incomplete, the fluidity of the mixture will be less than would be the case in a homogeneous solution. This conclusion can be deduced mathematically and it is verified experimentally. These experimental facts have been known for a long time and several theories have been proposed to account for them. We have indicated that some of these are not inconsistent with our explanation, though others are unnecessary if not untenable.

We wish to acknowledge indebtedness to Dr. R. E. Loving for suggestions in the preparation of this paper.

RICHMOND COLLEGE, RICHMOND, VIRGINIA.

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[CONTRIBUTIONS FROM THE HAVEMEYER LABORATORIES OF COLUMBIA UNIVERSITY, No. 197.]

# THE WEIGHT OF A FALLING DROP AND THE LAWS OF TATE. IX. THE DROP WEIGHTS OF THE ASSOCIATED LIQUIDS, WATER, ETHYL ALCOHOL, METHYL ALCOHOL AND ACETIC ACID; AND THE SURFACE TENSIONS AND CAPILLARY CONSTANTS CALCULATED FROM THEM.

BY J. LIVINGSTON R. MORGAN AND A. McD. McAFEE.

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In the previous papers of this series the modified definition of normal molecular weight in the liquid state,[1] *viz.*, the finding of a calculated value of $t_c$ in the relationship

$$w\left(\frac{M}{d}\right)^{\frac{2}{3}} = k_B(t_c - t - 6),$$

where $k_B$ is found by a similar equation for benzene, using for $t_c$ its observed critical temperature, 288.5°, has been applied to the drop weight results, on the Morgan drop weight apparatus, of forty-five (45) different liquids, with the result that all, with but four (4) exceptions, dimethylaniline, and the methyl, ethyl, and propyl formates, are found to be perfectly normal and non-associated, the value of $t_c$ remaining constant, within reasonable limits, at the various temperatures of observation. Slight differences are to be expected here, of course, due to variations in the densities, unless these are also determined on the sample of liquid used.

In the cases of the four exceptions, as has already been pointed out, the dimethylaniline probably undergoes a rapid and permanent decomposition, which affected, in this work, the result at the higher temperature of observation, but not that at the lower; while there are indications that the formates undergo, with increased temperature, a decomposition, or change of some sort, which persists for several days after the liquid cools slowly to a lower temperature, but not when it cools rapidly. For the

[1] Morgan, THIS JOURNAL, 33, 648–649 (1911).

present, then, these liquids must be considered as belonging in a class by themselves, the observed complications existing allowing them to be considered neither as typically non-associated, nor as typically associated.

The object of this paper is to present the results obtained with the new apparatus with the typical associated liquids, water, ethyl alcohol, methyl alcohol and acetic acid, where no complications of this sort exist. It is to be expected here that the calculated value of $t_c$ will change with the temperature of observation, increasing with an increase in that, but in such a way that the change should not persist when the temperature is decreased either slowly or rapidly—in other words, the value of $t_c$ from these typical liquids should under all conditions be a function of the temperature of observation, uninfluenced by that at which it was held previously.

The liquids used were all purified according to the methods advocated by previous workers on capillary rise, while the constant temperature bath, for temperatures from 0°–77°, was that described recently by Morgan.[1]

The drop weight results for benzene at 60.4°, from which the standard $k_B$ of the tip was found, are given in Table I.[2]

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

| $t$. | Wt. vessel + 30 drops. | Av. | Wt. vessel + 5 drops. | Av. | Wt. 1 drop. Mg. |
|---|---|---|---|---|---|
| 60.4 | 9.4232<br>9.4229 | 9.42305 | 8.7888<br>8.7888 | 8.7888 | 25.370 |

| $t$. | $d$. | $w$. | $w\left(\frac{M}{d}\right)^{\frac{2}{3}}$. | $k_B$. |
|---|---|---|---|---|
| 60.4 | 0.83583 | 25.370 | 521.979 | 2.3502 |

From this value of $k_B$, 2.3502, using the equation

$$k_B = 0.4224 \times 2r$$

(see No. 8), we find that the diameter of this tip was 5.56 mm.

In order that this value of $k_B$ might be checked, before using the tip for the new liquids, the drop weight at 60.3° of freshly distilled quinoline was determined, with the result given in Table II.

TABLE II.—QUINOLINE; M = 129.

| $t$. | Wt. vessel + 30 drops. | Av. | Wt. vessel + vapor. | Wt. 1 drop. Mg. |
|---|---|---|---|---|
| 60.3 | 9.9562<br>9.9560 | 9.9561 | 8.6487 | 43.580 |

| $t$. | $d$. | $w$. | $w\left(\frac{M}{d}\right)^{\frac{2}{3}}$ | $t_c$ from $k_B$ = 2.3502. |
|---|---|---|---|---|
| 60.3 | 1.0615 | 43.580 | 1069.3 | 521.3 |

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[1] THIS JOURNAL, 33, 344–349 (1911).

[2] The same value of $k_B$ was also found at other temperatures, the results for which need not be given.

As Morgan also found, from the results of Morgan and Higgins (see No. 4), the same $t_c$, 521.3°, for quinoline, this value of $k_B$, as the standard of the tip, is to be regarded as satisfactory.

In Tables III–VI inclusive, are given the experimental values for water, ethyl alcohol, methyl alcohol and acetic acid, at various temperatures of observation. The temperatures here, at 30° and below, were read on a certified thermometer, divided into fiftieths of a degree, those above being observed on one reading in tenths, also certified. With water, at first, the same difficulty observed by Rayleigh[1] was encountered, *i. e.*, a decrease in the weight of the drop after taking down the apparatus and repeating the measurement. This difficulty, due to impurity on the tip, was readily avoided, however, by cleaning the tip just before each determination with a sulfuric and chromic acid mixture, and washing with alcohol, ether, and finally, water. In this way very good checks were easily obtainable.

