than when the concentrations are the same with respect to numbers of grams.

5. Heydweiller's relationship, connecting the surface tension of solutions with the number of equivalents present and the ionization of the substance, was found to fail with our results in the case of calcium chloride, but at times to show up remarkably well with both zinc nitrate and sodium chromate.

LABORATORY OF PHYSICAL CHEMISTRY.

[CONTRIBUTIONS FROM THE CHEMICAL LABORATORIES OF COLUMBIA UNIVERSITY, No. 223.]

THE WEIGHT OF A FALLING DROP AND THE LAWS OF TATE, XVIII. THE DROP WEIGHTS, SURFACE TENSIONS AND CAPILLARY CONSTANTS OF AQUEOUS SOLUTIONS OF ETHYL, METHYL AND AMYL ALCOHOLS, AND OF ACETIC AND FORMIC ACID.[1]

BY J. LIVINGSTON R. MORGAN AND MARKS NEIDLE.

Received July 28, 1913.

In a previous paper[2] it was shown that when the *two non-associated liquids,* benzene and carbon tetrachloride, were mixed together *in equal parts by weight* a critical temperature could be calculated for the mixture from the drop weight or surface tension, which was practically the mean of those of the two individual constituents; the only assumption made being that the density of the mixture is the mean of those of the two individual constituents. This can be shown in a more striking and direct way, and without any assumption at all, by calculating for each individual liquid an equation expressing the change of its surface tension, which is determined *directly* from drop weight, with the temperature, and taking the mean of the two. If the surface tension of the mixture, 1 : 1, is then an additive property, this will be the equation giving its change with temperature. As Morgan and Thomssen worked at only one temperature, this calculated equation cannot be compared directly with an experimental one for the mixture; but a value from it can be calculated and then compared with the one value experimentally determined by them for the mixture. Proceeding in this way, we find that their results for the surface tensions of benzene and of carbon tetrachloride can be expressed by the equations $\gamma_{C_6H_6} = 30.498 - 0.1305t$ and $\gamma_{CCl_4} = 28.129 - 0.1156t$, which, for a mixture of equal parts by weight would give $\gamma_{mix.} = 29.314 - 0.1231t$, as the mean equation of change with the temperature.

At 23.6°, Morgan and Thomssen find $\gamma_{mix.} = 26.382$, whereas the above formula leads to the result $\gamma_{mix.} = 26.409$; a difference of but 0.027 dynes, or 0.1%.

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[1] For other papers of this series, see reference on p. 1821.

[2] Morgan and Thomssen, THIS JOURNAL, 33, 657–72 (1911).

That the surface tension of a mixture of non-associated liquids is an additive property has already been shown for this pair of liquids as well as for others, but in a less striking way. This is owing to the necessity, in the capillary rise method, of knowing the density of the mixture, or of assuming that neither liquid affects the other.[1] We may conclude, then, that *non-associated* liquids, according to the definitions of either Ramsay and Shields, or Morgan, lead to systems, when mixed, whose surface tensions can be readily calculated by simply considering that property as an additive one.

The object of this investigation was to ascertain, by aid of the Morgan drop-weight apparatus, just how the surface tension of a mixture of two *associated liquids* is related, if at all, to the surface tensions of the constituents. For this purpose the drop weights were determined, and the surface tensions and capillary constants calculated. The following substances were examined: mixtures of methyl alcohol, ethyl alcohol, acetic acid and formic acid, each with water, in fourteen concentrations of each, ranging from 100% of water to 100% of the pure constituent —all at 30°; and solutions of amyl alcohol in six concentrations, at the same temperature (the slight solubility of amyl alcohol in water prevents the formation of homogeneous solutions of more than about 2.5% of amyl alcohol). In addition to these, the temperature coefficients of surface tension and of the capillary constant were determined from the results at three to four temperatures for certain aqueous solutions of methyl alcohol, ethyl alcohol, acetic acid and formic acid.

