stant, the remainder of the curve (II or III) clearly will not justify the statement that the mass-action law is obeyed by this salt when $\gamma$ is obtained from freezing-point data. With cesium nitrate, therefore, as with the other strong electrolytes, the freezing point method cannot be relied upon to give correct values for $\gamma$, for the validity of the mass-action law is implicitly assumed whenever $\gamma$ is calculated by this method.

## 11. Summary.

1. The freezing point lowerings, densities, relative viscosities, and equivalent conductances of solutions of cesium nitrate, potassium chloride, and lithium chloride at 0° have been investigated and a complete set of these data are given in Tables V, VI, and VII. The data extend to normal solutions in the case of potassiun and lithium chlorides and to 0.5 normal in the case of cesium nitrate.

2. The cryohydric point for cesium nitrate is —1.254°.

3. When the freezing-point curves (Fig. 2, mole fraction of solute plotted against freezing-point lowering) for the three salts are compared with the curve of the "normal solute," potassium chloride is found to agree exactly up to about 0.5 normal, lithium chloride deviates decidedly in the direction of hydration while cesium nitrate deviates decidedly in the opposit direction. The conclusion is drawn that deviation from the behavior of a "normal solute" (an unhydrated non-electrolyte) cannot serve as a basis for the calculation of the degree of hydration of an electrolyte. Another method for making this calculation is outlined and, as a provisional result, about 9 molecules of water are found to be in combination with one of KCl and about 18 with one of LiCl in a half normal solution of the electrolyte.

4. The freezing-point data for cesium nitrate are compared with the data of Biltz and his conclusion, that this salt obeys the Mass Action Law, is only partially substantiated.

URBANA, ILL.

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[CONTRIBUTIONS FROM THE HAVEMEYER LABORATORIES OF COLUMBIA UNIVERSITY, No. 199.]

# THE WEIGHT OF A FALLING DROP AND THE LAWS OF TATE. X. THE DROP WEIGHTS OF SOME FURTHER ASSOCIATED AND NON-ASSOCIATED LIQUIDS, AND THE SURFACE TENSIONS AND CAPILLARY CONSTANTS CALCULATED FROM THEM.

BY J. LIVINGSTON, R. MORGAN AND F. T. OWEN.

Received September 19, 1911.

The associated and non-associated liquids used in this research were selected for the following purposes: (1) The further testing of the new definition of normal molecular weight in the liquid state;[1] (2) the further comparison of the surface tension and capillary-constant values calculated from the results of the Morgan drop weight apparatus[2] with those found by other observers from measurements of capillary rise; and (3) to supply additional data for a later quantitative study of the relationship existing between the drop weight, or the values derived from it, and the other physical and chemical properties of the liquid.

For convenience, and to avoid unnecessary loss of time in case of accident, two pieces of apparatus, with tips of different diameters, were employed, but it was not necessary in any case to complete the study of any liquid on one tip after having started it with the other. If an accident had happened, however, this would have been possible, as has already been brought out in a previous paper,[3] and just as it is possible to calculate values of $t_c$, or of the surface tension, or the capillary constant, from the results on one tip, which would be identical (within the limits of error) with those obtained by a similar calculation from the results with the same liquid at the same temperature on another tip. Thus for the same liquid, at the same temperature ($t_o$) we would have for the two tips the relationships

$$w'(M/d)^{2/3} = k'_B(t_c—t_o—6)$$

and

$$w''(M/d)^{2/3} = k''_B(t_c—t_o—6),$$

from which it is evident, since at the same temperature for the same liquid, M, $d$, $t_c$, and $t_o$ are identical in the two equations, that

$$w' : w'' : : k'_B : k''_B,$$

*the weight of a drop of liquid from one tip is related to that of the same liquid, at the same temperature, from another tip, as are the* $k_B$ *values of the two tips.*

By similar reasoning it can be shown that the $k_B$ values themselves of the two tips are related as the respective drop weights of benzene falling from them at the same temperature of observation ($t_o$), for then we would have

$$w'_B(78/d)^{2/3} = k'_B(288.5—t_o—6)$$

and

$$w''_B(78/d)^{2/3} = k''_B(288.5—t_o—6)$$

which would reduce to

$$w'_B : w''_B : : k'_B : k''_B.$$

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[1] Morgan, THIS JOURNAL, 33, 643–657 (1911). *The molecular weight of a liquid is to be regarded as normal (i. e., is identical with that as a gas) when* $t_c$ *in the equation* $w(M/d)^{2/3} = k_B(t_c—t_o—6)$ *is found to be constant at all temperatures of observation* ($t_o$), $k_B$ *being the value found for benzene on the same tip, when* $t_c$ *is taken as equal to the observed critical temperature, viz., 288°.5.*

[2] THIS JOURNAL, 33, 349–362 (1911).

[3] Morgan and Cann, THIS JOURNAL, 33, 1060–1071 (1911).

And in the same way the surface tension values can be calculated from the drop weight, for then we would have, *for the same liquid at the same temperature*,

$$\gamma(M/d)^{\frac{2}{3}} = K_B(t_c—t_o—6)$$

and

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

where M, $d$, $t_c$ and $t_o$ are the same and consequently

$$\gamma : w :: K_B : k_B$$

*i. e.*,

$$\gamma = w \times K_B/k_B,$$

$\gamma$ in dynes and $w$ in milligrams, being values at identical temperatures.