TABLE III.—WATER.

| *t*. | Weight vessel + 30 drops. | Av. | Wt. vessel + 5 drops. | Av. | Wt. 1 drop. Mg. |
|---|---|---|---|---|---|
| 0.0 | 11.1770 | 11.1770 | .... | 9.4905 | 84.325 |
| | 11.1770 | | 9.4905 | | |
| | 11.1770 | | 9.4905 | | |
| 1.8 | 11.1697 | 11.1695 | 9.4886 | 9.4886 | 84.045 |
| | 11.1693 | | 9.4886 | | |
| 4.0 | 11.1572 | 11.1572 | 9.4844 | 9.48445 | 83.638 |
| | 11.1572 | | 9.4845 | | |
| 6.0 | 11.1459 | 11.14625 | 9.4804 | 9.4804 | 83.293 |
| | 11.1466 | | 9.4807 | | |
| | ... | | 9.4801 | | |
| 7.5 | 11.1387 | 11.13852 | .... | 9.47798 | 83.027 |
| | 11.1382 | | 9.4781 | | |
| | 11.1389 | | 9.4780 | | |
| | 11.1385 | | 9.4778 | | |
| | 11.1383 | | 9.4780 | | |
| | 11.1385 | | .... | | |
| 12.95 | 11.1088 | 11.10845 | 9.4678 | 9.4678 | 82.033 |
| | 11.1081 | | 9.4678 | | |
| 15.0 | 11.0973 | 11.09686 | .... | 9.4640 | 81.643 |
| | 11.0964 | | 9.4640 | | |
| | 11.0969 | | 9.4640 | | |
| 17.0 | 11.0858 | 11.08626 | .... | 9.46045 | 81.291 |
| | 11.0862 | | 9.4605 | | |
| | 11.0868 | | 9.4604 | | |
| 19.25 | 11.0740 | 11.0740 | 9.4556 | 9.4556 | 80.920 |
| | 11.0740 | | 9.4556 | | |
| 22.5 | 11.0555 | 11.05565 | 9.4495 | 9.4495 | 80.308 |
| | 11.0558 | | 9.4495 | | |

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[1] *Phil. Mag.*, [5] 48, 324 (1899).

TABLE III.—(*Continued*).

| t | Wt. vessel + 30 drops. | Av. | Wt. vessel + 5 drops. | Av. | Wt. 1 drop. Mg. |
|---|---|---|---|---|---|
| 25.3 | 11.0422 | 11.04255 | 9.4464 | 9.4465 | 79.803 |
| | 11.0429 | | 9.4466 | | |
| 27.81 | 11.0275 | 11.0278 | 9.4409 | 9.44105 | 79.338 |
| | 11.0281 | | 9.4412 | | |
| 30.0 | 11.0174 | 11.0172 | 9.4383 | 9.4384 | 78.940 |
| | 11.0176 | | 9.4385 | | |
| | 11.0166 | | 9.4384 | | |
| 36.46 | 10.9797 | 10.98005 | 9.4252 | 9.42505 | 77.750 |
| | 10.9804 | | 9.4249 | | |
| 40.0 | 10.9608 | 10.9608 | 9.4195 | 9.4194 | 77.070 |
| | 10.9608 | | 9.4193 | | |
| 45.0 | 10.9323 | 10.9319 | 9.4105 | 9.4105 | 76.070 |
| | 10.9315 | | 9.4105 | | |
| 55.0 | 10.8735 | 10.87346 | .... | 9.3920 | 74.073 |
| | 10.8737 | | 9.3921 | | |
| | 10.8732 | | 9.3919 | | |
| 60.0 | 10.8456 | 10.8456 | 9.3825 | 9.38265 | 73.148 |
| | 10.8456 | | 9.3828 | | |
| 70.0 | 10.7821 | 10.7820 | 9.3604 | 9.36065 | 71.068 |
| | 10.7819 | | 9.3609 | | |
| 77.0 | 10.7410 | 10.7413 | .... | 9.3487 | 69.630 |
| | 10.7410 | | 9.3487 | | |
| | 10.7419 | | 9.3487 | | |

TABLE IV.—ETHYL ALCOHOL.

| t. | Wt. vessel + 30 drops. | Av. | Wt. vessel + 10 drops. | Av. | Wt. 1 drop. Mg. |
|---|---|---|---|---|---|
| 0.0 | 9.3168 | 9.3168 | 8.7988 | 8.7988 | 25.900 |
| | 9.3168 | | 8.7988 | | |
| | 9.3168 | | | | |
| 10.0 | 9.3969 | 9.39675 | 8.8964 | 8.8966 | 25.008 |
| | 9.3966 | | 8.8968 | | |
| 20.0 | 9.3702 | 9.3702 | 8.8878 | 8.8878 | 24.120 |
| | 9.3702 | | 8.8878 | | |
| 40.0 | 9.3197 | 9.31993 | .... | 8.8734 | 22.327 |
| | 9.3201 | | 8.8735 | | |
| | 9.3200 | | 8.8733 | | |
| 50.0 | 9.2955 | 9.2955 | 8.8660 | 8.86605 | 21.473 |
| | 9.2955 | | 8.8661 | | |
| 60.0 | 9.1663 | 9.16596 | .... | 8.7538 | 20.608 |
| | 9.1656 | | 8.7537 | | |
| | 9.1660 | | 8.7539 | | |
| 65.0 | 9.2613 | 9.26145 | 8.8575 | 8.85745 | 20.200 |
| | 9.2616 | | 8.8574 | | |
| 70.0 | 9.2506 | 9.25065 | 8.8539 | 8.8541 | 19.828 |
| | 9.2507 | | 8.8543 | | |