It is just in such cases as these that the drop-weight method shows its superiority over that depending upon capillary rise, as a means of finding the surface tension; for, as has been shown in previous papers, all influence of evaporation or any similar effect, can very readily be avoided in the drop-weight method, while it must always affect very considerably the results by capillary rise. This is especially true of solutions from which one constituent would evaporate, and thus cause a concentration change at the meniscus. The determination of the capillary rise of such liquids as we have studied would naturally be impossible *in vacuo*. The results of Ramsay and Aston on mixtures of pure organic liquids were possible by a method of this sort, only because they selected liquids which distilled nearly as chemical individuals, leaving a liquid behind of practically the same composition.

The ethyl alcohol used in this research was Kahlbaum's 99.8%. Treating this with quicklime and distilling did not change the drop weight so that this original sample was used and considered as 100%. It will be observed, from the table given later, that this 0.2% of water changed the surface tension of the alcohol only a few hundredths of one per cent. This probably is below the experimental error, and laborious attempts

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[1] Ramsay and Aston, *Z. physik. Chem.*, **15**, 91, (1894).

to remove the final traces of water were, therefore, considered unnecessary. The methyl alcohol and amyl alcohol were specially prepared for us by the Hoffman and Kropff Chemical Company. The Kahlbaum acetic acid was purified by the freezing-out method until the drop weight remained constant. The formic acid[1] was prepared by the Hoffman and Kropff Chemical Company, and further purified before use by several distillations under reduced pressure. All solutions were made up by weight.

Two tips were used in the course of the work. Their constants were found in the usual way by aid of benzene[2] and were later verified against water, the calculated surface tension being compared with the surface tension of water from the equation of change with the temperature given by Morgan and McAfee.[3] At 40°, Tip No. 1 gave an average drop weight of benzene of 27.592 milligrams, which leads to $K_B = 2.3012$. Tip No. 2 at 30° gave a drop weight for benzene of 28.912 milligrams, leading to $K_B = 2.2954$.

To calculate the surface tension in dynes per centimeter (γ) from the drop weight in milligrams, and the capillary constant (a^2) from the drop volume in milli-cubic centimeters (w/d), we have now the equations: $\gamma = 0.9190 \times w_1$; $a^2 = 0.1876 \times w_1/d$; and $\gamma = 0.9213 \times w_2$; $a^2 = 0.1881 \times w_2/d$.

By aid of these γ relations, it is now possible to verify the standardizations of the tips, for surface tensions calculated from the drop weights of water should, if the constants K_B are correct, agree with the results of the Morgan-McAfee equation. Tip No. 1, for example, leads from its drop weight of water by aid of the above equation to a surface tension at 40° of 69.348, which agrees within 0.03% with the calculated value. Tip No. 2 also led to satisfactory results in a similar way.

This verification was repeated from time to time during the work, that we might be certain that no accidental change had occurred in the size of the tips.

For the pure amyl alcohol and acetic acid, and for all solutions, the following modification of the usual method was adopted: The weighing vessel, containing some of the liquid was weighed with the stopper in, and then cooled by immersing it partly in cold water, to prevent any loss by evaporation when the stopper was removed to attach the vessel to its

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[1] This formic acid gave results when pure which checked the formula of Morgan and Stone (THIS JOURNAL, 35, 1512) within 0.03%, although the samples were of different origin and purified by different methods.

[2] For details of the standardization of a tip, see THIS JOURNAL, 33, 1713–27 (1911). All results in this paper are given in average to save space, although three or more determinations were always made of the weight of each number of drops, the agreement being within a few tenths of a milligram on 25 drops.

