D. Sc. 1915

[*From the* PROCEEDINGS OF THE ROYAL SOCIETY, A, VOL. 85, 1911.]

On the Ionic Solubility-product.

BY JAMES KENDALL, M.A., B.SC.

[*Reprinted from the* PROCEEDINGS OF THE ROYAL SOCIETY, A. Vol. 85]

On the Ionic Solubility-product.

By JAMES KENDALL, M.A., B.Sc. (Vans Dunlop Scholar in Chemistry, University of Edinburgh).

(Communicated by Prof. James Walker, F.R.S. Received February 16,—Read March 9, 1911.)

The theory of a constant ionic solubility-product was first advanced by Nernst,* from the analogy of the laws governing dissociation in gases. According to the principle of mass action, if the dissociation pressure of a system in equilibrium be changed by the introduction of an excess of either of the dissociated gases, combination takes place between them until equilibrium is restored. Thus, on the addition of either NH_3 or HCl to a system consisting of ammonium chloride in equilibrium with its dissociation products, ammonium chloride is produced. For each temperature, the product of the pressures of NH_3 and HCl is a constant. Similarly, Nernst found that the solubility of an electrolyte in water was reduced by the addition of any salt containing a common ion. The variations in the solubility of silver acetate (a sparingly soluble salt) in water containing known amounts of silver nitrate or sodium acetate were investigated, and the results obtained confirmed the view that a corresponding equilibrium law was here applicable. If we confine ourselves to substances of the simplest type RX, the law may be stated thus: "At a given temperature the solubility of a sparingly soluble electrolyte is dependent upon a constant, which is proportional to the product of the concentrations of the ions of the electrolyte."

The fundamental assumption made in the application of this law is that in a saturated solution of an electrolyte the undissociated salt in solution plays the part of an intermediary between the ions and the solid, being in equilibrium with the ions on the one hand and with the solid on the other. Consequently, so long as the solvent remains the same, the concentration of the undissociated salt is constant, however much the ionic concentrations may be separately varied by the introduction of other electrolytes; and the product of these ionic concentrations is also a constant.

Expressed algebraically, if s be the concentration of the saturated solution and m the degree of dissociation, m^2s^2 represents the solubility-product, and $(1-m)s$ the "constant undissociated value." These are connected, by the law of mass action, through the equation

$$m^2s^2 = (1-m)s.c,$$

where c is the dissociation constant.

---

* 'Zeits. physikal. Chem.,' 1889, vol. 4, p. 372.

The theoretical solubilities of two substances containing a common ion, in the presence of each other in aqueous solution, may now be established. Let a^2 and b^2 be their solubility-products, x and y their ionic concentrations in simultaneous solution. Then we have

$$x(x+y) = a^2, \quad y(x+y) = b^2,$$

$(x+y)$ being the concentration of the common ion. From this quadratic x and y are at once obtained.

If one of the substances is present not as a solid, but as a solution in water of known concentration s, the equations become

$$x(x+y) = a^2, \quad \frac{y(x+y)}{s-y} = c,$$

where c is the dissociation constant of the substance in solution. From these equations a cubic results, whence x and y are obtainable by trial.

In the above equations Ostwald's dilution law has been assumed, namely, that c is a constant for each particular electrolyte. This is true only in the case of weak acids and bases; for the majority of substances, the strong electrolytes, c is not constant, but increases with increase of concentration. Thus, with increase of concentration, the ratio of the ionised to the total substance dissolved becomes greater than the theoretical. The values of c for such a substance, however, can be determined for each concentration, and the value at saturation used to find the solubility-product. Noyes,* indeed, has used the values thus found not only for solubility determinations such as are indicated above, but also for the reverse problem of determining the degree of dissociation of a second substance by the solubility method.

The above assumption of a constant undissociated value has been attacked both theoretically and experimentally by Arrhenius.† Arrhenius showed that the assumption has no sound theoretical basis, and on determining the solubilities of silver salts of certain organic acids in water and in aqueous solutions containing excess of the corresponding sodium salts, he found that the undissociated value was not constant, but decreased with increase of concentration.

These results of Arrhenius have been investigated by Stieglitz.‡ Stieglitz, comparing this decrease of the undissociated part with the ratio of the ionic to the total strength, which, as mentioned above, increases beyond theoretical with increase of concentration, has formulated the hypothesis that the two

---

* 'Zeits. physikal. Chem.,' 1892, vol. 9, p. 603.

† 'Zeits. physikal. Chem.,' 1899, vol. 31, p. 197.

‡ 'Journ. Amer. Chem. Soc.,' 1908, vol. 30, p. 946.

effects counterbalance each other, and consequently restates the theory of the constant solubility-product in an empirical form. But the results of Arrhenius, as worked out in the above paper, give divergences in the solubility-product of from 5 to 10 per cent., and so long as such divergences exist unexplained, the theory can hardly be regarded as even empirically established; it remains no more than an approximation.

Previous investigations upon the simultaneous solubilities in water of two substances containing a common ion have been confined to those cases in which the substances examined have been of the same type, *i.e.* either both strong or both weak electrolytes. The case of two strong electrolytes has been most frequently examined, the special interest here lying in the question whether the law of mass action is, or is not, applicable. Fewer instances of the simpler case of two weak electrolytes have been investigated, but, in both types, the hypothesis of the constancy of the solubility-product has been considered to give results consistent with those obtained experimentally, although, even in dilute solutions, the agreement is only approximate. For instance, in a solution saturated simultaneously with thallium chloride and thallium bromate, the product of the ionic concentrations of each was found to be increased by about 5 per cent.* The saturated solutions of each of the above salts are (approximately) only one-fortieth normal.

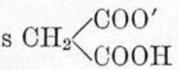
No experiments, however, have been made with two substances of opposite types—one strong and one weak electrolyte—and the primary object of the following research was to supply this deficiency. Here also arises the question of the applicability of the law of mass action. In preliminary experiments divergences from the theoretical result of several per cent. were obtained, similar to that given above. In parallel experiments on the two types already investigated even larger differences were observed, far exceeding the limits of experimental error. Finally a series of experiments on all the possible types of combination of two electrolytes was carried out, first with dilute and afterwards with more concentrated solutions, in order to ascertain the cause of these divergences, and more especially to discover whether they formed an inherent defect in the theory or could be explained away on other grounds.