TABLE V.—METHYL ALCOHOL.

| *t*. | Wt. vessel + 30 drops. | Av. | Wt. vessel + 10 drops. | Av. | Wt. 1 drop. Mg. |
|---|---|---|---|---|---|
| 0.0 | 9.4379 | | 8.9104 | | |
| | 9.4383 | 9.4379 | 8.9100 | 8.91026 | 26.382 |
| | 9.4375 | | 8.9104 | | |
| 20.0 | 9.3819 | | .... | | |
| | 9.3822 | 9.38223 | 8.8918 | 8.8917 | 24.527 |
| | 9.3826 | | 8.8916 | | |
| 30.0 | 9.3565 | 9.35665 | 8.8846 | 8.8840 | 23.603 |
| | 9.3568 | | 8.8846 | | |
| 40.0 | 9.3300 | 9.32975 | 8.8764 | 8.8765 | 22.663 |
| | 9.3295 | | 8.8766 | | |
| 50.0 | 9.3042 | | 8.8694 | | |
| | 9.3045 | 9.3045 | 8.8694 | 8.8694 | 21.755 |
| | 9.3048 | | 8.8694 | | |

TABLE VI.—ACETIC ACID.

| *t*. | Wt. vessel + 39 drops. | Av. | Wt. vessel + 10 drops. | Av. | Wt. 1 drop. Mg. |
|---|---|---|---|---|---|
| 20.0 | 9.5445 | | .... | | |
| | 9.5438 | 9.54417 | 8.9464 | 8.9464 | 29.889 |
| | 9.5439 | | 8.9464 | | |
| | 9.5445 | | 8.9464 | | |
| 40.0 | 9.4820 | | 8.9268 | | |
| | 9.4824 | 9.48246 | 8.9270 | 8.9270 | 27.773 |
| | 9.4830 | | 8.9272 | | |
| 60.0 | 9.4239 | | .... | | |
| | 9.4243 | 9.4242 | 8.9100 | 8.9100 | 25.710 |
| | 9.4244 | | 8.9100 | | |
| 70.0 | 9.3960 | 9.39625 | 8.9023 | 8.90225 | 24.700 |
| | 9.3965 | | 8.9022 | | |

Throughout in this work both ventilation tubes were connected to drying tubes, and pure dry air was bubbled through for some time before each determination, so that *all the results are for the liquids when saturated with air at the temperature of observation.*

Since these liquids, being associated, do not lead at all temperatures of observation to the same calculated value of $t_c$, it is necessary to find some means of transforming the above results of drop weight into surface tension in dynes per centimeter. In the previous papers, for this purpose, the ratio

$$w_t : \gamma_t :: k_B : K_B$$

has been used, the value of the constant of capillary rise, $K_B$, being found from the benzene values of the investigator whose work was to be compared. Since in this case all the observers whose results we shall consider have not determined benzene, it has seemed better to take for $K_B$ the mean of the values calculated from all the reliable *benzene* results by capillary rise to be found in the literature, using the observed temperature, 288.5°, for $t_c$. These mean values of $K_B$ are collected in Table VII.

TABLE VII.—MEAN VALUES OF $K_B$ FROM CAPILLARY RISE.

| | |
|---|---|
| Ramsay and Shields | $K_B = 2.1012$ |
| Ramsay and Aston | 2.1211 |
| Renard and Guye | 2.1108 |
| Walden | 2.1260 |
| Average, | $K_B = 2.1148$ |

From the drop weight in milligrams on this tip, then, we can calculate $\gamma$, the surface tension in dynes per centimeter at the same temperature, by aid of the relationship

$$\gamma_t = \frac{2.1148}{2.3502} w_t = 0.89984 w_t. \tag{1}$$

Since the volume of a drop, $\frac{w_t}{d_t}$, is proportional to the capillary constant, $a^2 = h \times r$, and this is more directly obtainable from the observed rise in a capillary tube than the surface tension is, for that requires a knowledge of the difference between the density of the liquid and that of the vapor, or of the air saturated with vapor, comparisons can also be made, and at times more satisfactorily, between drop volume and the capillary constant than between drop weight and the surface tension. We would have, then, the relationship

$$a^2 = \text{constant} \times \frac{w_t}{d_t},$$

in which we have only to calculate the value of the "constant" for the standard liquid, *benzene*.