Here again $K_B : k_B :: \gamma_B : w_B$, where $\gamma_B$ and $w_B$ are the respective values for benzene at the same temperature of observation ($t_o$), for

$$\gamma_B(78/d)^{\frac{2}{3}} = K_B(288.5—t_o—6)$$

and

$$w_B(78/d)^{\frac{2}{3}} = k_B(288.5—t_o—6),$$

the values of $t_o$ and $d$ being identical, so that

$$\gamma_B : w_B :: K_B : k_B.$$

Since no general relationship like the above holds for the capillary constant, $a^2$, the relationship between the drop volume (*i. e.*, drop weight at $t_o$/density at $t_o$) and the capillary constant can be found only by a direct comparison of individual results at various temperatures, and then finding the mean of the constant by which the drop volume must be multiplied to give the observed capillary constant. In a previous paper[1] it was shown that for a tip giving a value of $k_B = 2.3502$, $a^2$ (= height of ascension, times radius of bore) for benzene as found at a number of temperatures by four of the best modern workers with the capillary rise method can be obtained from the drop weight from that tip by aid of the equation

$$a_t^2 = 0.1837\, w'_t/d_t,$$

so that for any new tip, since the drop weight is proportional to the normal (benzene) constant of the tip, for

$$w'_t : w''_t :: k'_B : k''_B,$$

*i. e.*,

$$w'_t = k'_B/k'_B w''_t,$$

we have for *any* liquid from *any* tip

$$a_t^2 = 0.1837 \times 2.3502/k''_B \times w''_t/d_t$$

where $k''_B$ and $w''_t$ are the values for the new tip.

The benzene values for the two tips employed in this research are given in the table below, the mean value of $w$ from several determinations

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[1] Morgan and McAfee, THIS JOURNAL, **33**, 1275–1290 (1911).

(which varied among themselves as slightly as those given in the previous papers) being the one used.[1]

CALIBRATION WITH BENZENE. M = 78; $t_c$ = 288.5.

Tip No. I.

| $t$. | $d$. | $w$. | $w(M/d)^{2/3}$. | $k_B = \frac{w(M/d)^{2/3}}{288.5 - t_0 - 6}$. |
|---|---|---|---|---|
| 30.3 | 0.86792 | 30.088 | 603.68 | 2.3936 |
| | | Tip No. 2. | | |
| 30.1 | 0.86792 | 29.058 | 582.87 | 2.3098 |

To obtain the surface tension in dynes per centimeter from the drop weights then, we have the equations

$$\text{I.} \qquad \gamma = w_1 \times \frac{2.1148}{2.3936} = 0.88352 \times w_1; \qquad \textit{Tip No. I.}$$

$$\text{II.} \qquad \gamma = w_2 \times \frac{2.1148}{2.3098} = 0.91558 \times w_2; \qquad \textit{Tip No. II.}$$

where 2.1148 is the average value of $K_B$ for the surface tension of benzene from capillary rise, using $t_c$ = 288.5° and calculated from the work of the four best modern investigators.[2]

And to calculate the values of the capillary constant, as mentioned above, we have then only to make use of the equations:

$$\text{III.} \qquad a^2 = 0.1837 \frac{2.3502}{2.3936} \times w_1/d = 0.18037 \times w_1/d. \qquad \textit{Tip No. I.}$$

$$\text{IV.} \qquad a^2 = 0.1837 \frac{2.3502}{2.3098} \times w_2/d = 0.18691 \times w_2/d. \qquad \textit{Tip No II.}$$

From the $k_B$ values of the two tips given above we can also, of course, calculate the mean diameters of the tips, for in a previous paper[3] it was shown that

$$\text{diameter} = (k_B/0.4224)\ \text{mm.}$$

According to this relationship the diameter of tip No. I was 5.643 mm., while that of tip No. II was 5.445 mm.

In the following tables are given the results obtained with the 12 (7 non-associated, 5 associated) liquids studied, together with the calculated values of $t_c$, surface tension, and capillary constant, and, wherever it is possible, the similar values observed by other investigators.

*Methyl Hexyl Ketone*, $CH_3COC_6.H_{13}$; M = 128.13.

Kahlbaum's preparation, redistilled, density at 0° extrapolated, and that at 30.1° interpolated, from the results by Falk[4] on the same sample. *Tip No. I.*

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[1] In order to save space the mean only of the drop weight at the various temperatures is also given for the other liquids studied.

[2] Morgan and McAfee, *Loc. cit.*, 1280.

[3] Morgan and Cann, *Loc. cit.*

[4] THIS JOURNAL, 31, 86 and 806.

| $t$. | $d$. | $w$. | $w(M/d)^{\frac{2}{3}}$. | $t_c$ from $k_B = 2.3936$. |
|---|---|---|---|---|
| 0 | 0.8362 | 31.324 | 896.96 | 380.7 |
| 30.1 | 0.8106 | 28.202 | 824.47 | 380.5 |

It is evident that this liquid is perfectly normal and non-associated, the values of $t_c$ agreeing (0.05 per cent.) within the experimental error. Assuming a linear relationship between the drop weight and the temperature, and also between the drop volume and temperature, we find

$$w_t = 31.324 - 0.10372t,$$

and

$$v_t = w_t/d_t = 37.460 - 0.08864t,$$

from which it follows, by aid of equations I and III respectively, that

$$\gamma_t = \mathbf{27.675 - 0.09164}t$$

and

$$a_t^2 = \mathbf{6.757 - 0.016}t.$$

*Benzyl Cyanide*, $C_6H_5CH_2CN$; M = 117.1.