EXPERIMENTAL.

The substances used were acids of the simple type HX. Weak electrolytes: salicylic acid, $C_6H_4(OH).COOH$; ortho-nitrobenzoic acid, $C_6H_4(NO_2).COOH$; hippuric acid, $NH(CO.C_6H_5).CH_2.COOH$; formic acid,

---

* A. A. Noyes, 'Reports of Congress of Arts and Sciences, St. Louis,' vol. 4, p. 322.

H.COOH; acetic acid, $CH_3.COOH$; and malonic acid, $CH_2(COOH)_2$. (The last named was used only in such concentrations as allowed it to be considered as a monobasic acid, splitting up into the ions  $CH_2\left\langle\begin{array}{l}COO'\\COOH\end{array}\right.$ and H•). Strong electrolytes: hydrochloric acid; picric acid, $C_6H_2(OH)(NO_2)_3$; and trinitrometacresol or methyl picric acid, $1:3:2:4:6\text{-}C_6H(CH_3)(OH)(NO_2)_3$.

The solid acids were purified by recrystallisation from freshly-distilled water; small crystals suitable for the experiments being obtained by rapid cooling from a hot saturated solution. Samples tested gave sharp and distinct melting points. The liquid acids were purified by distilling, and rejecting the first and last portions of the distillate. In all cases solutions were made up with freshly-distilled water, and the glass vessels employed were well steamed out before first using.

The concentrations of the saturated solutions of certain of the above acids at 25° C. were first determined. A few grammes of the acid were placed in a glass-stoppered bottle, half filled with water; over the neck of the bottle a square of rubber sheeting was tied tightly, and the bottle was then clamped in the stirrer of a thermostat and rotated for several days. A measured quantity (25 to 100 c.c., according to the strength of the solution) was then removed by means of a pipette, the body of the bottle remaining in the thermostat. To the end of the pipette was fitted a filter-cover, to prevent the entrance of any crystals, and the pipette itself, when not in use, was kept in a glass tube immersed in the thermostat, so that it was at the same temperature as the solution, and no crystallising occurred inside it. The solution was titrated immediately against baryta, phenolphthalein being used as an indicator. The bottle was again circulated in the bath, and the solution tested every few days until a steady value was reached.

Another method, used for single acids only, was to make a saturated solution above 25° C., add a nucleus of crystals, and rotate in the thermostat as before until a constant titre was obtained. The true concentration of the saturated solution at 25° C. was thus approached from both directions.

Limits of Error.—The above experiments were performed in duplicate; divergences rarely exceeded 0·2 per cent., and were never greater than 0·4 per cent. The two methods also gave results agreeing well within this limit.

The temperature of the thermostat was maintained within 0°·1 C. of 25° C. The thermostat being very large, any change of temperature was correspondingly slow.

The baryta solution used, approximately 1/40 normal, was standardised against each of the acids. The different values obtained varied by less than 0·2 per cent. This, besides testifying to the purity of the acids used, allowed the employment of one mean value, greatly simplifying the calculations in subsequent experiments. With picric and methyl picric acids, the end point was at first difficult to distinguish, owing to the disturbing colour effect, but after some practice the first permanent change of tint could be detected quite accurately by using a comparison solution.

In most cases the saturation point was soon reached; methyl picric acid, however, attained its full value only after two months, picric acid not even then. It was found that the presence of a few drops of ligroin or benzene in the solution shortened the necessary time for methyl picric to a few days, but the end points reached differed from that obtained with pure water. Ligroin, in which the acid is moderately soluble, increased its solubility by 2 per cent.; benzene, in which it is freely soluble, by 6 per cent. A considerable difference was thus caused by the presence of the extremely small amounts of each in solution in the water. This is noteworthy in view of results afterwards obtained.

In Table I below the concentrations of the saturated solutions of the acids are given in normalities; from these, by means of the dissociation constant, the solubility-product and the "constant undissociated value" of each acid are obtained.

Table I.—Solubilities of Single Acids.

Acid.	Solubility.	Solubility product.	"Constant undissociated value."
Salicylic	0·01634 N	0·0000130	0·01273 N
o-nitrobenzoic	0·04360 N	0·0001849	0·03000 N
Methyl picric	0·01000 N	0·0000846	0·00080 N
" (ligroin present)	0·01019 N	—	—
" (benzene present)	0·01059 N	—	—
Hippuric	0·02048 N	0·0000041	0·01846 N

The following dissociation constants* were used above, and in calculating the theoretical results of subsequent experiments:—

Salicylic acid	0·00102	Formic acid	0·000214	Hippuric acid	0·000222
o-Nitrobenzoic acid	0·00616	Malonic acid	0·00158		

It was necessary to determine specially the values given above in the case of methyl picric acid, since the molecular conductivities of the acid and of its sodium salt had not been previously tabulated.

---

* Ostwald, 'Zeits. physikal. Chem.,' 1889, vol. 3, p. 418.

Molecular Conductivity of Methyl Picric Acid.

The sodium salt was first obtained by adding the requisite volume of sodium hydroxide solution (freshly prepared from metallic sodium and standardised by methyl picric acid) to a known weight of methyl picric acid. On evaporating the liquid to small bulk crystals were obtained, which were recrystallised from water and alcohol. Sodium picrate was also prepared by a similar method.

The values for the molecular conductivities obtained from these salts, however, were obviously too low. The salts were finally found to consist of a hydrate, the water from which could not be expelled under 100° C. Owing to their explosive nature it was inadvisable to heat the salts above this temperature.

By neutralisation, as before, and then direct addition of the requisite volume of water to bring the solution to N/32, solutions were obtained giving the following values for the molecular conductivity. Those for sodium picrate, given for comparison, are practically identical with Ostwald's values for that salt.*

v.	Sodium picrate.	Sodium methyl picrate.
32	72·9	71·3
64	76·1	73·4
128	78·1	75·2
256	79·7	76·9
512	81·2	78·6
1024	82·6	80·0
Whence—		
∞	85·7	83·1

The above results are the mean values of two determinations. Taking the values Na = 51·0, H = 349·5 (the mean of the values given by Ostwald and Kohlrausch), we obtain, for the maximum molecular conductivities of the acids, the values 384·2 and 381·6 respectively.