Since $a^2 = h \times r$, we can calculate the value of $a^2$ from the results of capillary rise, when the height and the radius of the tube are both known. As the comparison of $a^2$ and $w/d$ must be made at the same temperature, the values of $w$ for benzene must be calculated from the equation

$$w_t = \frac{2.3502\ (288.5 - t - 6)}{\left(\frac{78}{d_t}\right)^{\frac{2}{3}}},$$

which we know from work on other tips holds not only for 60.4° as above, but also at all other temperatures. In Table VIII are given the various values, $h$, $r$, $w$, and $d$ for *benzene* necessary for the calculation of the "constant," together with the mean value of this. All densities here are calculated from the formula

$$d_t = 0.9002145 - 0.00106596t.$$

TABLE VIII.—VALUES OF THE "CONSTANT" IN $a^2$ = CONSTANT × $\frac{w_t}{d_t}$ FOR BENZENE.

| $t_4$ | $h$. | $r$. | $w$. | $d$. | $\frac{w}{d}$. | $a^2$. | $\frac{a^2}{w/d}$=constant. |
|---|---|---|---|---|---|---|---|
| | | | Ramsay and Shields. | | | | |
| 80 | 3.945 | 0.012935 | 22.744 | 0.8149 | 27.910 | 5.103 | 0.18284 |
| 90 | 3.772 | 0.012935 | 21.433 | 0.8043 | 26.648 | 4.879 | 0.18309 |
| 100 | 3.603 | 0.012935 | 20.139 | 0.7936 | 25.377 | 4.661 | 0.18367 |
| | | | | | | Average, | 0.18320 |
| | | | Ramsay and Aston. | | | | |
| 11.2 | 3.642 | 0.01843 | 32.274 | 0.8883 | 36.333 | 6.712 | 0.18473 |
| 46.0 | 3.213 | 0.01843 | 27.346 | 0.8512 | 32.126 | 5.922 | 0.18432 |
| 78.0 | 2.810 | 0.01843 | 23.010 | 0.8171 | 28.161 | 5.179 | 0.18390 |
| | | | | | | Average, | 0.18432 |
| | | | Renard and Guye. | | | | |
| 11.4 | 4.346 | 0.01522 | 32.246 | 0.8881 | 36.309 | 6.615 | 0.18218 |
| 31.2 | 4.120 | 0.01522 | 29.417 | 0.8670 | 33.918 | 6.271 | 0.18482 |
| 55.1 | 3.744 | 0.01522 | 26.094 | 0.8415 | 31.009 | 5.698 | 0.18377 |
| 68.5 | 3.516 | 0.01522 | 24.277 | 0.8272 | 29.349 | 5.351 | 0.18234 |
| 78.3 | 3.385 | 0.01522 | 22.969 | 0.8167 | 28.124 | 5.152 | 0.18319 |
| | | | | | | Average, | 0.18326 |
| | | | Walden. | | | | |
| 18.1 | 3.392 | 0.0193 | 31.279 | 0.8809 | 35.508 | 6.547 | 0.18437 |
| 38.3 | 3.157 | 0.0193 | 28.417 | 0.8594 | 33.067 | 6.093 | 0.18427 |
| 41.0 | 3.122 | 0.0193 | 28.156 | 0.8565 | 32.874 | 6.026 | 0.18330 |
| | | | | | | Average, | 0.18398 |

The mean of all these average values is **0.1837.** For the transformation of the drop weight of ANY liquid in milligrams into the capillary constant at the same temperature, then, we have the relationship

$$a^2 = 0.1837 \times \frac{w_t}{d_t}. \tag{2}$$

In Table IX are given the values of $t_c$ for water calculated from the drop weights and the normal, benzene, constant, **2.3502.** This is a typical associated liquid, and the calculated value of $t_c$, as will be observed, increases with the temperature of observation.

Plotting the variation of the drop weight of water with the temperature shows that the relationship is not linear, the temperature coefficient increasing slightly with increased temperature. Treatment of the experimental results by the method of least squares, omitting the weight at 0°, leads to the formula

$$w_t = 84.317 - 0.1719t - 0.000247t^2, \tag{3}$$

for this tip, between 0° and 77°.

TABLE IX.—VALUES OF $t_c$ FOR WATER; M = 18.

| $t$. | $d$. | $w$. | $w\left(\frac{M}{d}\right)^{\frac{2}{3}}$. | $t_c$ from $k_B$ = 2.3502. |
|---|---|---|---|---|
| 0.0 | 0.99987 | 84.325 | 579.22 | 252.5 |
| 1.8 | 0.99996 | 84.045 | 577.26 | 253.5 |
| 4.0 | 1.00000 | 83.638 | 574.45 | 254.4 |
| 6.0 | 0.99997 | 83.293 | 572.09 | 255.4 |
| 7.5 | 0.99990 | 83.027 | 570.29 | 256.2 |
| 13.0 | 0.99940 | 82.033 | 563.65 | 258.8 |
| 15.0 | 0.99913 | 81.643 | 561.07 | 259.7 |
| 17.0 | 0.99897 | 81.291 | 558.71 | 260.7 |
| 19.3 | 0.99838 | 80.920 | 556.38 | 262.0 |
| 22.5 | 0.99768 | 80.308 | 552.43 | 263.6 |
| 25.3 | 0.99699 | 79.803 | 549.21 | 265.0 |
| 27.8 | 0.99632 | 79.338 | 546.26 | 266.2 |
| 30.0 | 0.99567 | 78.940 | 543.75 | 267.4 |
| 36.5 | 0.99336 | 77.750 | 536.39 | 270.7 |
| 40.0 | 0.99224 | 77.070 | 532.09 | 272.4 |
| 45.0 | 0.99025 | 76.070 | 525.89 | 274.8 |
| 55.0 | 0.98573 | 74.073 | 513.65 | 279.6 |
| 60.0 | 0.98324 | 73.148 | 508.10 | 282.2 |
| 70.0 | 0.97781 | 71.068 | 495.47 | 286.8 |
| 77.0 | 0.97368 | 69.630 | 486.82 | 290.1 |

Table X, in which the results of the application of this formula are given at the various temperatures, together with the observed values, shows the greatest variation between the calculated and observed values

TABLE X.—THE DROP WEIGHT OF WATER IN MILLIGRAMS.

