When the results of Series I and II are averaged with those of Series III, it is found that

If Ag = 107.930 As = 75.021
If Ag = 107.880 As = 74.957
If Ag = 107.850 As = 74.918

The atomic weight of arsenic will be further investigated in this laboratory.

The most important results of this research may be briefly summed up as follows:

1. Methods for the preparation of normal trisilver arsenate were devised.

2. It is shown that trisilver arsenate precipitated by means of trisodium arsenate probably contains occluded basic impurity.

3. It is shown that silver arsenate cannot be completely dried without fusion.

4. The specific gravity of unfused trisilver arsenate is found to be 6.66 at 25°/4°.

5. The per cent. of silver in silver arsenate is found to be 69.9616 by three closely agreeing methods.

6. With several assumed values for the atomic weight of silver referred to oxygen 16.000, the atomic weight of arsenic is found to have the following values:

If Ag = 107.93 As = 75.02
If Ag = 107.88 As = 74.96
If Ag = 107.85 As = 74.92

A grant from the Carnegie Institution of Washington has been of great assistance in the pursuit of this investigation. We are also indebted to the Cyrus M. Warren Fund for Research in Harvard University for much indispensable platinum apparatus.

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[CONTRIBUTIONS FROM THE HAVEMEYER LABORATORIES OF COLUMBIA UNIVERSITY, NO. 160.]

THE CALCULATION OF THE CRITICAL TEMPERATURE OF AN ASSOCIATED LIQUID FROM SURFACE TENSION RESULTS.

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Theoretical.

According to Ramsay and Shields[1] liquids may be divided into two great classes. One of these, the so-called *non-associated* liquids, following the law

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[1] *Z. physik. Chem.*, 12, 433–75 (1893).

$$\gamma_1(\mathrm{M}/d_1)^{2/3}_{t_1} = k\ (t_c—t_1—6), \qquad (1)$$

where by definition

$$k = \frac{\gamma_1(\mathrm{M}/d_1)^{2/3}_{t_1} — \gamma_2(\mathrm{M}/d_2)^{2/3}_{t_2}}{t_1—t_2};\text{[1]} \qquad (2)$$

while the other does not. The peculiarity of this latter class, the so-called *associated* liquids, lying in the fact that the k value, observed according to the definition, (2), is not a constant.

It will be seen, then, as Ramsay and Shields have already pointed out, that the critical temperature of any liquid in the first class can be calculated from the values of $\gamma\ (\mathrm{M}/d)^{2/3}$, observed at two temperatures, by first finding the exact value of k, for the liquid in question, by aid of (2), then substituting it, with one of the values of $\gamma\ (\mathrm{M}/d)^{2/3}$, in (1), and solving for t_c, the critical temperature. This process, of course, is simply an extrapolation to find the temperature at which the term $\gamma\ (\mathrm{M}/d)^{2/3}$ would become zero, for that must be the critical temperature, or a point 6° below it, for at the critical temperature (or this point 6° below it) all distinction between a liquid and its vapor must disappear, as well as the meniscus which ordinarily separates them.

For associated liquids, since k is found not to be constant, there is at present no similar, general, method for the calculation of the critical temperature from surface tension results. The object of this paper is to present such a general method, together with tests of it from the results of Ramsay and Shields.

The functional relationship between the term $\gamma(\mathrm{M}/d)^{2/3}$ and the temperature has apparently thus far only been found in the form employed by Ramsay and Shields, (1), in which the temperature is reckoned, not in the conventional manner, upward from the ice-point of water as zero, but *downward from the critical point taken as zero.* This method was perhaps at the time the best for their purposes, for it laid greater stress upon the fact to which they were calling attention, *viz.*, that the term $\gamma(\mathrm{M}/d)^{2/3}$ is *approximately equal in value for all non-associated liquids at corresponding temperatures*, *i. e.*, at those temperatures which are equally removed from the critical points.