The molecular conductivities of the acids themselves were then determined, and are given below, together with the values of the degree of dissociation (*m*) obtained therefrom :—

v.	Picric acid.	*m*.	Methyl picric acid.	*m*.
32	343·4	0·894	—	—
64	354·9	0·924	—	—
128	360·7	0·939	352·9	0·925
∞	384·2	1·0	381·6	1·0

---

* 'Allg. Chemie,' 1893, vol. 2, p. 751.

By drawing the curves of the values of m given above we obtain, by extrapolation, for N/100 methyl picric acid (the saturated strength at 25° C.) the value $m = 0{\cdot}92$. From this the solubility product and the "constant undissociated value" are obtained.

The above values for the molecular conductivities of the acids are in general agreement with those given for picric acid by Ostwald* and Rothmund;† but the degree of error may be fully 1 per cent. This would affect the degree of dissociation to the same extent; but, by trial from the equations, it was found that an error of 5 per cent. was required to affect the solubility determinations, afterwards made with the acids, beyond the limits of experimental error.

The conductivities were determined with a rotating commutator and galvanometer, more satisfactory results being obtained with this apparatus than with the usual induction coil and telephone, especially for the more dilute solutions.

In the determination of the solubility of one acid in the presence of another, the method of procedure was exactly similar to that already described for single acids. The experiments were of two classes: in the first, two solid acids were taken with water; in the second, one acid was present as a solid, the other as a solution in water of known strength. In all cases the end point was quickly reached, even methyl picric, in the presence of another acid, attaining the steady state in a few days.

The first investigations were of the simplest type, the two acids obeying Ostwald's dilution law. Of these, salicylic and *o*-nitrobenzoic acids are good examples, and a full series of experiments with these two acids was carried out, the results of which are shown in Table II (p. 207). Since they serve to illustrate the other cases, they are commented upon in detail.

It will be seen that the amount of acid in solution is in every case in excess of the theoretical. The divergences in Sections B and C increase with the strength of the original solution taken, and the greatest divergence is obtained in Section A, where both acids are present in the solid form. All the differences are far beyond the limits of experimental error.

There are, however, some small corrections to be made in the above figures. The results are given in normalities, whereas to be strictly comparable they should be expressed in gramme-molecules in 100 grm. of water. But this correction, instead of explaining the divergences, only increases them, for, as the solutions become more concentrated, the ratio of the weight of water present to the total weight becomes less, and the correction is thus a positive

---

* 'Zeits. physikal. Chem.,' 1887, vol. 1, p. 77.

† *Ibid.*, 1903, vol. 46, p. 845.

Table II.—Salicylic and *o*-Nitrobenzoic Acids.

Initial state.	Acid dissolved (theory).		Acid dissolved (expt.).	Divergences.
A. Solid salicylic	Salicylic =	0·01365 N		
Solid *o*-nitrobenzoic	*o*-Nitrobenzoic =	0·04314 N		
		0·05679 N	0·05843 N	+0·00164 N
B. Known solution salicylic, Solid *o*-nitrobenzoic—				
(*a*) Salicylic = 0·00937 N	*o*-Nitrobenzoic	0·04328 N	0·04357 N	+0·00029 N
(*b*) " = 0·01356 N		0·04316 N	0·04402 N	+0·00086 N
(*c*) " = 0·01624 N		0·04301 N	0·04413 N	+0·00112 N
C. Known solution *o*-nitrobenzoic, Solid salicylic—				
(*a*) *o*-Nitrobenzoic = 0·01565 N	Salicylic	0·01430 N	0·01447 N	+0·00017 N
(*b*) " = 0·04310 N		0·01366 N	0·01445 N	+0·00079 N
(*c*) " = 0·04358 N		0·01365 N	0·01439 N	+0·00074 N

one, and also increases with concentration. There must also be taken into account the increase of the density of the solution with concentration; this entails a smaller negative correction. The final correction is, therefore, small and positive, in most cases well within the limits of experimental error, and so does not materially affect the results. Density determinations, however, were always made, and in the table below a typical example of the correction is given. Another case is shown after Table III; all other tables give results in normalities only.

Corrections for Density, etc.

The corrections for Section B of Table II are here given. Densities were obtained by means of a 25 c.c. pipette and a weighing bottle, and are liable to an error of 0·0002.

Strength of salicylic acid solution taken.	Density.	Final strength (salicylic and *o*-nitrobenzoic acids).	Density.
—	0·9963	0·04360 N	0·9998
0·00937 N	0·9968	0·05294 N	1·0001
0·01356 N	0·9970	0·05758 N	1·0009
0·01624 N	0·9973	0·06037 N	1·0012

When we express these strengths in gramme-molecules per 100 grm. of water, we obtain the following values. The last column shows the correction necessary to transfer results in normalities to correct results. (For obtaining, however, the "effective" part of this correction, it is necessary to subtract the initial value of it from its value at the given concentration. An example is given below.)

Strength of salicylic solution.	Total titre.	*o*-Nitrobenzoic dissolved.	Correction.
—	0·04392	0·04392	+0·00032
0·00941	0·05340	0·04399	+0·00042
0·01362	0·05810	0·04448	+0·00046
0·01632	0·06093	0·04461	+0·00048

The "effective" correction is thus, even in the last case, only (0·00048 − 0·00032) = 0·00016. This is less than 0·3 per cent. of the whole titre.

In Sections B and C of Table II it will be seen that not only does the divergence from theory increase with increase of concentration, but that the actual amount of acid dissolved, instead of decreasing, at first rapidly and then more slowly, as demanded by the theory, either shows an increase or becomes practically constant. The divergences from theory are therefore fundamental. The result of another experiment will show this more clearly. A saturated solution of *o*-nitrobenzoic acid, of strength 0·04358 N, free from solid, was added to solid salicylic acid and shaken in the thermostat until constant. The strength was now 0·05797 N. Since the concentration of the hydrogen ion had been increased, the solution should be supersaturated with respect to *o*-nitrobenzoic acid. But on adding solid *o*-nitrobenzoic acid to the solution, and shaking again until the titre was constant, the concentration rose to 0·05845 N, *i.e.* the solution was not supersaturated, but unsaturated.