$$w_t = 84.317 - 0.1719t - 0.000247t^2.$$

| $t$. | $w$ calc. | $w$ obs. | Δ. |
|---|---|---|---|
| 0.0 | 84.317 | 84.325 | +0.008 |
| 1.8 | 84.008 | 84.045 | +0.037 |
| 4.0 | 83.625 | 83.638 | +0.013 |
| 6.0 | 83.277 | 83.293 | +0.016 |
| 7.5 | 83.014 | 83.027 | +0.013 |
| 13.0 | 82.040 | 82.033 | —0.007 |
| 15.0 | 81.682 | 81.643 | —0.039 |
| 17.0 | 81.323 | 81.291 | —0.032 |
| 19.3 | 80.907 | 80.920 | +0.013 |
| 22.5 | 80.324 | 80.308 | —0.016 |
| 25.3 | 79.810 | 79.803 | —0.007 |
| 27.8 | 79.347 | 79.338 | —0.009 |
| 30.0 | 78.938 | 79.940 | +0.002 |
| 36.5 | 77.714 | 77.750 | +0.036 |
| 40.0 | 77.046 | 77.070 | +0.024 |
| 45.0 | 76.081 | 76.070 | —0.011 |
| 55.0 | 74.115 | 74.073 | —0.042 |
| 60.0 | 73.114 | 73.148 | +0.034 |
| 70.0 | 71.051 | 71.068 | +0.017 |
| 77.0 | 69.617 | 69.630 | +0.013 |

to be 0.057 per cent., while the general agreement is very much better. In short, then, *we may use the results of this equation in place of the experimental values in all cases of comparison.*

Naturally, the surface tensions calculated from the above drop weights, since they are proportional to them, will also be in curvilinear relationship with the temperature. Unfortunately, the table of values from capillary rise given in Landolt-Börnstein-Meyerhoffer (p. 102, 1905) is made up from the work of Volkmann, 6–30° (1895), and from Brunner (1847) to 80°, and shows the relationship to be nearly linear, and sharply divided into two distinct portions of differing slope, joining at 40°, so that a direct comparison of the results of the two methods could at best show agreement only in places. The values of surface tension, calculated from the equation

$$\gamma_t = 75.872 - 0.1547t - 0.000222t^2, \qquad (4)$$

obtained by multiplying each term of the above drop weight equation by **0.89984,** are given for every 5° from 0–80° in Table XI, together with the values to be found in Landolt-Börnstein-Meyerhoffer, and those observed by Ramsay and Shields.

TABLE XI.—SURFACE TENSION OF WATER IN DYNES PER CM.[1]

| $t$. | From eq. (4). | V. & B. | % Δ. | R. & S. |
|---|---|---|---|---|
| 0 | 75.872 | 75.49 | —0.50 | 73.21 |
| 5 | 75.092 | 74.75 | —0.46 | ... |
| 10 | 74.303 | 74.01 | —0.40 | 71.94 |
| 15 | 73.501 | 73.26 | —0.33 | ... |
| 20 | 72.690 | 72.53 | —0.22 | 70.60 |
| 25 | 71.867 | 71.78 | —0.12 | ... |
| 30 | 71.031 | 71.03 | 0.00 | 69.10 |
| 35 | 70.188 | 70.29 | +0.14 | ... |
| 40 | 69.332 | 69.54 | +0.30 | 67.50 |
| 45 | 68.465 | 68.6 | +0.20 | ... |
| 50 | 67.587 | 67.8 | +0.31 | 65.98 |
| 55 | 66.692 | 66.9 | +0.31 | ... |
| 60 | 65.798 | 66.0 | +0.30 | 64.27 |
| 65 | 64.878 | 65.1 | +0.34 | ... |
| 70 | 63.965 | 64.2 | +0.37 | 62.55 |
| 75 | 63.021 | 63.3 | +0.44 | ... |
| 80 | 62.075 | 62.3 | +0.37 | 60.84 |

The irregular variation of the values of Volkmann and Brunner from those of drop weight, although not very great, plainly shows that the type of curve expressing their results is quite different from the perfect parabola found for the surface tensions as found from drop weight, the

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[1] Magni (*Atti accad. Lincei*, 20, 33 (1911)) finds for water at 18°, by the method based upon the pressure necessary to form an air bubble, the value 73.065 dynes, while equation (4) at this temperature leads to 73.022, a difference of but 0.06%. This is for water when saturated with air in both cases.

two curves touching only at 30°, while the Ramsay and Shields' values are lower throughout, by about 3.5 per cent. at 0°, and by 2 per cent. at 80°. Such a difference is perhaps to be expected, as far as concerns the results of Ramsay and Shields, for they worked in the absence of air, and at a pressure equal to the vapor pressure of the liquid. It is only at the boiling point, 100°, then, that their conditions would correspond to those under which the drop weight was determined, for then only would the pressure be atmospheric and the liquid in both cases free from air. As will be observed, the agreement improves with increased temperature, so that it is possible that at 100° the values observed would correspond.