It is possible, however, to express this functional relationship in another form, without the use of the critical temperature. And this form, as will be seen, is to be preferred, for it leads to a more satisfactory and general result, being applicable not only to non-associated liquids, but also, with a slight change, to those for which Ramsay and Shields found k to be inconstant, *i. e.*, to associated liquids.

[1] γ, here, is the surface tension in dynes per centimeter, M the molecular weight, d_1 and d_2 the densities at the temperatures t_1 and t_2, t_c the critical temperature of the liquid, and k a constant with a mean value of approximately 2.12 ergs.

For non-associated liquids, since $\gamma(M/d)^{2/3}$ is a linear function of the temperature, this relationship may be written in the simple form

$$\gamma(M/d)^{2/3}_t = A + Pt, \tag{3}$$

where A is the value of $\gamma(M/d)^{2/3}$, for the liquid in question, at 0°, B is the change in $\gamma(M/d)^{2/3}$ per degree, and t is the centigrade temperature. While A, here, will have a different value for each liquid, B is approximately a constant for all non-associated liquids, for, by definition, it is identical with the term k of Ramsay and Shields; and has a negative value, for $\gamma(M/d)^{2/3}$ decreases with increased temperature. This, of course, can be shown by differentiating (3) with respect to $\gamma(M/d)^{2/3}$ and t, from which we find

$$d/dt[\gamma(M/d)^{2/3}_t] = B = k.$$

Equation (3), then, can be written in the form

$$\gamma(M/d)^{2/3}_t = \gamma(M/d)^{2/3}_0 + kt, \tag{4}$$

where, from (1), $\gamma(M/d)^{2/3}_0 = A = k(t_c - 6)$.

To calculate the critical temperature of the non-associated liquid by (4) it is simply necessary to make the left-hand member, $\gamma(M/d)^{2/3}_t$, zero, and find the value of t which would make it so. This temperature, according to the work of Ramsay and Shields, is usually 6° below the critical temperature. Proceeding in this way, we find

$$\gamma(M/d)^{2/3}_{t_c-6} = 0 = \gamma(M/d)^{2/3}_0 + k(t_c - 6),$$

or

$$t_c = \frac{\gamma(M/d)^{2/3}_0}{k} + 6, \tag{5}$$

from which, knowing the value of $\gamma(M/d)^{2/3}$ for the liquid at 0°, and the general constant k, we can solve for t_c, the critical temperature.

Although equation (3) would lead to the same results as those already found for the critical temperatures of non-associated liquids by Ramsay and Shields, (1), it lends itself more readily, owing to its form, to the application to the experimental results of the method of least squares, for the exact evaluation of the term B ($= k$), than the form they have used, and that method, granting an equal possibility of error in all the results, leads to a much fairer smoothed curve than any that could be obtained by the visual plotting of the results. Then, after the mean values of A and B, from the consideration of *all* the results, have been found, the one, final, value of the critical temperature can be calculated by aid of (5). This method would also probably lead to a better, general, average value of k than that at present accepted and obtained from form (1).[1]

[1] To find the values of A and B (3) by the method of least squares, the various, n, values of $\gamma(M/d)^{2/3}_t$, at their proper temperatures, are inserted, together with these values of t, in n equations of the forms (3), each having two unknowns, A and B. Then

When the liquid is *associated, i. e.*, when k is not constant, and $\gamma(M/d)^{2/3}$ is no longer a linear function of the temperature, equation (3) can be made to apply by the addition to it of a third constant, also negative, as is (B), with the square of the temperature as its coefficient. Equation (3) is thus transformed, *for associated liquids*, into the form

$$\gamma(M/d)_t^{2/3} = A + Bt + Ct^2, \qquad (6)$$

where, as in (3), A is equal to the value of $\gamma(M/d)^{2/3}$ at 0°. Differentiating (6) with respect to $\gamma(M/d)^{2/3}$ and t, we find