[3] THIS JOURNAL, 33, 1275–90 (1911).

plug. The whole apparatus was then placed in the constant temperature water bath and allowed to stand for from 20 to 30 minutes—and the desired number of drops allowed to form and fall very slowly. It is not necessary here to allow the first drop to hang for 5 minutes, as in the original method, for the vessel has already been saturated from the larger amount of liquid put in the weighing vessel, previous to setting up. Before removing the weighing vessel at the end of the experiment, naturally, it was again cooled, to prevent loss of vapor in removing the vessel from the apparatus and when inserting the stopper. The gain in weight was then the weight of the number of drops taken. In order to make sure that the liquid originally placed in the weighing vessel did not lose in weight while standing in the apparatus, several blanks were made. A typical blank was the following: A 75% solution of methyl alcohol in water was allowed to stand in the weighing vessel, while the whole apparatus remained for 50 minutes in the water bath at 60° when the loss in weight was found to be but 0.4 milligram, which may be considered as negligible, in comparison with the weight of the 20 to 30 drops used in the determination.

The great advantage of this method is that when the first drop of liquid is run over on the tip, and exposed to the air space of the weighing vessel, no change takes place in it, for that space is already saturated with just the vapor which it itself would produce—and the drop forms and falls, retaining throughout its original concentration.

In the following tables are grouped together the average values of the drop weights found, and those of the surface tension and capillary constant calculated, together with the other data necessary for the calculation:

AQUEOUS SOLUTIONS OF ETHYL ALCOHOL AT 30° C.—TIP NO. 1.

Wt. Per cent.	Density.[1]	Grams per 100 cc.	Drop wt.	Surf. tens.	Cap. const.
0.000	0.9958	0.000	77.290	71.030	14.564
0.979	0.9940	0.973	71.380	65.600	13.472
2.143	0.9918	2.125	66.210	60.847	12.524
4.994	0.9868	4.928	57.820	53.137	10.992
10.385	0.9783	10.156	48.605	44.668	9.321
17.979	0.9671	17.39	40.600	37.311	7.876
25.00	0.9563	23.91	35.843	32.941	7.031
29.98	0.9476	28.41	33.534	30.818	6.639
34.89	0.9383	32.74	31.879	29.297	6.374
50.00	0.9058	45.29	28.859	26.521	5.977
60.04	0.8830	53.01	27.587	25.352	5.861
71.85	0.8547	61.44	26.331	24.198	5.779
75.06	0.8470	63.58	25.952	23.850	5.748
84.57	0.8212	69.45	24.824	22.813	5.671
95.57	0.7939	75.88	23.230	21.348	5.489
100.00	0.7810	78.10	22.585	20.756	5.425

[1] The densities here are taken from Landolt-Börnstein-Meyerhoffer's Tabellen.

AQUEOUS SOLUTIONS OF METHYL ALCOHOL AT 30° C.—TIP NO. 2.

Wt. Per cent.	Density.	Grams per 100 cc.	Drop wt.	Surf. tens.	Cap. const.
0.000	0.9958[1]	0.000	77.290[2]	71.030	14.564
1.011	0.9939	1.005	73.940	68.120	13.993
2.500	0.9912	2.478	70.384	64.845	13.357
4.997	0.9867	4.931	65.444	60.294	12.476
9.994	0.9781	9.775	58.245	53.661	11.201
15.00	0.9703	14.56	52.987	48.817	10.272
20.00	0.9628	19.26	48.729	44.894	9.520
25.00	0.9549	23.87	45.380	41.809	8.939
29.98	0.9473	28.40	42.409	39.071	8.604
39.98	0.9289	37.14	37.920	34.936	7.679
50.00	0.9091	45.46	34.563	31.843	7.151
60.00	0.8876	53.26	31.880	29.371	6.756
70.00	0.8637	60.46	29.533	27.209	6.432
75.00	0.8514	63.86	28.409	26.173	6.276
80.03	0.8384	67.10	27.303	25.154	6.126
90.01	0.8114	73.04	25.073	23.100	5.813
100.00	0.7825	78.25	22.834	21.037	5.489

AQUEOUS SOLUTIONS OF AMYL ALCOHOL AT 30° C.—TIP NO. 2.