Kahlbaum's preparation, redistilled. Densities interpolated from Falk's[1] observations on this sample. *Tip No. I.*

| $t$. | $d$. | $w$. | $w(M/d)^{\frac{2}{3}}$. | $t_c$ from $k_B = 2.3936$. |
|---|---|---|---|---|
| 45 | 0.9981 | 42.654 | 1022.20 | 478.1 |
| 60 | 0.9850 | 40.772 | 985.77 | 477.8 |

This compound, according to the new definition of normal molecular weight, is non-associated, the deviation in the value of $t_c$ being less that 0.1 per cent. Assuming linear relationships, we have

$$w_t = 48.302 - 0.1255t$$

and

$$v_t = 46.763 - 0.0895t,$$

from which by aid of I and III we find

$$\gamma_t = \mathbf{42.676 - 0.1109}t$$

and

$$a_t^2 = \mathbf{8.435 - 0.01614}t.$$

*Benzaldehyde*, $C_6H_5CHO$; M = 106.05.

Preparation of Kahlbaum's, redistilled. Densities from Kopp.[2] *Tip No. I.*

| | | | | |
|---|---|---|---|---|
| 30.2 | 1.0349 | 42.358 | 927.56 | 423.7 |
| 50.0 | 1.0169 | 39.914 | 884.33 | 425.5 |

At 20° Landolt finds a density of 1.0473 (his only value) as compared to 1.0442 of Kopp, which would leave some doubt as to the accuracy of Kopp's figures. The value of $w$ at 50° here was determined immediately after the distillation, while that at 30.2° was not found until the following day. Considering these two facts, especially in view of the

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[1] *Loc. cit.*

[2] Liebig's *Ann.*, 94, 316 (1855).

known instability of this substance, it is more than probable that the liquid is normal and non-associated, for the above discrepancy in the values of $t_c$ of 1.8°, *i. e.*, of 0.42 per cent. can readily be ascribed to them.

From capillary rise Ramsay and Shields find for this liquid:

| $t$. | $d$. | $\gamma$. | $\gamma(M/d)^{\frac{2}{3}}$. | $t_c$ from $k_B = 2.1012$. |
|---|---|---|---|---|
| 15.4 | 1.0480 | 39.19 | 850.6 | 426.3 |
| 78.3 | 0.9915 | 31.72 | 714.4 | 424.3 |

Regarding the temperature change of drop weight, as well as drop volume, as linear we find

$$w_t = 46.084 - 0.1234t$$

and

$$v_t = 43.491 - 0.0848t,$$

the application of I and III giving

$$\gamma_t = \mathbf{40.716 - 0.109}t$$

and

$$a_t^2 = \mathbf{7.844 - 0.0153}t.$$

Interpolating between the values of Ramsay and Shields, we find for $\gamma$ and $a^2$ the following values compared with those from the above equation:

| $t$. | $\gamma$ M & O. | $\gamma$ R & S. | $a^2$M & O. | $a^2$ R & S. |
|---|---|---|---|---|
| 30.2 | 37.424 | 37.43 | 7.382 | 7.360 |
| 50.0 | 35.266 | 35.09 | 7.079 | 7.014 |

*Piperidine*, $CH_2(CH_2CH_2)NH$; M = 85.08.

Kahlbaum preparation, redistilled. *Tip No. I.* Above 30° the liquid in the apparatus turned yellow, so that no determinations above that point were attempted. The densities here were taken from the formula

$$d_t = 0.88125 - 0.000991t$$

obtained as a mean of the equations found from the densities employed by Ramsay and Shields and by Ramsay and Aston, *viz.:* 0.88025 — 0.000995$t$, and 0.8822 — 0.000987$t$, for it seems to agree better in general with the results obtained by others than do theirs; thus at 0° Ladenburg and Roth[1] find 0.8810. The values calculated for $t_c$ here are

| $t$. | $d$. | $w$. | $w(M/d)^{\frac{2}{3}}$. | $t_c$ from $k_B = 2.3936$. |
|---|---|---|---|---|
| 0 | 0.88125 | 35.720 | 751.73 | 320.1 |
| 30 | 0.85152 | 31.648 | 681.45 | 320.7 |

from which it is evident that the liquid is perfectly normal in its behavior, and non-associated.

The values of $t_c$, as well as those quantities from which that is derived, as found by Ramsay and Shields and by Ramsay and Aston, are given in the following tables:

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[1] *Ber.*, 17, 513.