$$d/dt[\gamma(M/d)_t^{2/3}] = k_t = B + 2Ct, \qquad (7)$$

from which it is obvious that $B = k_0$, *i. e.*, B is equal to the value of k at 0°. Differentiating (7) with respect to k and t, we obtain

$$dk/dt = 2C,$$

or

$$C = \tfrac{1}{2}dk/dt.$$

Substituting these values of A, B, and C in equation (6) we find, for *associated liquids*,

$$\gamma(M/d)_t^{2/3} = \gamma(M/d)_0^{2/3} + k_0 t + \tfrac{1}{2}dk/dt\, t^2, \qquad (8)$$

or

$$\gamma(M/d)_t^{2/3} = \gamma(M/d)_0^{2/3} + (k_0 + \tfrac{1}{2}dk/dt\, t)t,$$

as compared to the value

$$\gamma(M/d)_t^{2/3} = \gamma(M/d)_0^{2/3} + kt,$$

which we found above for *non-associated liquids*.

While, as we have seen for *non-associated liquids*,

$$k = \text{constant},$$

for *associated liquids*, from (7)

$$k_t = k_0 + dk/dt\, t. \qquad (9)$$

k is thus a linear function of the temperature for associated liquids, and increases with the temperature up to the critical point, where it attains a maximum value. The behavior of k with varying temperature, for associated liquids, is similar, then, to that of $\gamma(M/d)^{2/3}$ for non-associated

each of these n equations is multiplied by the coefficient of its A (here 1) and the sum of the n equations, so treated, is taken as normal equation 1. Next, each of the original n equations is multiplied by the coefficient of its B (*i. e.*, by t), and the sum of these n, so treated, taken as normal equation 2. Simultaneous solution of these two normal equations for A and B gives then their mean values. These values, found by this method, are such that the sum of the squares of the discrepancies (residuals) observed in the original n equations, when the values of the unknowns, A and B as found, are substituted in them, is a minimum, and the sum of the discrepancies (added algebraically) is zero.

In case there are three, instead of two constants, a third normal equation is formed by taking the sum of the n original equations, after each has been multiplied by the coefficient of its third constant. From these three normal equations the three unknown constants can then be simultaneously evaluated.

liquids, both are linear functions of the temperature; but, when $\gamma\ M/d^{2/3}$ is zero at the critical point (or 6° below it), k is a maximum; while at the negative value of the critical temperature (or 6° above it), if such a temperature could be attained, k would be equal to zero. At zero degrees, k has a value equal to one-half its maximum value.

For the calculation of the critical temperature of an *associated liquid*, naturally, we may employ either (8) or (9). With (8), of course, just as with (4), we find the value $(t_c—6)$ which satisfies the equation when $\gamma(M/d)^{2/3}_t$ is made equal to zero. The critical temperature, then, will be one of the two possible values (which one would probably always be obvious) found by solution of the equation

$$t_c = 6 (-) \frac{k_0}{dk/dt} \pm \sqrt{\frac{\gamma(M/d)^{2/3}_0}{{}^1/_2 dk/dt} + \left(\frac{k_0}{dk/dt}\right)^2}. \qquad (10)$$

Using equation (9) for this purpose, we find the temperature at which k becomes equal to zero. This, of course, from what has been said above, will be seen to be 6° above the *negative* value of the critical temperature. We have, for example,

$$O = k_0 + dk/dt[-(t_c - 6)]$$

i. e.,

$$t_c = \frac{k_0}{dk/dt} + 6. \qquad (11)$$

The maximum value of k, from what we have already seen, can obviously be found, either by multiplying the value of k at 0° by 2, or by solving the equation

$$k_{max.} = k_0 + dk/dt(t_c - 6), \qquad (12)$$

which is, of course, practically the same thing, for $k_0 = dk/dt(t_c - 6)$.