0.000	0.9958[3]	0.000	77.290[2]	71.030	14.564
0.250	0.9954	0.249	58.300	53.712	11.017
0.500	0.9950	0.498	50.100	46.157	9.471
0.750	0.9946	0.746	44.769	41.247	8.467
1.000	0.9942	0.994	40.845	37.631	7.728
1.500	0.9934	1.490	35.280	32.504	6.680
2.000	0.9926	1.985	31.116	28.667	5.897
2.498	0.9921	2.478	27.924	25.726	5.294
100.000	....	....	24.200	22.296	....

AQUEOUS SOLUTIONS OF ACETIC ACID AT 30°.—TIP NO. 1.

0.000	0.9958[4]	0.000	77.290	71.030	14.564
1.000	0.9972	0.997	73.544[5]	67.756	13.873
2.475	0.9979	2.470	69.462[5]	63.995	13.093
5.001	1.0025	5.014	64.512[5]	59.435	12.104
10.01	1.0090	10.100	58.215	53.500	10.824
14.98	1.0152	15.21	53.675[5]	49.451	9.945
20.09	1.0212	20.52	50.550	46.455	9.286
30.09	1.0322	31.06	45.995	42.269	8.360
40.11	1.0417	41.78	42.844	39.374	7.716
49.96	1.0494	52.43	40.380	37.109	7.219
60.05	1.0554	63.38	38.123	35.035	6.777
69.91	1.0591	74.04	36.016	33.099	6.380
79.88	1.0599	84.67	33.761	31.026	5.976
90.04	1.0554	95.03	30.205	28.677	5.547
100.00	1.0384	103.84	27.992	25.725	5.057

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[1] Extrapolated from the same source.

[2] Tip No. 1.

[3] Densities from the "Tabellen" on the assumption that equal concentrations lowered the density of water at 30° by the same amount as at 20°.

[4] Densities from the "Tabellen."

[5] Tip No. 2.

Aqueous Solutions of Formic Acid at 30° C.—Tip No. 2.

Wt. Per cent.	Density.[1]	Gm. per 100 cc.	Drop wt.	Surf. tens.	Cap. const.
0.000	0.9958	0.0000	77.290[1]	71.030	14.564
1.000	0.9995	0.9995	75.780	69.816	14.261
2.500	1.0029	2.573	73.835	68.024	13.848
5.000	1.0090	5.045	71.319	65.706	13.295
10.00	1.0198	10.198	67.362	62.061	12.425
15.00	1.0309	15.46	64.252	59.197	11.724
20.00	1.0423	20.85	61.779	56.917	11.149
25.00	1.0538	26.37	59.904	55.190	10.693
30.01	1.0653	31.97	58.152	53.575	10.268
40.00	1.0881	43.52	54.992	50.664	9.507
50.00	1.1113	55.57	52.222	48.112	8.839
60.00	1.1326	67.96	49.637	45.731	8.244
70.00	1.1544	80.81	46.934	43.240	7.648
75.00	1.1651	87.38	45.577	41.990	7.358
80.01	1.1743	93.96	44.180	40.703	7.077
90.00	1.1942	107.48	41.274	38.026	6.501
100.00	1.2089	120.89	38.295	35.281	5.959

In the following tables are given the results for the solutions we have studied, at the various temperatures employed. Here, after the drop weights had been determined, the equations for their variation with the temperature were found, by the aid of the method of least squares, and these equations transformed, by multiplying each term by the proper constant for the tip, into equations giving the variation of the surface tension in dynes with the temperature. And the same transformation was made with the equations representing the change in the drop volume (drop weight/density) with the temperature. From them, therefore, could be found the value of the capillary constant (a^2, the height of ascension in a capillary tube with a bore radius of 1 millimeter, under ideal conditions) at any desired temperature. In order to save space the results and equations for the drop weight and the drop volume are omitted, only the derived values and equations being given.

Aqueous Solutions of Ethyl Alcohol.

