for acetoacetic ethyl ester they are 2.15, 2.21, 2.11, 2.14, 2.14, 2.13, 3.01. Only a few calculations will serve to show that no work *could* be accurate enough to give absolute constancy to the temperature coefficient k_1 so calculated. Assuming that $\gamma(M/d)^{2/3}$ for a liquid at 10° is 771.2 and at 20° is 750, we obtain for k a value of 2.12. If now, however, our experiment had led to 771.1 and 750.1, k would become 2.10 in place of 2.12; a difference of 1%, due to two experimental errors of 0.013% each. If, in addition, the effect of an error in the temperature reading is added, the original experimental error will be still further multiplied in k. In view of this it would hardly seem possible to base any theory upon slight changes in the value of k.

The agreement of our values for γ and a^2 with those of Schenck and Ellenberger is good for acetyl acetone, and remarkable in the case of aceto-acetic ethyl ester; while, for the latter, the results of Ramsay and Shields are slightly higher. Acetyl acetone is undoubtedly associated, but aceto-acetic ethyl ester is probably non-associated, as only a very slight change in the density values would make t_c perfectly constant. As it is, the variation is but slight

Methyl cinnamate, ethyl cinnamate, monoacetin and amyl succinate are all associated and all have been previously studied by Walden and Swinne. In the case of methyl cinnamate, the values for γ and a^2, as found by Walden and Swinne, are smaller than ours; this is the only case, thus far, that comparison has shown their values to be smaller than ours. In the cases of the other liquids, larger values are found throughout by Walden and Swinne.

Phenyl hydrazine is shown to be associated, but the values for γ and a^2 are very much smaller than those of Turner and Merry.

Summary.

The results of this investigation may be summarized as follows:

1. Twenty-five organic liquids have been studied by aid of the Morgan drop-weight apparatus, of which nine have proven to be normal and non-associated, according to the definition requiring constancy in the value of t_c calculated at all temperatures of observation; and the other sixteen associated.

2. In some cases the agreement between our results, all of which are calculated to surface tensions and capillary constants, with those of other observers by the capillary rise method, is very remarkable—while in the other cases the results differ widely. This latter is observed especially with those liquids which are difficult to obtain and retain in the pure state. This may have much to do with the discrepancy.

3. The order of magnitude of the surface tensions of the ortho, meta and para arrangements in the case of toluonitrile, is shown by our work, as well as by that of Turner and Merry, to differ from the usual order noted by Feustel; for the meta position leads to the smallest surface tension here, making the order ortho, para, and meta, in place of the usual ortho, meta and para.

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.[1]

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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

$$t_c = \frac{w(M/d)^{2/3}}{K_B} + t_0 + 6,$$

where w and d are, repectively, the drop weight and density of the liquid at the temperature of observation, t_0, 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 γ 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.[2]

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

$$K_B = 2.3197.$$

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[1] For other papers of this series see reference in preceding article.

[2] THIS JOURNAL, 33, 1275–90 (1911).

[3] Only the average of three or more actual observations are given here to save space.