Constant, but Abnormal, Values of k.—This idea of a maximum value of k, which need not be as large as the general, average, value, 2.12, is, of course, more important for the calculation of the factor of association than for the calculation of the critical temperature. It may be said here, however, that by the use of (1), assuming that the critical temperature is the important factor in the fixing of the value of k, it can be shown from the results of Ramsay and Shields, that such a thing is by no means improbable or uncommon.

Thus, for acetone, which is regarded as an associated liquid, they find the following results:

t.	$\gamma(M/d)^{2/3}$.	k.
16.8	406.1	
		1.818
46.4	352.3	
		1.818
78.3	294.3	

Considering this abnormal value of k as constant, by (1) we find the critical temperature to be 246.2°, where the values 246.1°, 237.5°, 234.4°, and 232.8° have been found experimentally.[1] To give the lowest of these values, 232.8°, k would have to be but slightly higher, *viz.*, 1.93, which is still much lower than the average, general, value 2.12.

Further, Ramsay and Shields find the following results:

Propionic Acid.

t.	$\gamma(M/d)^{2/3}$.	k.
16.6	466.3	
		1.446
46.4	423.2	
		1.443
79.6	375.3	
		1.390
132.5	301.8	

k, here, within the experimental error, practically remains constant. By aid of formula (1), using the value of $\gamma(M/d)^{2/3}$ at 16.6°, and $k = 1.446$, we find 345° as the critical temperature, as against the experimental values 339.9°, 337.6°, and 326.8° noted in the "Tabellen." Here, also, k would have to be but slightly larger, and constant, to give a very good agreement with the experimental values.

It must be conceded, then, that, in addition to the liquids which show a constant, normal, value of k, and those giving a k value which is a linear function of the temperature, attaining its maximum value at the critical point, we also have a class which exhibits a constant, *but abnormally low*, value of k. Of course it must be remembered in this connection that the results given are few, and that even a slight error in $\gamma(M/d)^{2/3}$ or t would cause a large error in k. This is possibly the cause of the slight *decrease* observed in the case of propionic acid, as well as in other cases, which do not enable us thus to calculate the correct critical temperature.

Whether the above k values are attained slowly, *i. e.*, were smaller at the lower temperatures, or are constant throughout the entire temperature scale, cannot be decided, of course, owing to the lack of experimental data at those temperatures. It would seem, necessary, however, from what we have considered above, that they be either constant throughout, *though abnormal*, or increase continually, but very gradually, up to the critical point, at which they would attain a maximum value. Further, it is hardly possible in these cases for the maximum to be nearly as large as 2.12, nor is it likely that the maximum value could be attained at any temperature below the critical point.[2]

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[1] Landolt-Börnstein-Meyerhoffer, *Tabellen*, 1905, p. 182.

[2] Other investigators have also observed constant, but abnormally low, values of k, which lead to the correct critical values. Such liquids are HI, HBr, H_2S, H_3P and HCl.

Application of the Formulas to Experimental Results.

Below are given the results obtained by the application of the above formulas to the values of surface tension, as found by Ramsay and Shields, for the associated liquids, methyl alcohol, water, ethyl alcohol, and acetic acid, the only ones which have been sufficiently studied experimentally for the purpose.

Methyl Alcohol.—The experimental results for $\gamma(M/d)^{2/3}$ at various temperatures, from 20° to 230°, as obtained by Ramsay and Shields by the method of capillary rise, are given in Table I, in the column headed $\gamma(M/d)^{2/3}_{R \& S}$. The constants of equations (6) and (8) for this liquid were obtained by treating the 18 equations in the form (6), t varying from 20° to 230°, by the method of least squares, as described briefly above. The values so found are as follows:

$$\begin{aligned} A &= \gamma(M/d)_0^{2/3} &&= 282.66 \\ B &= \quad k_0 &&= -0.7726 \\ C &= \tfrac{1}{2}dk/dt &&= -0.0016864 \end{aligned}$$

so that (6) and (8), for methyl alcohol, may be written in the form

$$\gamma(M/d)_t^{2/3} = 282.66 - 0.7726t - 0.0016864t^2, \qquad (13)$$

and (9) becomes

$$k_t = -0.7726 - 0.0033728t.$$

The results obtained by the use of (13) are given in Table I in the column headed $\gamma(M/d)^{2/3}$ calc. Comparison of these values with the experimental ones from which the formula (13) was derived shows that while the agreement is fair at most of the temperatures, (13) leads to

TABLE I.