25% Av. Mol. Wt. = 21.25.				50% Av. Mol. Wt. = 25.90.			
t.	*d.*	γ.	a^2.	*t.*	*d.*	γ.	a^2.
0	0.9712	36.455	7.664	0	0.9294	28.391	6.237
10	0.9667	35.186	7.429	10	0.9218	27.768	6.150
20	0.9619	34.014	7.218	20	0.9140	27.145	6.064
30	0.9563	32.940	7.031	30	0.9058	26.522	5.978

$\gamma_t = 36.455 - 0.1318t + 0.000486t^2$ $\qquad$ $\gamma_t = 28.391 - 0.0623t$

$a_t^2 = 7.644 - 0.0247t + 0.00012t^2$ $\qquad$ $a_t^2 = 6.237 - 0.0086t$

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[1] The densities here were interpolated from the results of Drucker (*Ann. d. Phys.*, **28,** 217; **38,** 1018) who gives them at 25° based on water at 25° and at 35° based on water at 35°. The mean of the two values was taken as equal to density at 30°, based on water at 30°; and this was recalculated so as to be based on water at 4°.

AQUEOUS SOLUTIONS ETHYL ALCOHOL (*Continued*).

75% Av. Mol. Wt. = 33.13.

t.	d.	γ.	a^2.
0	0.8725	26.157	6.121
10	0.8643	25.406	6.002
20	0.8558	24.654	5.882
30	0.8472	23.903	5.761

$\gamma_t = 26.157 - 0.0752t$

$a_t^2 = 6.121 - 0.0120t$

95.57% Av. Mol. Wt. = 43.08.

t.	d.	γ.	a^2.
0	0.8195	23.681	5.900
10	0.8113	22.915	5.767
20	0.8027	22.150	5.634
30	0.7939	21.384	5.499

$\gamma_t = 23.681 - 0.0766t$

$a_t^2 = 5.900 - 0.0133t$

100% Mol. Wt. = 46.05.

t.	d.	γ.	a^2.
0	0.8063	23.090	5.847
10	0.7979	22.312	5.709
20	0.7895	21.534	5.569
30	0.7810	20.756	5.426

$\gamma_t = 23.090 - 0.0778t$

$a_t^2 = 5.847 - 0.0140t$

AQUEOUS SOLUTIONS OF METHYL ALCOHOL.

25% Av. Mol. Wt. = 20.23.

t.	d.	γ.	a^2.
0	0.9667	44.818	9.466
10	0.9633	43.807	9.285
20	0.9594	42.796	9.108
30	0.9549	41.785	8.934

$\gamma_t = 44.818 - 0.1011t$

$a_t^2 = 9.466 - 0.0177t$

50% Av. Mol. Wt. = 23.05.

t.	d.	γ.	a^2.
0	0.9287	34.309	7.543
10	0.9222	33.406	7.414
20	0.9157	32.664	7.283
30	0.9091	31.841	7.151

$\gamma_t = 34.309 - 0.0823t$

$a_t^2 = 7.543 - 0.0131t$

75% Av. Mol. Wt. = 26.87.

0	0.8753	28.618	6.675
10	0.8673	27.804	6.545
20	0.8594	26.991	6.412
30	0.8514	26.177	6.278

$\gamma_t = 28.618 - 0.0814t$

$a^2 = 6.675 - 0.0133t$

100% Av. Mol. Wt. = 32.03.

0	0.8102	23.447	5.909
10	0.8010	22.650	5.773
20	0.7918	21.853	5.635
30	0.7825	21.057	5.494

$\gamma_t = 23.447 - 0.0797t$

$a_t^2 = 5.909 - 0.0138t$

AQUEOUS SOLUTIONS OF ACETIC ACID.

25% Av. Mol. Wt. = 21.83.

t.	d.	γ.	a^2.
10	1.0375	45.763	9.006
20	1.0324	44.956	8.891
30	1.0268	44.148	8.779
40	1.0207	43.340	8.669

$\gamma_t = 46.571 - 0.0808t$

$a_t^2 = 9.118 - 0.0112t$

50% Av. Mol. Wt. = 27.72.

t.	d.	γ.	a^2.
10	1.0654	38.684	7.413
20	1.0575	37.878	7.313
30	1.0494	37.071	7.213
40	1.0410	36.265	7.113

$\gamma_t = 39.491 - 0.0807t$

$a_t^2 = 7.513 - 0.010t$

75% Av. Mol. Wt. = 37.90.