A comparison of the three results of Sections A, B (*b*), and C (*b*) is interesting. The concentrations of the solutions originally taken in B (*b*) and C (*b*) are, as nearly as possible, those shown by A to be theoretically saturated in presence of the other acid. The final titre should therefore be the same in all three cases. Instead of the theoretical value of 0·05679 N, however, the three values obtained are 0·05843 N, 0·05758 N, and 0·05755 N respectively, which differ widely not only from the theoretical value but also from each other. The presence of solid acid allows an excess beyond theory to be dissolved; this is allowed in the case of both acids in A, in the case of *o*-nitrobenzoic only in B (*b*), and in the case of salicylic only in C (*b*). Hence we may expect the divergence in A to be equal, as a first approximation, to the sum of the divergences in B (*b*) and C (*b*). The experimental results are 0·00164 N and (0·00086 N + 0·00079 N) = 0·00165 N. (See Table II.)

In Sections B (*c*) and C (*c*) saturated solutions (free from solid) of the one acid were taken, and treated with the other solid. Further consideration of the results is left over until the remaining experiments on this and other types are given.

The results of other experiments with two weak acids are given in Table III, which shows the solubilities of salicylic and *o*-nitrobenzoic acids in known solutions of formic and malonic acids. In all cases the differences from theory are small and negative, but by making the corrections for density, etc., such differences are either destroyed or converted into small positive divergences, in all cases within error limits of the theoretical result. A typical series of corrections is given in Table IIIA.

Table III.—Remaining Experiments with Two Weak Acids.

Initial state.	Acid dissolved (theory).	Acid dissolved (expt.).	Divergences.
A. Known solutions formic,			
Solid salicylic—	Salicylic		
(*a*) Formic = 0·05168 N	0·01539 N	0·01531 N	−0·00008 N
(*b*) „ = 0·09977 N	0·01496 N	0·01474 N	−0·00022 N
B. Known solutions formic,			
Solid *o*-nitrobenzoic—	*o*-Nitrobenzoic		
(*a*) Formic = 0·05168 N	0·04320 N	0·04304 N	−0·00016 N
(*b*) „ = 0·09977 N	0·04289 N	0·04266 N	−0·00023 N
C. Known solutions malonic,			
Solid salicylic—	Salicylic		
(*a*) Malonic = 0·03126 N	0·01502 N	0·01485 N	−0·00017 N
(*b*) „ = 0·10088 N	0·01417 N	0·01408 N	−0·00009 N
(*c*) „ = 0·20036 N	0·01378 N	0·01362 N	−0·00016 N
D. Known solutions malonic,			
Solid *o*-nitrobenzoic—	*o*-Nitrobenzoic		
(*a*) Malonic = 0·03126 N	0·04285 N	0·04279 N	−0·00006 N
(*b*) „ = 0·10088 N	0·04159 N	0·04153 N	−0·00006 N
(*c*) „ = 0·20036 N	0·03992 N	0·03967 N	−0·00025 N

Table IIIA.—Corrections for Density, etc.

Known solutions formic acid } (see Table III, Section A).
Solid salicylic acid }

Strength of formic acid solution taken.	Density.	Final strength (formic and salicylic acids).	Density.
—	0·9963	0·01634 N	0·9973
0·05168 N	0·9966	0·06699 N	0·9976
0·09977 N	0·9969	0·11451 N	0·9978

Expressing these strengths in gramme-molecules per 100 grm. water, we have :—

Strength of formic solution.	Total titre.	Salicylic dissolved.	Correction.
—	0·01642	0·01642	+0·00008
0·05198	0·06745	0·01547	+0·00016
0·10054	0·11553	0·01499	+0·00025

The "effective" correction is only $(0{\cdot}00025 - 0{\cdot}00008) = 0{\cdot}00017$ at the greatest concentration. This is less than 0·2 per cent. of the whole titre.

In the next table there are given the results of experiments with two strong acids. For the calculation of the theoretical results the following table of dissociation values for hydrochloric acid was used:—

$$\begin{array}{lllll} v = & 16 & 32 & 64 & 128, \\ m = & 0{\cdot}935 & 0{\cdot}953 & 0{\cdot}966 & 0{\cdot}972. \end{array}$$

The dissociation values of picric and methyl picric acids at various dilutions have already been given.

Table IV.—Experiments with Two Strong Acids.

Initial state.	Acid dissolved (theory).	Acid dissolved (expt.).	Divergences.
A. Known solutions hydrochloric,			
Solid methyl picric—	Methyl picric		
(*a*) Hydrochloric = 0·00895 N	0·00669 N	0·00641 N	−0·00028 N
(*b*) ,, = 0·01593 N	0·00510 N	0·00487 N	−0·00023 N
B. Known solution picric acid,			
Solid methyl picric—	Methyl picric		
(*a*) Picric acid = 0·01013 N	0·00651 N	0·00702 N	+0·00051 N

Here also divergences from theoretical results are obtained; negative in the case of methyl picric and hydrochloric, positive in the case of methyl picric and picric acids.

Table V gives examples of weak acids (salicylic and *o*-nitrobenzoic) dissolved in known solutions of a strong acid (hydrochloric). The divergences are pronounced, and in the negative direction. In the example A (*b*) it will be seen that the decrease is large enough, although the hydrochloric acid solution is only one-thirtieth normal (rather more than a gramme per litre), to bring the total amount of salicylic acid dissolved below its "constant undissociated value." A corresponding result was obtained by Arrhenius (*loc. cit.*) only with more concentrated solutions of two strong electrolytes.

Table V.—Weak Acids in Hydrochloric Acid Solutions.

Initial state.	Acid dissolved (theory).	Acid dissolved (expt.).	Divergences.
A. Known solutions hydrochloric, Solid salicylic acid—	Salicylic		
(*a*) Hydrochloric = 0·01786 N	0·01345 N	0·01290 N	−0·00055 N
(*b*) ,, = 0·03573 N	0·01310 N	0·01238 N	−0·00072 N
B. Known solutions hydrochloric, Solid *o*-nitrobenzoic acid—	*o*-Nitrobenzoic		
(*a*) Hydrochloric = 0·01786 N	0·03753 N	0·03681 N	−0·00072 N
(*b*) ,, = 0·03573 N	0·03478 N	0·03390 N	−0·00088 N

Table VI below completes the series by giving those cases in which a strong acid (methyl picric) was dissolved in known solutions of weak acids (salicylic and *o*-nitrobenzoic). In the case of methyl picric and salicylic acids a full investigation was made, similar to that carried out with salicylic and *o*-nitrobenzoic acids.