Methyl Alcohol.

t.	$\gamma(M/d)^{2/3}$ R. & S.	$\gamma(M/d)^{2/3}$ calc.
20	271.4	266.5
70	216.2	220.3
80	206.6	210.1
90	196.3	199.5
100	186.7	188.5
110	176.7	177.3
120	166.3	165.7
130	154.8	153.7
140	142.9	141.4
150	131.3	128.8
160	118.1	116.0
170	104.8	102.6
180	91.0	89.0
190	76.4	75.7
200	60.6	60.7
210	45.4	46.0
220	29.2	31.1
230	13.4	15.8

values which are too small at the lowest temperature, and too high at the highest. This means, of course, that the critical temperature calculated by aid of (10), from the values found for $\gamma(M/d)_0^{2/3}$, k_0, and $\frac{1}{2}dk/dt$ would be *too high*, and that by aid of equation (11) would be *too low*. To get a better agreement at the low temperatures it would be necessary to use a larger value for $\gamma(M/d)_0^{2/3}$, and this, as will be seen in the cases of ethyl alcohol and acetic acid, would lead to a larger value of k° and a smaller one for $\frac{1}{2}dk/dt$; this would cause (11) to give a better, higher, result for the critical temperature.

We might expect, then, from the above, that the mean of the critical temperatures, as found by (10) and (11) would be nearer correct than either alone, which is shown to be true by the results.

Equation (10) leads to the value

$$t_c = 246.1^\circ,$$

while (11) gives

$$t_c = 235.1^\circ,$$

the experimental value being

$$t_c = 240^\circ;$$

and the mean of (10) and (11) giving

$$t_c = 240.6^\circ.$$

Here it will be seen, the formula (13) does not give exact values at either extreme of temperature, consequently the taking of the mean value for the critical temperature is justified. In most cases, of course, fewer results would be available, and a formula could readily be found which would give good results either for the high, or for the low, temperatures; then the result of either (10) or (11), according to circumstances, would be taken as correct. This was not done here, since neither extreme was exactly in agreement. The non-holding of (6) for very large temperature intervals is discussed later.

It may be mentioned here that the experimental result of $\gamma(M/d)^{2/3}$ at 70° is probably too low, for Ramsay[1] finds by aid of a somewhat complicated, empirical, formula, derived by Rose-Innes, the same value as that found by (13), and as his calculated results at other temperatures agree exceedingly well with experiment, it would seem that this one result is decidedly in error.

Water.—The only results for $\gamma(M/d)^{2/3}$ for water, as given by Ramsay and Shields, are from 0° to 140°. Treating these, which are given in Table II, by the method of least squares, we find the constants of (6) and (8) to be

$$\begin{aligned} A &= \gamma(M/d)_0^{2/3} = 503.06 \\ B &= \quad k_0 \quad = -0.87187 \end{aligned}$$

and

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[1] *Z. physik. Chem.*, **15**, 106–116 (1894).

$$C = \tfrac{1}{2}dk/dt = -0.001228,$$

so that for water we have the relation

$$\gamma(M/d)_t^{2/3} = 503.06 - 0.87187t - 0.001228t^2.$$

The results of this formula are given in the column headed $\gamma(M/d)^{2/3}$ calc. and agree excellently with the values from which the equation was derived.

TABLE II.