Ramsay and Shields, $k_B$ = 2.1012.

| | | | | |
|---|---|---|---|---|
| 16.5 | 0.8640 | 29.89 | 637.1 | 325.7 |
| 46.4 | 0.8337 | 26.43 | 576.8 | 326.9 |
| 78.4 | 0.8024 | 22.75 | 509.3 | 326.8 |

Ramsay and Aston, $k_B$ = 2.1212.

| | | | | |
|---|---|---|---|---|
| 15.2 | 0.8670 | 29.67 | 635.6 | 320.9 |
| 46.2 | 0.8363 | 26.21 | 570.7 | 321.7 |
| 78.4 | 0.8048 | 22.46 | 501.8 | 321.0 |
| 132.5 | 0.7256 | 16.72 | 390.6 | 322.6 |

Assuming the relationships to be linear we find for drop weight and for drop volume from this tip the equations

$$w_t = 35.720 - 0.1357t$$

and

$$v_t = 40.534 - 0.1122t,$$

from which it follows from I and III that

$$\gamma_t = \mathbf{31.559 - 0.1199}t$$

and

$$a_t^2 = \mathbf{7.311 - 0.02024}t;$$

while from 16.5° to 46.4° Ramsay and Shields find $\gamma_t = 31.79 - 0.1155t$ and Ramsay and Aston $\gamma_t = 31.35 - 0.11t$; and $a_t^2 = 7.392 - 0.0205t$ and $a_t^2 = 7.260 - 0.0187t$, respectively.

From these relationships we find at 0° and 30° the various values of $\gamma$ and $a^2$ to be:

| | $\gamma$M & O. | $\gamma$R & S. | $\gamma$R & A. | $a^2$M & O. | $a^2$R & S. | $a^2$R & A. |
|---|---|---|---|---|---|---|
| 0 | 31.559 | 31.79 | 31.36 | 7.311 | 7.392 | 7.260 |
| 30 | 27.962 | 28.32 | 28.03 | 6.704 | 6.777 | 6.700 |

*Diisoamyl*, $((CH_3)_2CHCH_2CH_2)_2$; M = 142.18; $t_c$ obs. = 402°.

Kahlbaum preparation, redistilled. Density at 0° from Wurtz;[1] that at the others interpolated from the results of Falk on this same sample. With *Tip No. I* the following results were obtained:

| $t$. | $d$. | $w$. | $w(M/d)^{\frac{2}{3}}$. | $t_c$ from $k_B$ = 2.3936. |
|---|---|---|---|---|
| 0 | 0.7413 | 26.114 | 868.50 | 368.3 |
| 30 | 0.7161 | 23.344 | 794.48 | 368.0 |

It is evident that this liquid, also, is non-associated.

The variation with temperature of the drop weight, assuming it to be linear, is

$$w_t = 26.114 - 0.09203t$$

and that of the drop volume is

$$v_t = 35.227 - 0.0873t$$

which by aid of I and III lead to

$$\gamma_t = \mathbf{23.072 - 0.08131}t$$

and

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[1] *Jahresber. Fortschritte d. Chem.*, **8**, 573.

$$a^2 = \mathbf{6.354 - 0.01575}t.$$

The only measurements of the capillary rise of this liquid are those by Schiff which lead to the quite different values $a^2_{2.6} = 6.603$ and $a^2_{189.1} = 3.579$ as compared to 6.313 and 3.848 (the latter extrapolated through 129°) from the above formula.

*Isoamyl Acetate*, $C_2H_3O_2C_5H_{11}$; M = 130.11.

Kahlbaum preparation, redistilled. Densities from Bolle and Guye.[1] *Tip No. II.*

| $t$. | $d$. | $w$. | $w(M/d)^{\frac{2}{3}}$. | $t_C$ from $k_B$ = 2.3098. |
|---|---|---|---|---|
| 0 | 0.8941 | 28.076 | 776.80 | 342.4 |
| 49.7 | 0.8444 | 23.032 | 662.01 | 342.4 |

This liquid, according to the definition, is perfectly normal and non-associated. From the above values, assuming linear relationships, we find

$$w_t = 28.076 - 0.1015t,$$

and

$$v_t = 31.401 - 0.0830t,$$

from which it follows, employing II and IV, that

$$\gamma_t = \mathbf{25.706 - 0.09293}t$$

and

$$a^2_t = \mathbf{5.869 - 0.01551}t.$$

No results of capillary rise are to be found in the literature.

*Nitrobenzene*, $C_6H_5NO_2$; M = 123.05.

Kahlbaum preparation, redistilled. Densities from Guye and Baud,[2] $d_t = 1.3057 - 0.000845(t-11) - 0.00000125(t-11)^2$. *Tip No. II.*

| $t$. | $d$. | $w$. | $w(M/d)^{\frac{2}{3}}$. | $t_C$ from $k_B$ = 2.3098. |
|---|---|---|---|---|
| 30.2 | 1.1908 | 44.950 | 989.82 | 464.8 |
| 49.7 | 1.1729 | 42.592 | 947.42 | 466.0 |

From capillary rise the following results have been obtained:

Guye and Baud, $k_B$ = 2.1012.

| $t$. | $d$. | $\gamma$. | $\gamma(M/d)^{\frac{2}{3}}$. | $t_C$. |
|---|---|---|---|---|
| 9.4 | 1.2090 | 43.80 | 954.5 | 465.4 |
| 55.5 | 1.1680 | 38.41 | 856.5 | 469.2 |
| 98.8 | 1.1240 | 33.26 | 760.9 | 467.0 |
| 153.0 | 1.0625 | 27.40 | 650.8 | 469.0 |
| | Ramsay and Shields, $k_B$ = 2.1012. | | | |
| 13.6 | 1.188 | 42.75 | 942.8 | 468.3 |
| 78.4 | 1.124 | 34.89 | 798.2 | 464.3 |
| 156.2 | 1.047 | 26.94 | 646.0 | 469.7 |

Owing to the varying values found by various observers for the density of this liquid, the results from drop weight may be taken as showing that

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[1] *J. chim. phys.*, 3, 39 (1905).