Table VI.—Methyl Picric Acid and Weak Acids.

Initial state.	Acid dissolved (theory).		Acid dissolved (expt.).	Divergences.
A. Known solution *o*-nitrobenzoic, Solid methyl picric acid—				
(*a*) *o*-nitrobenzoic = 0·01975 N	Methyl picric	0·00736 N	0·00800 N	+0·00066 N
B. Solid salicylic acid .... Solid methyl picric acid	Salicylic = Methyl picric =	0·01404 N 0·00935 N		
		0·02339 N	0·02613 N	+0·00274 N
C. Known solutions salicylic acid, Solid methyl picric acid—				
(*a*) Salicylic = 0·00981 N	Methyl picric	0·00955 N	0·01063 N	+0·00108 N
(*b*) ,, = 0·01393 N		0·00935 N	0·01072 N	+0·00137 N
D. Known solution methyl picric, Solid salicylic acid—				
(*a*) Methyl picric = 0·00938 N	Salicylic	0·01404 N	0·01532 N	+0·00128 N

The results of sections B, C (*b*), and D may be compared. In the two latter the strengths of the original solutions are those shown by B to be theoretically saturated in presence of the other acid. (Compare Table II.) The divergence in B may be expected to be equal to the sum of the other two divergences, to a first approximation. The experimental results are 0·00274 N and (0·00137 N + 0·00128 N) = 0·00265 N.

The differences in Table VI are all large and positive. It will be seen that methyl picric acid is more soluble in salicylic acid solutions than in pure water.

In none of the above tables is the theory exactly followed, and a further experiment was performed, to ascertain whether the divergences obtained were superposable. A known solution of hydrochloric acid was taken, and two weak acids (salicylic and *o*-nitrobenzoic acids) added. The differences to be expected from theory were estimated by interpolation from the results of the preceding tables, and compared with the difference experimentally obtained.

Table VII.—Two Weak Acids in Hydrochloric Acid Solution.

Initial state.	Acid dissolved (theory).	Acid dissolved (expt.).	Divergence.
Known hydrochloric acid solution, Solid salicylic acid, „ *o*-nitrobenzoic acid—	Salicylic = 0·01316 N *o*-Nitrobenzoic = 0·03608 N		
(*a*) Hydrochloric = 0·02957 N...	0·04924 N	0·04935 N	+0·00011 N

The following divergences were to be expected (see Tables II and V):—

(*a*) Due to solid salicylic and solution of *o*-nitrobenzoic	+0·0006 N.
(*b*) Due to solid *o*-nitrobenzoic and solution of salicylic	+0·0008 N.
(*c*) Due to solid salicylic and solution of hydrochloric	−0·0006 N.
(*d*) Due to solid *o*-nitrobenzoic and solution of hydrochloric	−0·0008 N.

The solution should therefore be approximately of theoretical strength if the various differences are superposable. Seeing that the accuracy of a large number of experiments is involved in the values of the expected divergences given above, the experimental result agrees with this supposition well within the limits of error.

A general consideration of the results in Tables II to VII shows that the theory holds strictly in none of the possible combinations of acids. It makes no difference whether they are both weak, both strong, or one of each type; similar divergences of several per cent. are obtained in every case. And these divergences, though usually numerically small, are fundamental in each direction; the upper limit consistent with the theory—the total solubility in pure water—and the lower limit—the "constant undissociated value"—are both passed in very dilute solutions.

Now, on an examination of the tables, the following rule appears to hold:

that an increase beyond theoretical is obtained when two acids chemically similar (*i.e.*, salicylic and *o*-nitrobenzoic) are present in solution, and a decrease when two acids chemically dissimilar (*i.e.*, salicylic and hydrochloric) are present. This rule seems to be quite general, and not dependent at all upon the types of the two acids. In Table III the two acids are of neither very similar nor very dissimilar character, and the divergences obtained are but slight, and within error limits of the theoretical. There may be an increase or a decrease, but, at the concentrations tested, it is too small a percentage of the total titre to be perceived.

The fact that a solution of one acid can dissolve more of a chemically similar acid than theory demands, leads to the inquiry whether the ionic effect of the acids upon each other is not also accompanied by a solvent effect. The small quantity of the first acid in solution might, by its solvent action upon the second acid, cause an appreciable increase in the result. That the cause is quite adequate may be seen from the relatively large increase in the solubility of methyl picric acid in water in the presence of small quantities of ligroin or benzene dissolved in the water, as before described. A decrease below the theoretical result would be accounted for, under this view, by the comparative insolubility of the two acids in each other.

The divergence from theory would thus steadily increase with increase of concentration, and this is actually the case. Stronger confirmation, however, is given to the hypothesis by the results of the two series of experiments carried out with salicylic and *o*-nitrobenzoic acids, and with salicylic and methyl picric acids, respectively. When both acids are present in the solid form, both exert a solvent effect, and this is, to a first approximation, found to be the sum of their two separate solvent effects, determined by suppressing the solid form of one acid, and having it present instead as a solution, theoretically saturated in the presence of the other acid.

To test the above view further it is necessary to perform a series of experiments with one solid and one liquid acid, the solubility of the solid acid in the liquid one being either much greater or much less than its solubility in pure water. From the solubility results obtained by treating the solid acid with known solutions of the liquid acid in water it can then be seen whether the increase or decrease from theory is capable of being accounted for in this way.

The case of salicylic or *o*-nitrobenzoic with formic acid is a good example, both solids being much more soluble in formic acid than in water. The above, however, were the only cases in which no definite increase or decrease from theoretical was observed, the error limit obscuring the result at the concentrations tested.

Another series of experiments was therefore carried out with more concentrated solutions, both in the above and in other cases. The method of estimating volumetrically with baryta here became impracticable, owing to the overwhelming concentration of the solvent acid compared with that of the acid dissolved, in which latter small variations were consequently impossible to measure.

The method employed was that of evaporation. The solutions were prepared in the same manner as already described, 25 c.c. of the liquid were pipetted out into a weighed evaporating dish, and evaporated down to dryness. The amount of the dissolved solid was then found by weighing, and its titre in the solution directly calculated. The cases investigated were :—

(*a*) In solutions of formic acid : Salicylic acid, hippuric acid.
(*b*) In solutions of acetic acid : Salicylic acid.
(*c*) In solutions of hydrochloric : Salicylic acid, *o*-nitrobenzoic acid.