Most of the workers, by various methods, who have employed fairly large limits of temperature, have found the same parabolic type of curve representing the relationship of surface tension with temperature, as that found from the drop weight. Weinberg,[1] for example, finds for water, between 1° and 74° the equation

$$\gamma_t = \gamma_0\ (1 - 0.0020532t - 0.0000028432t^2).$$

Writing equations (3) and (4) in this form, we obtain

$$w_t = w_0\ (1 - 0.0020386t - 0.0000029294t^2)$$

and

$$\gamma_t = \gamma_0\ (1 - 0.0020386t - 0.0000029294t^2).$$

Writing the equations in this form, where the value at any temperature is found as a percentage of its value at 0°, enables us to compare the variation with the temperature of two proportional properties which may be expressed in entirely different units, and that without the use of any specific quantities. That the two curves, that from Weinberg and that from drop weight, are in fact perfectly parallel, even though the coefficients of $t$ and $t^2$ do differ very slightly, can be shown by calculating the values of the function at two extreme temperatures, in terms of its value at 0°. Thus at 20° Weinberg's value of $\gamma$ is equal to $0.9580 \times \gamma_0$, where the value from drop weight is $0.9578 \times \gamma_0$, while at 80° we have $0.91755 \times \gamma_0$ for Weinberg, as compared to $0.91813 \times \gamma_0$ for the value from drop weight, a difference of but 0.06 per cent. This agreement in relative value is all the more remarkable from the fact that Weinberg used a method based upon the force necessary to draw a copper ring away from the surface of the water, and found an absolute value at 0° considerably larger (7 per cent.) than that from drop weight, *the percentage variation in the surface tension with the temperature, however, being practically exactly identical according to both methods.*

The comparison of the results of the drop weight and capillary rise methods can perhaps be made through the value of the capillary constant,

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[1] *Z. physik. Chem.*, 10, 34–50 (1892).

$a^2$, which is equal to the height of ascension times the radius of the tube, for, as most observers have noted, this quantity for water stands in linear relationship to the temperature. In Table XII are given the experimental values of the capillary constant, assuming it to be proportional to the drop volume, *i. e.*, from the equation $a_t^2 = 0.1837 \frac{w_t}{d_t}$, together with the corresponding values calculated by aid of the equation

$$a_t^2 = 15.493 - 0.0308t, \qquad (5)$$

obtained by combining the equations $\frac{w_t}{d_t} = 84.337 - 0.1678t$, and $a_t^2 = 0.1837 \frac{w_t}{d_t}$.

TABLE XII.—VALUES OF THE CAPILLARY CONSTANT FOR WATER.

| $t$. | $a^2$ from (5). | $a^2$ obs. from (2). | Δ. |
|---|---|---|---|
| 0.0 | 15.493 | 15.493 | 0.0 |
| 1.8 | 15.438 | 15.440 | +0.002 |
| 4.0 | 15.370 | 15.364 | —0.006 |
| 6.0 | 15.308 | 15.301 | —0.007 |
| 7.5 | 15.262 | 15.254 | —0.008 |
| 13.0 | 15.093 | 15.078 | —0.015 |
| 15.0 | 15.033 | 15.011 | —0.022 |
| 17.0 | 14.969 | 14.949 | —0.020 |
| 19.3 | 14.899 | 14.889 | —0.010 |
| 22.5 | 14.800 | 14.787 | —0.013 |
| 25.3 | 14.714 | 14.704 | —0.010 |
| 27.8 | 14.637 | 14.628 | —0.009 |
| 30.0 | 14.569 | 14.564 | —0.005 |
| 36.5 | 14.369 | 14.378 | +0.009 |
| 40.0 | 14.261 | 14.269 | +0.008 |
| 45.0 | 14.107 | 14.112 | +0.005 |
| 55.0 | 13.799 | 13.804 | +0.005 |
| 60.0 | 13.645 | 13.667 | +0.022 |
| 70.0 | 13.337 | 13.352 | +0.015 |
| 77.0 | 13.121 | 13.137 | +0.016 |

It will be observed that although this relation is not perfectly linear, a negative variation existing at one extreme, while a positive one is observed at the other, thus pointing to a slight curvature, it may be considered as linear, without involving unreasonable error.

Writing this equation for $a^2$ in the percentage form, *viz.*,

$$a_t^2 = a_0^2\,(1 - 0.001987t),$$

$a_0^2$ being equal to 15.493 mm., and comparing it with Weinberg's similar formula

$$a_t^2 = a_0^2\,(1 - 0.001975t),$$

we find again, as is to be expected from the similar relationship for surface tension, a perfect and complete parallelism, with respect to the variation with temperature, between the results calculated from drop weight, and those, by an entirely different method, of Weinberg. Further, Weinberg finds from the work of eleven of the most reliable observers of capillary rise that the mean temperature coefficient of the capillary constant is 0.00200, as compared to the above value, 0.001987, as found from drop weight, a difference, which for 80° would amount to less than one-tenth of 1 per cent., *i. e.*, that between $0.9400 \times a_0^2$, and $0.9408 \times a_0^2$. Weinberg finds further that the mean value of $a_0^2$ from the work of thirty of the best observers of capillary rise is 15.350 ± 0.188, while the mean value of all observers, excluding those of eight pioneers, is 15.40, for ninety-six individual determinations, as compared to the value of 15.493 from drop weight. It is to be remembered in this connection that the values of $\gamma$ and $a^2$ from drop weight are only relative, which may account for the difference between the drop weight value, based upon the benzene values of four modern, accurate, workers, and the mean of all observers. The absolute value as found from capillary rise is dependent primarily upon the accuracy with which the radius of the capillary tube is measured, and it is thought that the diameters from which the benzene value we have used is calculated are probably more accurate, owing to our refined, present-day methods of measuring small distances, than those upon which the older capillary rise results were based. It is for this reason that it is thought that *the values given above for $\gamma_t$ and $a_t^2$ may be regarded as standard, not only as to variation with the temperature, but also in absolute value.*