[2] *Arch. sci. phys. et nat. Geneva*, [4] 11, 466 (1901).

it is non-associated notwithstanding the discrepancy of 1.2° in $t_c$. The values of $w_t$ and $v_t$ found above, assuming linear relationships, lead to the equations

$$w_t = 48.601 - 0.1209t$$

and

$$v_t = 39.970 - 0.07359t$$

from which by II and IV we obtain

$$\gamma_t = \mathbf{44.498 - 0.1107}t$$

and

$$a^2_t = \mathbf{7.471 - 0.01376}t.$$

Walden[1] expresses the results of Guye and Baud by means of the equations

$$\gamma_t = 44.945 - 0.1178t$$

and

$$a^2_t = 7.533 - 0.01492t.$$

A comparison of the values from these equations at the temperatures 30.2° and 49,7° with the values from the equations from drop weight as well as those interpolated from Ramsay and Shields is made in the following table:

Values of $a^2$ and of $\gamma$.

| $t$. | $a^2$M & O. | $a^3$W. | $a^2$R & S. | $\gamma$M & O. | $\gamma$W. | $\gamma$R & S. |
|---|---|---|---|---|---|---|
| 30.2 | 7.055 | 7.072 | 7.080 | 41.155 | 41.387 | 40.74 |
| 49.7 | 6.787 | 6.791 | 6.776 | 38.996 | 39.090 | 37.38 |

The striking thing about these results is that while the Ramsay and Shields values differ widely for $\gamma$, they are in good agreement with the others as far as concerns $a^2$. This, of course, is due to the fact that Ramsay and Shields used the quite different densities of Kopp, which affect the results $\gamma = {}^1/_2 \times h \times d \times r$, while the $a^2$ values are simply the product of the height and the radius. The values of $\gamma$ calculated from the drop weight are of course independent of the density, while those for $a^2$ are calculated with a knowledge of that factor.

### *Methyl Ethyl Ketone*, $CH_3COC_2H_5$; M = 72.06.

Sample from Eimer and Amend, prepared by Emerson. Densities from the volumes of Thorpe and Jones.[2] The drop weights from *Tip No. II*, together with those calculated from the equation found from them by the method of least squares, are given below:

$$w_t = 28.358 - 0.1279t + 0.000199t^2.$$

| $t$. | $w$ (obs.). | $w$ (from equation). | Δ. |
|---|---|---|---|
| 0 | 28.353 | 28.358 | +0.005 |
| 15 | 26.514 | 26.484 | —0.030 |
| 30 | 24.664 | 24.700 | +0.036 |
| 45 | 23.020 | 23.005 | —0.015 |

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[1] *Z. physik. Chem.*, **65**, 142 (1908).

[2] *J. Chem. Soc.*, **63**, 283 (1893).

while the drop volumes are

$$v_t = 34.190 - 0.11434t + 0.0001709t^2.$$

| $t$. | $w/d$. | $v$ (from equation). | Δ. |
|---|---|---|---|
| 0 | 34.176 | 34.190 | +0.014 |
| 15 | 32.553 | 32.513 | —0.040 |
| 30 | 30.874 | 30.914 | +0.040 |
| 45 | 29.404 | 29.391 | —0.013 |

The application of the new definition of normal molecular weight leads to the following values of $t_c$:

| $t$. | $d$. | $w$. | $w(M/d)^{\frac{2}{3}}$. | $t_c$ from $k_B = 2.3098$. |
|---|---|---|---|---|
| 0 | 0.82961 | 28.353 | 556.09 | 246.8 |
| 15 | 0.81449 | 26.514 | 526.47 | 249.0 |
| 30 | 0.79886 | 24.664 | 496.13 | 250.8 |
| 45 | 0.78288 | 23.020 | 469.28 | 254.2 |

from which it is evident that the liquid is abnormal, *i. e.*, associated.

No values from capillary rise are to be found in the literature but the application of II and IV to the drop weight and drop volume equations lead to

$$\gamma_t = 25.964 - 0.1171t + 0.0001822t^2$$

and

$$a_t^2 = 6.391 - 0.02137t + 0.00003194t^2.$$

*Diethyl Ketone*, $C_2H_5COC_2H_5$; M = 86.08.

Sample obtained through Eimer and Amend from Emerson, redistilled within 0.1°. Densities calculated from the volumes given by Thorpe and Jones.[1] The observed drop weights from *Tip No. I*, as well as those calculated from the equation derived from them, are as follows:

$$w_t = 29.394 - 0.1133t.$$

| $t$. | $w$ (obs.). | $w$ (from equation). | Δ. |
|---|---|---|---|
| 0 | 29.404 | 29.394 | —0.010 |
| 15 | 27.696 | 27.694 | —0.002 |
| 30.1 | 25.958 | 25.984 | +0.026 |
| 45 | 24.310 | 24.295 | +0.015 |

while for drop volumes we have

$$v_t = 25.253 - 0.10634t - 0.0001787t^2.$$

| $t$. | $w/d$ (obs.). | $v$ (from equation). | Δ. |
|---|---|---|---|
| 0 | 35.278 | 35.253 | —0.025 |
| 15 | 33.618 | 33.698 | +0.080 |
| 30.1 | 32.300 | 32.214 | —0.086 |
| 45 | 28.800 | 28.830 | +0.030 |