Water.

t.	γ $(M/d)^{2/3}$ R. & S.	γ $(M/d)^{2/3}$ calc.
0	502.9	503.06
10	494.2	494.22
20	485.3	485.13
30	476.1	475.80
40	466.3	466.21
50	456.4	456.40
60	446.2	446.33
70	435.9	436.01
80	425.3	425.45
90	414.6	414.73
100	403.5	403.59
110	392.3	392.30
120	380.7	380.75
130	369.1	368.96
140	357.0	356.93

Here, of course, we would expect (11) to give the better result, for the agreement at these comparatively low temperatures is very good. Equation (10), on the other hand, could hardly be expected to lead to a satisfactory value of critical temperature, for it would mean the extrapolation of a large quantity to its zero value through more than 200°.

Equation (11), here, leads to the value

$$t_c = 361°,$$

as compared to the experimental ones of 358.1°, 364.3°, and 365°, noted in the "Tabellen." Equation (10) leads to an incorrect value, 383.6°, as expected.

Ethyl Alcohol.—In this case, just as with methyl alcohol, we have too many results for the simple treatment possible for water. Applying to all the results for $\gamma(M/d)^{2/3}$ from 20° to 230°, inclusive, as given in Table III, the method of least squares, we find the values

$$A = \gamma(M/d)_0^{2/3} = 347.26$$
$$B = k_0 = -0.8772$$

and

$$C = \tfrac{1}{2}dk/dt = -0.002377,$$

so that equations (6) and (8) may be written

$$\gamma(M/d)_t^{2/3} = 347.26 - 0.8772t - 0.002377t^2, \qquad (14)$$

the results of which are given in column 3 of the table.

TABLE III.

Ethyl Alcohol (14).

t.	$\gamma(M/d)^{2/3}$ R. & S.	$\gamma(M/d)^{2/3}$ calc.
20	331.0	328.7
40	307.3	308.37
60	284.8	286.07
80	261.2	261.87
90	247.9	249.06
100	235.0	235.77
110	221.7	222.01
120	208.0	207.77
130	193.3	193.05
140	178.8	177.86
150	163.0	162.20
160	147.2	146.06
170	130.1	129.44
180	112.6	112.34
190	94.9	94.78
200	75.7	76.74
210	57.1	58.22
220	39.2	39.22
230	19.8	19.76

The agreement here, though indifferent at the lower temperatures, is remarkable at the higher ones, and consequently we could expect an excellent value of the critical temperature by (10), and a poor one by (11). By equation (10) we find

$$t_c = 245.7^\circ,$$

as compared to the experimental value

$$t_c = 243.1^\circ.$$

In order that equation (11) might also be used here, for that is the important one for the calculation of the critical temperature, since in all cases one would simply make observations at the lower temperatures, the relationship between $\gamma(M/d)^{2/3}$ and the lower temperatures was found in the following way: The k values from the results for $\gamma(M/d)^{2/3}$ from 20° to 160°, as calculated by Ramsay,[1] and said by him to represent fairly the experimental results, were plotted against the mean temperatures, and a straight line drawn to slightly favor the lower temperatures. From this plot it was found that $k^\circ = -0.952$, and $\frac{1}{2}dk/dt = -0.002$. These values were then substituted in an equation obtained by adding together the three normal equations found by treating the results for $\gamma(M/d)^{2/3}$, from 20° to 160°, inclusive, and gave $A = \gamma(M/d)_0^{2/3} = 350.2$. In Table IV the results of equations (6) and (8) in the form

$$\gamma(M/d)_t^{2/3} = 350.2 - 0.952t - 0.002t^2, \qquad (15)$$

are compared with those of Ramsay, from which the equation was de-

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[1] *Loc. cit.*

rived, and the experimental values at the same temperatures, of Ramsay and Shields.[1] The agreement, it will be noticed, is excellent.

TABLE IV.