10	1.0794	33.819	6.397
20	1.0697	32.916	6.283
30	1.0600	32.014	6.166
40	1.0501	31.112	6.049

$\gamma_t = 34.722 - 0.0903t$

$a_t^2 = 6.514 - 0.0117t$

100% Av. Mol. Wt. = 60.03.

20	1.0497	26.701	5.194
30	1.0384	25.733	5.060
40	1.0273	24.764	4.922

$\gamma_t = 28.639 - 0.0969t$

$a_t^2 = 5.466 - 0.0136t$

Aqueous Solutions of Formic Acid.

25% Av. Mol. Wt. = 21.23.				50% Av. Mol. Wt. = 25.82.			
t.	*d*.	γ.	a^2.	*t*.	*d*.	γ.	a^2.
25	1.0570	55.665	10.752	25	1.1155	48.585	8.893
30	1.0538	55.186	10.692	30	1.1113	48.101	8.837
35	1.0504	54.706	10.634	35	1.1070	47.618	8.782

$\gamma_t = 58.061 - 0.0959t$

$a_t^2 = 11.040 - 0.0116t$

$\gamma_t = 51.000 - 0.0967t$

$a_t^2 = 9.167 - 0.011t$

75% Av. Mol. Wt. = 33.13.

t.	*d*.	γ.	a^2.
25	1.1702	42.494	7.414
30	1.1651	41.985	7.358
35	1.1599	41.476	7.301

$\gamma_t = 45.038 - 0.01018t$

$a_t^2 = 7.697 - 0.0113t$

Discussion of the Results.

The curves representing the change in surface tension (the directly determined factor in the drop-weight method, without any necessity of knowledge as to the density) with the percentage composition of the solution, are very much of the same type for all the five liquids studied above in this way. In all cases the first addition caused a very considerable drop in the surface tension. The drop in the surface tension of water caused by the addition of very small amounts of amyl alcohol, is especially striking, and immediately suggests itself as the basis of a very delicate method for estimation of the amount of that substance when it is alone present in water solution. Thus the presence in solution of even so small an amount as 0.25% changes the surface tension of water from 71.03 to 53.713, or nearly 25% at 30°, while the following changes are observed for other concentrations: for 0.5%, nearly 38% change; for 0.75%, 42%; for 1%, 47%; and for 2.5% (which is near the saturation point at this temperature) the change is 64%.

Ethyl alcohol depresses the surface tension of water more than the same percentage of either methyl alcohol or acetic acid, which have pretty much the same effect, or of formic acid which causes a much smaller change.

It is impossible to represent any of these variations in surface tension with a change in concentration by a simple formula. For this reason all values observed are presented here. The curves for acetic acid and ethyl alcohol show points of inflection, as does also that for formic acid, to a slight degree. In the case of formic acid, from about 45% to 100% the curve is almost a straight line; for methyl alcohol, from 60% to 100%, it is actually a straight line.

Duclaux[1] has found that *for aqueous solutions of homologous alcohols and acids the ratio of the percentage concentration of any two homologues,*

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[1] *Ann. chim. phys.*, [5] 13, 76 (1878).

in the solutions exhibiting the same surface tension, is constant. This rule has been tested by applying to it our values for the three alcohols, and the two acids. The result is fairly satisfactory, as will be observed from a glance at the following table, in which the results are taken from the plotted curves:

γ.	$\frac{C(MeOH)}{C(EtOH)}$.	$\frac{C(EtOH)}{C(AmOH)}$.	γ.	$\frac{C(\text{Formic acid})}{C(\text{Acetic acid})}$.
46	1.95	18.3	51	3.18
48	1.98	18.3	55	3.13
50	2.01	18.9	56	3.08
52	2.04	18.9	57	3.05
54	2.08	18.9	59	3.05
56	2.10	18.9	61	3.06
58	2.11	19.0	63	3.04
60	2.11	19.0	64	3.05
62	2.13	18.9	65	3.05
64	2.10	18.9	..	....