The application of the definition of normal molecular weight leads to the following values of $t_c$:

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[1] *Loc. cit.*

| $t$. | $d$. | $w$. | $w(M/d)^{\frac{2}{3}}$. | $t_c$ from $k_B = 2.3936$. |
|---|---|---|---|---|
| 0 | 0.83350 | 29.404 | 647.25 | 276.4 |
| 15 | 0.82384 | 27.696 | 618.11 | 278.7 |
| 30.1 | 0.80365 | 25.958 | 585.46 | 280.7 |
| 45 | 0.78929 | 24.310 | 554.92 | 282.8 |

from which it is clear that the liquid is abnormal, *i. e.*, associated. The use of I and III leads here with the equations for $w_t$ and $v_t$ to

$$\gamma_t = 25.970 - 0.1001t$$

$$a_t^2 = 6.363 - 0.01919t + 0.00003225t^2$$

but no values from capillary rise are to be found in the literature.

### *Propyl Alcohol*, $C_3H_7OH$; M = 60.06.

Kahlbaum preparation, redistilled. Densities are from Young.[1] The drop weights found and calculated from an equation are as follows: *Tip No. I.*

$$w_t = 27.817 - 0.08857t.$$

| .. | $w$ (obs.). | $w$ (from equation). | Δ. |
|---|---|---|---|
| —5.7 | 28.362 | 28.322 | —0.040 |
| +0.2 | 27.740 | 27.799 | +0.059 |
| 7.1 | 27.188 | 27.188 | 0.000 |
| 22.4 | 25.872 | 25.833 | —0.039 |
| 34.5 | 24.744 | 24.761 | +0.017 |
| 58.2 | 22.636 | 22.662 | +0.026 |
| 70.2 | 21.620 | 21.599 | —0.021 |

The drop volumes ($w_t/d_t$) given below are at temperatures at which Young gives values for the density, the values of $w$ being those from the above equation.

$$vt = 33.950 - 0.07586t - 0.0000502t_8.$$

| $t$. | $d$. | $w$. | $w/d$. | $v$ (from equation). | Δ. |
|---|---|---|---|---|---|
| 0 | 0.8193 | 27.817 | 33.952 | 33.950 | —0.002 |
| 20 | 0.8035 | 26.046 | 32.416 | 32.413 | —0.003 |
| 40 | 0.7875 | 24.274 | 30.824 | 30.836 | +0.012 |
| 60 | 0.7700 | 22.503 | 29.225 | 29.217 | —0.008 |

That propyl alcohol is abnormal in molecular weight, *i. e.*, is associated, is shown by the following values of $t_c$ (a fact which is also confirmed by results from capillary rise):

| $t$. | $d$. | $w$. | $w(M/d)^{\frac{2}{3}}$. | $t_c$ from $k_B = 2.3936$. |
|---|---|---|---|---|
| 0 | 0.8193 | 27.817 | 487.24 | 209.6 |
| 20 | 0.8035 | 26.046 | 462.18 | 219.1 |
| 40 | 0.7875 | 24.274 | 436.55 | 228.4 |
| 60 | 0.7700 | 22.503 | 410.81 | 237.6 |

From the above equations for $w$ and $v$, we find, by aid of I and III, the following values for $\gamma$ and $a^2$:

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[1] *Proc. Roy. Soc. Dub.*, **12** (N. S.), 442 (1910).

$$\gamma_t = 24.577 - 0.07825t$$

and

$$a_t^2 = 6.124 - 0.01368t - 0.00000906t^2.$$

A comparison of the values of $\gamma$ and $a^2$ found from these equations with those found by other observers (Renard and Guye, Ramsay and Shields) by the method of capillary rise is made in the two tables below, at the temperatures at which they worked. All numbers which are in parentheses are found by interpolating or extrapolating, using the temperature coefficient found from the two nearest figures; this is also true with all the other tables given later.

*Values of $\gamma$.*

| $t$. | M & O (from equation). | R & G. | R & S. |
|---|---|---|---|
| 10.2 | 23.778 | *23.69* | (24.34) |
| 16.4 | 23.294 | (23.19) | *23.82* |
| 36.0 | 21.760 | *21.61* | (22.15) |
| 44.5 | 21.095 | *21.05* | (21.41) |
| 46.3 | 20.954 | (20.90) | *21.29* |
| 57.8 | 20.054 | *19.97* | (20.35) |
| 65.9 | 19.420 | *19.27* | (19.68) |
| 75.8 | 18.646[1] | *18.33* | (18.87) |
| 78.3 | 18.450[1] | (18.19) | *18.67* |
| 90.6 | 17.488[1] | *17.48* | (17.66) |

*Values of $a^2$.*

| $t$. | M & O. | R & G. | R & S. |
|---|---|---|---|
| 5.8 | 6.044 | (6.007) | (6.181) Schiff *6.223* |
| 10.2 | 5.984 | *5.943* | (6.112) |
| 16.4 | 5.897 | (5.852) | *6.014* |
| 36.0 | 5.620 | *5.565* | (5.704) |
| 44.5 | 5.497 | *5.468* | (5.570) |
| 46.3 | 5.465 | (5.441) | *5.543* |
| 57.8 | 5.303 | *5.268* | (5.364) |
| 65.9 | 5.183 | *5.132* | (5.237) |
| 75.8 | 5.035[1] | *4.934* | (5.083) |
| 78.3 | 4.997[1] | (4.916) | *5.045* |
| 90.6 | 4.810[1] | *4.771* | (4.853) |
| 97.1 | 4.710[1] | (4.699)[1] | (4.752) Schiff *4.718* |

As will be observed from the above the values from drop weight always lie between those found by Renard and Guye and those of Ramsay and Shields, more closely approaching, however, those of the former.