Solutions containing hippuric acid could be evaporated down on the steam-bath without loss of solid by volatilisation; those containing salicylic and *o*-nitrobenzoic acids, since these proved to be more or less volatile with steam, were allowed to evaporate slowly at the ordinary temperature.

The residues obtained weighed from 0·1 to 0·04 of a gramme; the error limit in the latter case is about 1 per cent. Experiments performed in duplicate gave results agreeing together within this limit, and the results of this method, as tested with some of the more dilute solutions, were closely concordant with those obtained volumetrically.

The results obtained are shown in both tabular and graphic form. Some volumetric determinations are also given in the tables, both for the purpose of comparison with the gravimetric results and for use in the accompanying curves.

Results are expressed, as before, in normalities. The corrections described in the volumetric determinations, although much larger here owing to the greater concentrations of the solutions used, are not applied. That due to density change is never so much as 1 per cent. of the total, and is therefore still within the limits of experimental error. That due to replacement of water by acid is as much as 10 per cent. of the total in the most concentrated solutions, but since we are here considering the solvent actions of both water and acid, it is preferable to compare solutions containing equal weights of total solvent than those containing equal weights of water, and such solutions are represented, within error limits, in the uncorrected figures below.

Table VIII.—Gravimetric Determinations.

A. Salicylic Acid in Solutions of Formic Acid. (See fig., p. 216.)

Strength of formic acid solution (per cent.).	Weight of residue from 25 c.c. (in grms.).	Strength of dissolved acid (gravimetrically).	Strength of dissolved acid (volumetrically).
0	0·0563	0·01631 N	0·01634 N
0·24	—	—	0·01531 N
0·46	—	—	0·01474 N
0·625	0·0512	0·01484 N	—
1·25	0·0516	0·01496 N	—
2·5	0·0530	0·01536 N	—
5	0·0592	0·01716 N	—
10	0·0725	0·02101 N	—

B. Hippuric Acid in Solutions of Formic Acid. (See fig.)

Strength of formic acid solution (per cent.).	Weight of residue from 25 c.c. (in grms.).	Strength of dissolved acid (gravimetrically).	Strength of dissolved acid (volumetrically).
0	0·0915	0·02045 N	0·02048 N
1·25	0·0901	0·02014 N	—
2·5	0·0930	0·02078 N	—
5	0·1018	0·02275 N	—
10	0·1191	0·02661 N	—

C. Salicylic Acid in Solutions of Acetic Acid. (See fig.)

Strength of acetic acid solution (per cent.).	Weight of residue from 25 c.c. (in grms.).	Strength of acid dissolved (gravimetrically).
0	0·0563	0·01631 N
0·625	0·0584	0·01691 N
1·25	0·0602	0·01745 N
2·5	0·0636	0·01846 N
5	0·0710	0·02059 N

D. Salicylic Acid in Solutions of Hydrochloric Acid. (See fig.)

Strength of hydrochloric acid solution.	Weight of residue from 25 c.c. (in grms.).	Strength of dissolved acid (gravimetrically).	Strength of dissolved acid (volumetrically).
—	0·0563	0·01631 N	0·01634 N
0·0179 N	—	—	0·01290 N
0·0357 N	—	—	0·01238 N
0·125 N	0·0419	0·01214 N	—
0·25 N	0·0412	0·01194 N	—
0·5 N	0·0387	0·01123 N	—

E. *o*-Nitrobenzoic Acid in Solutions of Hydrochloric Acid. (See fig.)

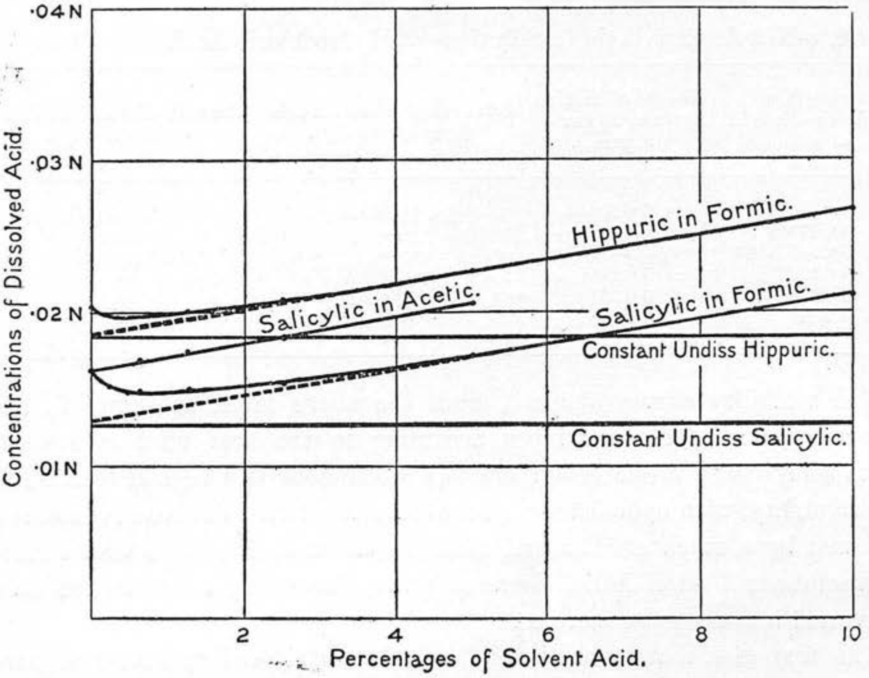
Strength of hydrochloric acid solution.	Weight of residue from 25 c.c. (in grms.).	Strength of dissolved acid (gravimetrically).	Strength of dissolved acid (volumetrically).
—	0·1804	0·04320 N	0·04360 N
0·0179 N	—	—	0·03681 N
0·0357 N	—	—	0·03390 N
0·125 N	0·1245	0·02980 N	—
0·25 N	0·1221	0·02922 N	—
0·5 N	0·1188	0·02846 N	—