The agreement here, for the ratio of ethyl and amyl alcohols, is very good, but for the other combinations a trend in the results seems certain.

The results for the pure liquids—ethyl alcohol, methyl alcohol, and acetic acid—differ slightly from those previously given by Morgan and McAfee,[1] and the discrepancy is not constant—which proves that on neither side could it be a question of a constant error. The water values agreed perfectly in the two investigations. After examining a number of carefully purified samples of the liquids, it was concluded that these, slightly smaller, results are the correct ones, and that the fault probably lies in slight impurities present in the samples used in that previous work, where no such care in purification was thought necessary.

In addition to the results for the solutions at various temperatures given in the above tables, we have also calculated, for each solution, the values of its Ramsay and Shields' constant, k by aid of the equation

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

This was done to ascertain whether or not it would give any indication at all of the dis-association of the two associated constituents, as a result of the solution of the one in the other. This should be apparent if the theory to that effect of Jones and Lindsay[2] is correct. It may be said here[3] that the values of k found for the solutions are invariably smaller than that of pure water or those of the other pure constituents; whereas, if the theory were true, and the Ramsay and Shields' constant could prove it to be so, the value of k would be larger for the solution than the values

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[1] THIS JOURNAL, **33**, 1275–90 (1911).

[2] *Am. Chem. Jour.*, **28**, 329 (1902).

[3] The results have not been included in the tables to save space.

for the pure constituents and approach more nearly the normal, non-associated value of 2.12. Whether it be the fault of the theory; or of the inability of the Ramsay and Shields' constant to show such a change, is, of course, impossible here to state, or even to theorize upon.

The average molecular weights here are found by dividing the weight of each constituent by its molecular weight as a gas. The summation of the two, then, will give the total number of mols present in solution in the known weight of the mixture. From this the *average* molecular weight of the substances present will be given by simple division. It might be mentioned here that Ramsay and Aston, in their work on mixtures of organic liquids, have followed a different method of calculation, for apparently they regard the average molecular weight of any mixed liquid, containing equal parts by weight, as simply the mean of the two constituent molecular weights, which is plainly incorrect.

Summary.

The results of this investigation may be briefly summarized as follows:

1. The drop weights at 30° of many concentrations each of aqueous solutions of ethyl, methyl, and amyl alcohols, and of acetic and formic acids have been determined. From them the values of the surface tension and of the capillary constant have been calculated.

2. The variation with the temperature of the surface tension and of the capillary constant, have also been found for certain selected concentrations of aqueous solutions of the compounds mentioned.

3. The very large effect of even minute amounts of amyl alcohol on the surface tension of water is shown—and attention is called to the fact that this might be made the basis of a very delicate method for the quantitative estimation of this substance in water.

4. The relationship of Duclaux—that, for aqueous solution of homologous alcohols and acids, the ratio of the concentrations of any two homologues in the solutions exhibiting the same surface tensions is constant—is confirmed.

5. Calculation of the Ramsay and Shields' constant for solutions of these associated liquids does not show it to approach the normal value, 2.12, more closely than the constituents themselves[1]—as it should if each of the associated liquids dis-associates the other, according to the theory advanced by Jones and Lindsay.

6. Associated liquids, when mixed, do not give for the mixture a surface tension equal to the mean of the two constituent surface tensions—which would seem to be a characteristic of the mixture of two non-associated liquids. On obtaining further evidence of this fact, it is possible that a new definition of normal molecular weight in the liquid state may result.

LABORATORY OF PHYSICAL CHEMISTRY.

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[1] In fact, it is always smaller.