All attempts to calculate the critical temperature of water by the method employed on the results of Ramsay and Shields by Morgan[1] proved futile, due apparently to the fact that the observations were not carried to a high enough temperature to fix accurately the values of the coefficients of $t$ and $t^2$. The method of least squares applied to the values of the molecular function $w\left(\frac{M}{d}\right)^{\frac{2}{3}}$ for water lead to the equation

$$\left[w\left(\frac{M}{d}\right)^{\frac{2}{3}}\right]_t = 578.96 - 1.55t - 0.00052t^2,$$

which gives a value of the critical temperature which is absurd. It is significant here that an equation from the Ramsay and Shields values up to 80° only, as these were, and not to 140° as Morgan's were, also leads to an absurd value. It may be said here, as showing the great effect of the high temperatures in fixing the values of the coefficients of the first and second powers of the temperature, that the equation which would practically give the critical temperature, 365°, for water is

$$\left[w\left(\frac{M}{d}\right)^{\frac{2}{3}}\right]_t = 579.22 - 1.0817t - 0.0015t^2,$$

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[1] THIS JOURNAL, 31, 309–322 (1909).

*which gives an identical value with experiment at 0° and one of 482.99 at 80°, as compared to the experimental one of 483.03, but which could not be found except with a previous knowledge of the experimental critical temperature. With values at higher temperatures, this equation would not only hold, but would also be the only one that could be found by the method of least squares, and thus would lead, without a knowledge of the experimental value, to the true critical temperature of the liquid.* It is quite evident, then, that for associated liquids, results at the higher temperatures must be at hand in order that the method of least squares may lead to coefficients of $t$ and $t^2$ which are sufficiently accurate to allow the calculation of an unknown critical temperature.

The values of $t_c$ calculated from the experimental values at the various temperatures of observation, by aid of the benzene constant, 2.3502, for ethyl alcohol, methyl alcohol, and acetic acid, are given in Table XIII. As will be observed in all cases, just as with water, the values increase with increased temperature of observation.

TABLE XIII.—VALUES OF $t_c$ FROM $k_B = 2.3502$.

Ethyl alcohol, M = 46; $t_c$ obs. = 243.1°.

| $t$. | $d$. | $w$. | $w\left(\frac{M}{d}\right)^{\frac{2}{3}}$. | $t_c$. |
|---|---|---|---|---|
| 0 | 0.8095 | 25.900 | 382.82 | 168.9 |
| 10 | 0.8014 | 25.008 | 372.12 | 174.3 |
| 20 | 0.7926 | 24.120 | 361.56 | 179.8 |
| 40 | 0.7754 | 22.327 | 339.61 | 190.5 |
| 50 | 0.7663 | 21.473 | 329.20 | 196.1 |
| 60 | 0.7572 | 20.608 | 318.47 | 201.5 |
| 65 | 0.7523 | 20.200 | 313.52 | 204.4 |
| 70 | 0.7474 | 19.828 | 309.09 | 207.5 |
| Methyl alcohol, M = 32; $t_c$ obs. = 240°. | | | | |
| 0 | 0.8100 | 26.382 | 306.01 | 136.2 |
| 20 | 0.7905 | 24.527 | 289.16 | 149.0 |
| 30 | 0.7830 | 23.603 | 280.04 | 155.2 |
| 40 | 0.7745 | 22.663 | 270.85 | 161.3 |
| 50 | 0.7650 | 21.755 | 262.15 | 167.5 |
| Acetic acid, M = 60; $t_c$ = 321.5°. | | | | |
| 20 | 1.0491 | 29.889 | 443.68 | 214.8 |
| 40 | 1.0284 | 27.773 | 417.78 | 223.8 |
| 60 | 1.0060 | 25.710 | 392.47 | 233.0 |
| 70 | 0.9948 | 24.700 | 379.87 | 237.6 |

The relationship existing between the drop weight (and also the surface tension, of course) and the temperature for methyl alcohol and acetic acid is very satisfactorily linear, as it also is for ethyl alcohol up to 60°, although at 65° and 70° there is a distinct and sharp curvature, the reason for which is not apparent.

For methyl alcohol, between 0° and 50°, we have the relationship

$$w_t = 26.382 - 0.0927t = 26.382\,(1 - 0.003514t);$$

for ethyl alcohol, between 0° and 60°,

$$w_t = 25.888 - 0.0883t = 25.888\,(1 - 0.00341t);$$

and for acetic acid, calculated from 20°–70°,

$$w_t = 31.949 - 0.1038t = 31.949\,(1 - 0.00325t).$$

Transforming these equations for drop weights into surface tensions, by multiplication with 0.89984, we find for methyl alcohol

$$\gamma_t = 23.740 - 0.0834t = 23.740\,(1 - 0.003514t);$$

for ethyl alcohol

$$\gamma_t = 23.295 - 0.0795t = 23.295\,(1 - 0.00341t);$$

and for acetic acid

$$\gamma_t = 28.749 - 0.0933t = 28.749\,(1 - 0.00325t),$$

all in dynes per centimeter.