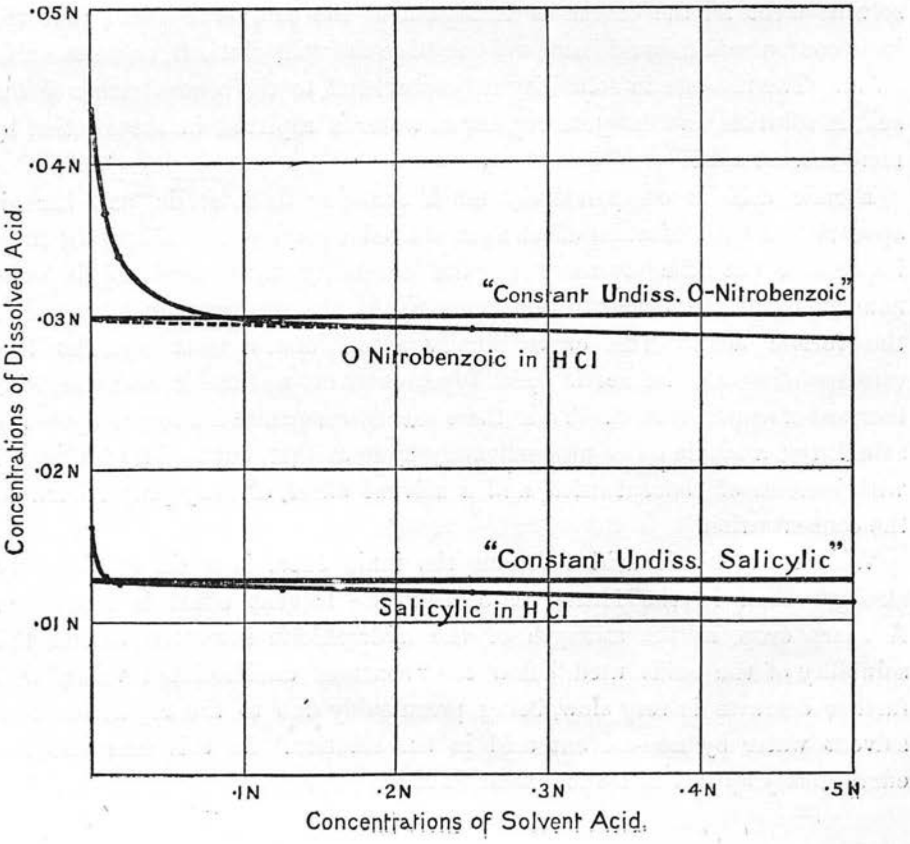
The solubility curves obtained from the above table, as shown in the diagrams, consist of three types, according to the acid used as solvent. With solutions of acetic acid there is a continuous and regular increase in the solubility, with hydrochloric solutions a sharp initial decrease is obtained, followed by a much smaller and more regular decrease, while with formic acid solutions a small initial decrease is with increasing concentration soon converted into a regular increase.

The first case, that of acetic acid, may be considered as a case of pure solvent effect, for the degree of ionisation of the acid is so small that the ionic concentration could have, even in concentrated solutions, no measurable effect. The increase in solubility is proportional to the concentration of the acid in solution, and is quite regular as water is replaced in the solution by more solvent acid.

Formic acid is comparatively much stronger than acetic, and here it appears that the ionisation effect upon the acids employed is at first the more important, but the decrease in the solubility thus produced is soon neutralised, as the concentration increases, by the greater solvent power of the formic acid. The curve finally approximates to a straight line corresponding to the acetic acid type, showing a regular increase with increase of concentration. Thus there are two separate influences upon the solubility; an ionic effect proportionally large at first, but rapidly falling off with increase of concentration, and a solvent effect, directly proportional to the concentration.

With hydrochloric acid solutions the ionic effect is again considerably stronger than in the former case, and the solvent effect is negligible. A sharp drop, as the strength of the hydrochloric increases, carries the solubility of the acids used below the "constant undissociated value," and further decrease is very slow, being presumably due to the replacement of solvent water by non-solvent acid in the solution. In this case also the curve finally approximates to a straight line.


·04 N
·03 N
·02 N
·01 N
Concentrations of Dissolved Acid.
Hippuric in Formic.
Salicylic in Acetic.
Salicylic in Formic.
Constant Undiss Hippuric.
Constant Undiss Salicylic.
2
4
6
8
10
Percentages of Solvent Acid.


·05 N
·04 N
·03 N
·02 N
·01 N
Concentrations of Dissolved Acid.
"Constant Undiss. O-Nitrobenzoic"
O Nitrobenzoic in HCl
"Constant Undiss. Salicylic"
Salicylic in HCl
·1 N
·2 N
·3 N
·4 N
·5 N
Concentrations of Solvent Acid.

If these straight lines are produced backwards to meet the axis, it will be seen that they do so at or near the point of the so-called "constant undissociated value." (The only exception is in the case of salicylic in acetic acid, but this is practically a case of pure solubility.) Thus, if we consider these lines as dividing lines, we may regard the solubility of one acid in aqueous solutions of another as consisting of two portions:—

(*a*) An undissociated portion (below the line), increasing or decreasing regularly, according as the acid is more or less soluble in the solvent acid than in water.

(*b*) A dissociated portion (above the line), decreasing more or less rapidly according to the ionic strength of the solvent acid. This decrease is not regular, but is proportionally greater the less concentrated the solution is, falling off as the dissociated portion is suppressed by increase of concentration.

The solvent effect, acting directly upon the undissociated portion, will also indirectly affect the dissociated part of the substance in solution, since this must remain in equilibrium with the undissociated part. In the curves given, the acids exist in solution mainly in the undissociated state, hence this indirect effect is but small, and soon becomes negligible with increase of concentration, owing to the almost total suppression of the ionised part. In solutions of strong electrolytes, however, the indirect may be greater than the direct effect; hence the solubility curves in such cases will not finally approximate to straight lines which cut the axis, when produced backwards, at or very near to the "constant undissociated value." The case of salicylic acid in solutions of acetic acid is another example of the inapplicability of the rule in the event of the ionised portion persisting in appreciable quantity at all concentrations of the solvent acid.

The experimental divergences obtained from the values indicated by the theory of the constant solubility-product can thus be accounted for in all cases by this solvent effect. The divergences, positive or negative, are caused by the solvent influence of the two substances upon each other, and this, as shown in the above tables, is positive when the substances are chemically similar in character, negative when they are dissimilar. The amount of the divergence due to each acid can also, as in the case of salicylic and *o*-nitrobenzoic acids, be obtained to a first approximation.