Ethyl Alcohol (15).

t.	$\gamma(M/d)^{2/3}$ R. & S.	$\gamma(M/d)^{2/3}$ R.	$\gamma(M/d)^{2/3}$ calc.
20	331.0	331.0	330.4
40	307.3	309.0	308.9
60	284.8	285.8	285.9
80	261.2	261.1	261.2
100	235.0	235.1	235.0
120	208.0	207.3	207.2
140	178.8	177.8	177.7
160	147.2	146.4	146.7

Using these values in equation (11) we find

$$t_c = 244^\circ,$$

in place of the experimental value, above mentioned,

$$t_c = 243.1^\circ.$$

Acetic Acid.—Equations (6) and (8), when the method of least squares is applied to all the results, as given in Table V, *i. e.*, from 20° to 300°, become

$$\gamma(M/d)_t^{2/3} = 378.04 - 0.6607t - 0.001762t^2. \qquad (16)$$

TABLE V.

Acetic Acid (16).

t.	$\gamma(M/d)^{2/3}$ R. & S.	$\gamma(M/d)^{2/3}$ calc.
20	371.2	364.1
130	261.5	262.4
140	250.2	251.0
150	238.4	239.3
160	226.3	227.2
170	213.9	214.8
180	200.2	202.0
190	187.9	188.9
200	174.9	175.4
210	160.5	161.6
220	146.9	147.5
230	132.1	132.0
240	117.5	118.0
250	101.5	102.7
260	86.0	87.2
270	71.6	71.2
280	54.8	54.9
290	39.9	38.3
300	25.1	21.3

Comparison of the values from this with those by experiment shows that the agreement is very poor at the low temperatures, good for the

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[1] $\gamma(M/d)_t^{2/3}$ becomes zero by (15) at 243.4°.

intermediate ones, and very good for the very high temperatures, although $\gamma(M/d)^{2/3}$, as calculated for the highest temperature, is too small. Naturally, we would expect here, then, that the critical temperature calculated by (10) would be somewhat too small, and that by (11) absurd. Equation (10), in fact, leads to the value

$$t_c = 318.1^\circ,$$

as compared to the experimental value

$$t_c = 321.5^\circ.$$

In order that (11) might be applied to this case, as it was to that of ethyl alcohol, the k values from the results up to 180° by Ramsay, some of which were not found experimentally, but were included to give the relationship at low temperatures (the general agreement when both are given justifying their use), were plotted against the mean temperatures. From this plot, by aid of the sum of the three normal equations, just as with ethyl alcohol, equations (6) and (8) were reduced to the form

$$\gamma(M/d)_t^{2/3} = 387.5 - 0.804t - 0.00128t^2, \qquad (17)$$

the results of which, compared with Ramsay's values, and those found, at the same temperatures, by Ramsay and Shields, are given in Table VI.[1]

TABLE VI.

Acetic Acid (17).

t.	$\gamma\ (M/d)^{2/3}$ R. & S.	$\gamma\ (M/d)^{2/3}$ R.	$\gamma\ (M/d)^{2/3}$ calc.
20	371.2	371.1	370.9
40	.....	353.2	353.3
60	.....	334.4	334.6
80	.....	314.8	315.0
100	.....	294.3	294.3
120	.....	272.7	272.6
140	250.2	250.0	249.8
160	226.3	226.1	226.1
180	200.2	201.2	201.3

These values of k_0 and $\frac{1}{2}dk/dt$ in (11) lead to

$$t_c = 320.1^\circ,$$

the experimental value, as given above, being

$$t_c = 321.5^\circ.$$

Discussion of the Results.

It will be noted from the above that equations (6) and (8), which are simply interpolation formulas, do not hold exactly for very great temperature intervals; *i. e.*, when they give exact agreement at the higher temperatures, they do not do so at the lower ones; and *vice versa*. This at once makes it seem necessary to include in them another term, involving t^3, but since the experimental results at the higher temperatures

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[1] $\gamma(M/d)_t^{2/3}$ according to (17) becomes zero at 319.5°.

must be burdened with a greater error[1] than those at the lower points, so that the same weight cannot be conceded to all the results, a necessity in this form of the method of least squares, it was not thought necessary to undertake this very laborious task just for the purpose of obtaining an equation which might account for this error and hold for a greater range of temperature than those found above.