Transforming the drop weights at the various temperatures into drop volumes, by dividing by the density at that temperature, and the linear equation of the variation of this property with the temperature, into that for the capillary constant, by multiplying each term by the factor 0.1837, we find for the above liquids the following equations for the change of $a^2$, the capillary constant, with the temperature. For methyl alcohol

$$a_t^2 = 5.996 - 0.01543t = 5.996\,(1 - 0.00257t);$$

for ethyl alcohol

$$a_t^2 = 5.876 - 0.01455t = 5.876\,(1 - 0.002476t);$$

and for acetic acid

$$a_t^2 = 5.5027 - 0.0135t = 5.5027\,(1 - 0.00245t).$$

Without taking up too much space in a comparison of the above values of $\gamma$ and $a^2$ with those found by other methods and workers, it may be said that for ethyl alcohol Timberg[1] found, by measurement of the radius of curvature of an air bubble under the liquid, the equations

$$\gamma_t = \gamma_0\,(1 - 0.0034t)$$

$$a_t^2 = a_0^2\,(1 - 0.002784t),$$

which shows perfect agreement in temperature coefficient, as far as concerns $\gamma$, with the result from drop weight, and differs but slightly, due to the use of different densities probably, from that for $a^2$; although again, as for water in the case of Weinberg, the zero values are considerably higher, *viz.*, 6.074 for $a^2$.

Table XIV gives the various values of $a^2$ at 20° for ethyl alcohol.

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[1] *Wied. Ann.*, 30, 545–561 (1887).

TABLE XIV.—$a^2$ FOR ETHYL ALCOHOL AT 20°.

| Observer. | $a^2$. |
|---|---|
| Morgan and McAfee | 5.597 |
| Ramsay and Shields | 5.663 |
| Magie[1] | 5.599 |
| Quincke[1] | 5.659 |
| Timberg | 5.736 |
| Schiff[2] from 5.5° and 78° | 5.721 |
| Renard and Guye[3] | 5.709 |

Only two observers, Ramsay and Shields, and Schiff have studied methyl alcohol, the former at 20° and 70°, and higher temperatures, and Schiff at 7.3° and 64.2°, Schiff's results for the capillary constant from these two temperatures may be expressed by the equation

$$a_t^2 = 6.128 - 0.016t = 6.128\ (1 - 0.0026t);$$

while from Ramsay and Shields can be found

$$a_t^2 = 6.169 - 0.019t = 6.169\ (1 - 0.003t);$$

*i. e.*, Schiff's percentage temperature coefficient is practically identical with that from drop weight, or rather drop volume, while Ramsay and Shields is somewhat higher. In Table XV are compared the values of $a^2$ for this liquid at three temperatures, which will show the point at which the values of Ramsay and Shields cross those found from the drop weight.

TABLE XV.—VALUES OF $a^2$ FOR METHYL ALCOHOL.

| Observer. | 20°. | 40°. | 50°. |
|---|---|---|---|
| Morgan and McAfee | 5.688 | 5.380 | 5.226 |
| Schiff | 5.808 | 5.488 | 5.328 |
| Ramsay and Shields | 5.789 | 5.409 | 5.219 |

Acetic acid, also, has been studied only by Schiff and Ramsay and Shields: the former at two temperatures, the latter at 20° and then at 130° and higher. Schiff's results for the capillary constant may be expressed by the equation

$$a_t^2 = 5.627 - 0.015t = 5.627\ (1 - 0.00267t).$$

The values of $a^2$ for this liquid at 20° are compared in Table XVI.

TABLE XVI.—VALUES OF $a^2$ AT 20° FOR ACETIC ACID.

| Observer. | $a^2$. |
|---|---|
| Morgan and McAfee | 5.237 |
| Schiff | 5.327 |
| Ramsay and Shields | 5.019 |

Here the values from drop weight, as will be observed, lie between

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[1] *Wied. Ann.*, 25, 421–437 (1885).

[2] *Ann.*, 223, 69 (1884).

[3] *J. chim. phys.*, 7, 100 (1907).

those of Ramsay and Shields, the percentage temperature coefficient of Schiff being slightly larger.

All attempts to calculate the critical temperatures of ethyl alcohol and acetic acid, by the method of Morgan,[1] based upon the finding of an equation for the variation of $w\left(\frac{M}{d}\right)^{\frac{2}{3}}$ with the temperature, and involving the temperature and the square of the temperature, failed, owing to the change in the drop weight relation, and also in that of the function, at 60°, for ethyl alcohol, and from the fact that the few points for acetic acid (the highest being 251° below the critical 321°) seemed rather to indicate a linear relationship with the temperature.

In the case of methyl alcohol, just as with water, the equation of a curve could be derived from the experimental critical temperature which agreed well with the experimental results. This equation is

$$w_t = 306.01 - 0.0795t - 0.0017t^2.$$

Morgan's equation (11),[1] based upon the relationship of the coefficients of $t$ and $t^2$ leads from this equation to a critical temperature of 240°, while his equation (10) based upon the temperature at which the function $w\left(\frac{M}{d}\right)^{\frac{2}{3}}$ becomes zero, leads to 256°, the experimental value being 240°.

The question as to the real molecular weight, or the factor of association, in the case of these liquids has not been considered here, for it can best be treated in a later paper.

## Conclusions.

The results of this investigation may be summarized as follows:

1. The drop weights of water, ethyl alcohol, methyl alcohol, and acetic acid have been determined at various temperatures, and equations giving the surface tensions and capillary constants of these liquids calculated from them.

2. It is shown that in each case the new definition of normal molecular weight as a liquid does not hold, for the value of $t_c$ calculated from the normal benzene constant does not remain constant, but increases with an increase in the temperature of observation. These liquids therefore, according to that definition, are not normal, but associated.

3. It is again shown that for finding either surface tension or the capillary constant of a liquid, the drop weight method is more consistent than any other, leading not only to a smaller variable error, but probably also to a truer absolute value.

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[1] *Loc. cit.*