*Propionitrile*, $C_2H_5CN$; M = 55.04.

Kahlbaum preparation, redistilled. Densities from Thorpe.[2]

$d_t$ 0.80101 — 0.0009815$t$ — 0.000000125$t^2$. *Tip No. I.*

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[1] Extrapolated.

[2] *Trans. Chem. Soc.*, 37, 141 and 327.

$$w_t = 31.942 - 0.11657t.$$

| $t$. | $w$ (obs.). | $w$ (from equation). | Δ. |
|---|---|---|---|
| 6.5 | 31.190 | 31.185 | —0.005 |
| 17.7 | 29.859 | 29.879 | +0.020 |
| 37.7 | 27.560 | 27.547 | —0.013 |
| 60.3 | 24.950 | 24.913 | —0.037 |
| 71.2 | 23.608 | 23.642 | +0.034 |

$$v_t = 39.840 - 0.09066t - 0.0002045t^2.$$

|  | $d$ (Thorpe). | $w$ (from equation). | $w/d$. | $v$ (from equation). | Δ. |
|---|---|---|---|---|---|
| 0 | 0.80101 | 31.942 | 39.877 | 39.840 | —0.037 |
| 20 | 0.78117 | 29.611 | 37.906 | 37.945 | +0.039 |
| 40 | 0.76093 | 27.279 | 35.850 | 35.886 | +0.036 |
| 60 | 0.74027 | 24.948 | 33.701 | 32.664 | —0.037 |

That this liquid, also, is abnormal, *i. e.*, associated according to the new definition, is shown by the following $t_c$ values at the above even temperatures.

| $t$. | $w(M/d)^{\frac{2}{3}}$. | $t_c$ from $k_B = 2.4936$. |
|---|---|---|
| 0 | 535.87 | 229.9 At 16.8° R. and S. find 238.7° |
| 20 | 515.14 | 237.0 |
| 40 | 473.57 | 243.9 |
| 60 | 441.13 | 250.3 At 61.8° R. and G. find 249.7° |

From the equations for drop weight and drop volume, we find, using I and III,

$$\gamma_t = \mathbf{28.221 - 0.103}t$$
$$a^2_t = \mathbf{7.186 - 0.01635}t\mathbf{ - 0.00003689}t^2.$$

In the table below the values of $\gamma$ and $a^2$ as found by aid of these equations are compared with those found at other temperatures by the capillary rise method.

|  | Values of $\gamma$. |  |  |  | Values of $a^2$. |  |  |
|---|---|---|---|---|---|---|---|
| $t$. | M & O. | R & S. | R & G. | $t$. | M & O. | R & S. | R & G. |
| 11.8 | 27.006 | (27.21) | *27.29* | 11.8 | 6.988 | (7.030) | *7.038* |
| 16.8 | 26.491 | *26.68* | (26.74) | 16.8 | 6.901 | *6.933* | (6.913) |
| 31.3 | 24.997 | (25.14) | *25.13* | 31.3 | 6.638 | (6.652) | *6.652* |
| 46.4 | 23.442 | *23.55* | (23.39) | 46.4 | 6.348 | *6.358* | (6.329) |
| 48.1 | 23.267 | (23.36) | *23.19* | 61.8 | 6.035 | (6.018) | *6.000* |
| 61.8 | 21.856 | (21.91) | *21.69* | 78.1 | 5.685[1] | (5.657) | *5.631* |
| 78.1 | 20.177[1] | (20.18) | *19.92* | 78.3 | 5.681[1] | *5.653* | (5.627) |
| 78.3 | 20.156[1] | *20.18* | (19.90) | 89.9 | 5.417[1] | (5.397) | *5.382* |
| 89.9 | 18.961[1] | (18.93) | *18.67* | 97.0 | 5.253[1] | (5.240) | (5.232) Schiff *5.453* |

### *Acetone*, $CH_3COCH_3$; M = 58.05.

Kahlbaum preparation, redistilled. Densities from Thorpe's volumes. *Tip No. II.*

$$w_t = 27.666 - 0.1339t.$$

| $t$. | $w$ (obs.). | $w$ (from equation). | Δ. |
|---|---|---|---|
| 15 | 25.674 | 25.657 | —0.017 |
| 30.1 | 23.610 | 23.636 | +0.026 |
| 60 | 19.642 | 19.632 | —0.010 |

$$v_t = 33.993 - 0.1296t.$$

| $t$. | $d$. | ($w$ obs./$d$). | $v$ (from equation). | Δ. |
|---|---|---|---|---|
| 15 | 0.80177 | 32.022 | 32.049 | +0.027 |
| 30.1 | 0.78348 | 30.135 | 30.092 | —0.043 |
| 60 | 0.74962 | 26.203 | 26.217 | +0.014 |