In case the constants found cause (6) and (8) to express accurately the variation of $\gamma(M/d)^{2/3}$ at very high temperatures, as when results are already at hand, such as those above for the alcohols and acetic acid, the critical temperature is then to be most accurately calculated by (10).

When, on the other hand, the constants found cause the equations to hold accurately for the lower temperatures, and this would be the general case, if measurements were to be made for the purpose, equation (11) would give the better result, and is to be used for the calculation of the critical temperature.

Summary.

In this paper the following points have been brought out:

1. It is possible to express, for a very considerable range of temperature, the experimental results for the molecular surface tension of an associated liquid in the form

$$\gamma(M/d)_t^{2/3} = \gamma(M/d)_0^{2/3} - k_0 t - \tfrac{1}{2} dk/dt\, t^2;$$

where, if the temperature range is too great, one set of coefficients can be found which will give an exceedingly good agreement at the low temperatures, while another set will give an equally good agreement at very high temperatures.

2. In case the above expression gives a close agreement at the very high temperatures, the critical temperature of the liquid can be found by simply setting $\gamma(M/d)^{2/3}$ equal to zero, and solving for the corresponding temperature, which is 6° less than the critical temperature.

3. In case the above expression holds accurately at the low temperatures, and this would generally be the case where measurements were made for the purpose, the critical temperature can be calculated by aid of the first differential coefficient of the equation, *i. e.*,

$$k_t = k_0 + dk/dt\, t,$$

which, solved for the critical temperature, since k equals zero at 6° above the *negative* critical temperature, gives

$$t_c = \frac{k_0}{dk/dt} + 6.$$

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[1] This includes the error in reading the smaller rise in the capillary tube, and those in the determination of the density and the temperature, which are much greater than they are at the lower temperature.

4. While the *k* of Ramsay and Shields is a constant for non-associated liquids, $\gamma(M/d)^{2/3}$ becoming zero at 6° below the critical temperature, *k* for *associated* liquids is found to be a linear function of the temperature, which attains a maximum value at 6° below the critical temperature, and consequently would become zero at 6° above the *negative* critical temperature, if such a point could be attained.

5. A third class of liquids, based upon their *k* values, is formed by acetone and propionic acid, which show a constant, but compared to 2.12, abnormally low value of *k*.

6. The above formulas are applied, for the calculation of critical temperature, with exceedingly good results, to the values of $\gamma(M/d)^{2/3}$ as found by Ramsay and Shields for methyl alcohol, water, ethyl alcohol, and acetic acid.

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THE HYDRATION OF IONS DETERMINED BY TRANSFERENCE EXPERIMENTS IN THE PRESENCE OF A NON-ELECTROLYTE.

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I. Introduction.

Since 1900, evidence has been gradually accumulating which points strongly to the existence of hydrated ions in aqueous solutions of electrolytes. Practically all of this evidence, however, has been of a nature which in law would be classed as "circumstantial." It is probably for this reason that the importance of the part played by "solvation" in the process of electrolytic dissociation is only now beginning to receive general recognition among the advocates of the Ionic Theory. Indeed, with but few exceptions, the standard text-books on physical and electrochemistry, in use to-day, treat the ion simply as an atom or atom group possessing an electric charge and having an independent existence within the solution. If hydration is spoken of at all in this connection, it is usually referred to very briefly as a possible explanation of certain peculiarities in the mobilities of some of the ions.

The present investigation was undertaken for the purpose of studying hydration by a method which would not only yield direct and definite results with respect to the existence of hydrated ions, but which would also yield quantitative data concerning the relative degree of hydration of the different ions. The principle at the basis of the method employed is very simple. It the ions are hydrated, not only the electrolyte but also some of the water should be transferred from one electrode to