The values of $t_c$ calculated for this liquid show it, also, to be abnormal, *i. e.*, *associated.*

| $t$. | $w(M/d)^{\frac{2}{3}}$. | $t_c$ from $k_B = 2.3098$. |
|---|---|---|
| 15 | 445.99 | 214.1 |
| 30.1 | 416.50 | 216.5 |
| 60 | 356.86 | 220.5 |

From the above weight and volume relations, by aid of II and IV, we obtain

$$\gamma_t = 25.330 - 0.1226t$$

and

$$a^2_t = 6.354 - 0.02422t.$$

The values of $\gamma$ and $a^2$ observed by the various investigators (Ramsay and Shields, Dutoit and Friederich, and Renard and Guye), or interpolated or extrapolated from their work, are compared with those calculated from the above equations in the following tables:

Values of $\gamma$.

| $t$. | M & O. | R & S. | D & F. | R & G. |
|---|---|---|---|---|
| —1.2 | 25.477[1] | (25.58) | *25.76* | (25.41) |
| 12.9 | 23.748[1] | (23.83) | (24.00) | *23.96* |
| 16.8 | 23.271 | *23.35* | (23.61) | (23.56) |
| 21.0 | 22.755 | (22.83) | (22.98) | *23.13* |
| 21.8 | 22.657 | (22.73) | *22.89* | (23.02) |
| 30.0 | 21.652 | (21.71) | (21.62) | *21.93* |
| 33.8 | 21.186 | (21.24) | *21.03* | (21.50) |
| 44.1 | 19.923 | (19.96) | (19.92) | *20.33* |
| 46.4 | 19.641 | *19.68* | (19.67) | (20.09) |
| 55.1 | 18.575 | (18.64) | (18.72) | *19.19* |
| 56.6 | 18.513 | (18.59) | *18.67* | (19.14) |
| 78.3 | 15.730[1] | *15.90* | (16.22) | (16.78) |

Values of $a^2$.

| $t$. | M & O. | R & S. | D & F. | R & G. |
|---|---|---|---|---|
| 1.2 | 6.383[1] | (6.380) | *6.410* | (6.324) |
| 12.9 | 6.042[1] | (6.052) | (6.038) | *6.074* |
| 16.8 | 5.974 | *5.958* | (5.935) | (6.005) |
| 21.0 | 5.845 | (5.857) | (5.824) | *5.931* |
| 21.8 | 5.826 | (5.838) | *5.802* | (5.910) |
| 30.0 | 5.627 | (5.641) | (5.617) | *5.693* |
| 33.8 | 5.535 | (5.550) | *5.532* | (5.608) |
| 44.1 | 5.286 | (5.303) | (5.292) | *5.378* |
| 46.4 | 5.230 | *5.246* | (5.238) | (5.332) |
| 55.1 | 5.019 | (5.029) | (5.037) | *5.159* |
| 55.6 | 5.007 | (5.016) | *5.025* | (5.149) |
| 78.3 | 4.458[1] | *4.456* | 4.496 | (4.695) |

Just as with nitrobenzene, the agreement in the $a^2$ values here is better than that of the $\gamma$ values. It must be remembered again in this connection that the surface tensions from capillary rise are dependent upon the density, and the various observers have not all used the same values while the $\gamma$ value from drop weight is independent of density, except that of benzene, for it is from the $\gamma$ values of that only that the constant for the transformation of $w$ into $\gamma$ is found. The $a^2$ values, on the other hand, are dependent, when found from drop weight, upon the density, while those from capillary rise are directly observed. The better agreement of the $a^2$ values, then, is a proof that the densities we have employed (Thorpe's) are the correct ones, for they transform directly observed drop weight results into indirect values agreeing with the directly observed capillary rise, or would transform directly observed capillary rise values into calculated surface tensions agreeing with those found directly from directly observed drop weights.

## Summary.

I. On the basis of the new definition of normal molecular weight in the liquid state, the finding of a calculated value of $t_c$ independent of the temperature of observation ($t_o$) in the equation $w(\mathrm{M}/d)^{\frac{2}{3}} = k_{\mathrm{B}}(t_c - t_o - 6)$, where $k_{\mathrm{B}}$ is found from the same equation for *benzene* at all temperatures when its observed critical point, 288.5°, is used as $t_c$, it is shown that methyl hexyl ketone, benzyl cyanide, benzaldehyde, piperidine, diisoamyl, isoamyl acetate, and nitrobenzene are perfectly normal, *i. e.*, non-associated, the calculated $t_c$ remaining constant within the limits of error. Methyl ethyl ketone, diethyl ketone, propyl alcohol, propionitrile, and acetone on the other hand are abnormal, *i. e.*, associated, for the values of $t_c$ calculated for them increase with increased temperature of observation.

II. The values of surface tension in dynes, $\gamma$, and of the capillary constant $a^2$, calculated respectively from the drop weights and the drop volumes, are found to agree with the values observed from capillary rise even better than these do when found by different observers, for in most cases where comparison is possible, the values from the drop weight method lie between those found by the investigators on capillary rise.

III. Equations giving the variation of the surface tension $\gamma$ and the capillary const. $a^2$, as found from the drop weight, are given for all the above liquids, that for $\gamma$ being especially important for it is independent of any knowledge of the density of the liquid, a cause of variation, all too often encountered in the results by the capillary rise method. The values of $a^2$, on the other hand, are here dependent upon the density, but as great care has been taken in the selection of the observed values, those of Thorpe or Young being used when possible, it is thought that great stress may also be laid upon them.

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