The existence of this solvent effect renders it evident that the reverse problem, attempted by Noyes, of calculating the degree of dissociation of one substance by determining its solubilities in water and in a known solution of another substance containing a common ion, may sometimes lead to very erroneous results. In any case the results of such a determination must be uncertain, since a wide variation in the assumed degree of dissociation corresponds in most instances to a very small change in the solubility, any decrease in undissociated substance dissolved being almost entirely balanced by an increase in dissociated, and *vice versâ.* This fact explains also why, although the degrees of dissociation of the strong acids used in the above research are not yet accurately determined, being liable to an uncertainty of several per cent. in dilute solutions, the solubility results of other acids with them, as calculated from these values, are subject to a much smaller degree of error.

In conclusion, I have much pleasure in expressing my thanks to Prof. Walker, at whose suggestion and under whose direction the above research was carried out, for his advice and assistance during the whole period of its execution.

HARRISON AND SONS, Printers in Ordinary to His Majesty, St. Martin's Lane.

THE VELOCITY OF THE HYDROGEN ION, AND A GENERAL DISSOCIATION FORMULA FOR ACIDS.

BY

JAMES KENDALL, M.A., B.Sc.
(Vans Dunlop Scholar in Chemistry, University of Edinburgh).

From the Transactions of the Chemical Society, 1912 Vol. 101

CXXXVIII.—*The Velocity of the Hydrogen Ion, and a General Dissociation Formula for Acids.*

By James Kendall, M.A., B.Sc. (Vans Dunlop Scholar in Chemistry, University of Edinburgh).

Whilst the mobilities of most of the common ions have been definitely determined to an accuracy of one-tenth of a unit, the value for the velocity of the hydrogen ion, which is the most important from theoretical considerations, is not known more exactly than within several units. The experimental difficulties in the two methods available for the determination of ionic velocities are here much greater than is the case with other ions. In conductivity measurements the impurities contained in the water used have prevented the accurate determination of the equivalent conductivities of acids at very high dilutions, and no trustworthy correction for the influence of these impurities has yet been applied, as has been done for salts. The values obtained from the measurement of migration ratios are also less accurate, since the preponderating mobility of the hydrogen ion causes a small error in the ratio obtained to exert a comparatively large influence on the ionic velocity deduced from it. The results from both methods have proved very conflicting, as the following figures, which are the results of the chief researches on the mobility of the hydrogen ion, will serve to show. All values are expressed in terms of the reciprocal ohm.

Ostwald, from conductivity measurements with hydrochloric acid, obtained the value 342 at 25° (*Zeitsch. physikal. Chem.*, 1888, **2**, 842), and employed this figure in the calculation of the dissociation constants of all the weak acids subsequently examined (*Zeitsch. physikal. Chem.*, 1889, **3**, 172). The value was afterwards raised to 347 ("Lehrbuch der Allgemeinen Chemie," 1893, **2**, 675).

Kohlrausch ("Leitvermögen der Electrolyte," 1898, pp. 107–10, 200) deduced, by the application of an empirical formula to the results of conductivity measurements with dilute solutions of hydrochloric and nitric acids, the provisional value of 318 at 18°, or 352 at 25°. Until recently the above values of Ostwald and Kohlrausch have been adopted for the calculation of dissociation ratios.

The measurement of migration ratios was not of sufficient accuracy to be used for the purpose of determining the velocity of the hydrogen ion until an improved apparatus was devised by Noyes (*Zeitsch. physikal. Chem.*, 1901, **36**, 69). With this, a determination of the mobility by the method of migration ratios was attempted by Noyes and Sammet (*Zeitsch. physikal. Chem.*, 1903, **43**, 49), hydrochloric acid being used as the electrolyte. The unexpectedly high value of 365 was obtained.

It has been shown by Rothmund and Drucker (*Zeitsch. physikal. Chem.*, 1903, **46**, 827), in the course of an investigation on the dissociation of picric acid, that lower values for the velocity of the hydrogen ion give results for the degree of dissociation which are more satisfactory than those obtained with the use of Kohlrausch's figure, 352. A value as low as 338 is suggested, and tested with several strong acids. The subject is further developed by Drucker in a later paper (*Zeitsch. physikal. Chem.*, 1904, **49**, 563), where it is demonstrated that $H^{\cdot} = 312$ at 18° (that is, 345 at 25°) gives more satisfactory values for the dissociation constants of weak acids than does the higher figure of Kohlrausch.

The results of the investigations of several observers, both on conductivities and on migration ratios, are collected and compared by Drucker in a third paper (*Zeitsch. Elektrochem.*, 1907, **13**, 81). The measurements of the equivalent conductivities of dilute solutions of hydrochloric and nitric acids by Goodwin and Haskell (*Proc. Amer. Acad.*, 1904, **40**, 399), and of sulphuric acid by Whetham (*Zeitsch. physikal. Chem.*, 1906, **55**, 200), are combined with the migration ratios obtained with the same acids by Jahn and his pupils (*Zeitsch. physikal. Chem.*, 1901, **37**, 707) and Tower (*J. Amer. Chem. Soc.*, 1904, **26**, 1039) respectively. The mean value deduced for the velocity of the hydrogen ion is 313 at 18°, or 346 at 25°. From the results obtained it is inferred that the figure given by Kohlrausch is certainly too high.

Kohlrausch (*Zeitsch. Elektrochem.*, 1907, **13**, 333), whilst admitting that his former value was claimed to be merely an approximation, takes also into account further migration ratios recently determined by Jahn and his pupils (*Zeitsch. physikal. Chem.*, 1907, **58**, 641), and puts forward as the most probable value for the velocity of the hydrogen ion the figure 315 at 18°, or 348 at 25°.

Gorke (*Zeitsch. physikal. Chem.*, 1908, **61**, 495) obtained, by the measurement of the equivalent conductivities of dilute solutions of picric acid, the value 353 at 25°.

Noyes and Kato (*Zeitsch. physikal. Chem.*, 1908, **62**, 420), from the migration ratios obtained with dilute solutions of nitric and hydrochloric acids, were led to the conclusion that the velocity of the hydrogen ion varies considerably with the concentration. For solutions under one-thousandth normal its value may be taken as 315 at 18° (that is, 348 at 25°); for more concentrated solutions it is several per cent. higher. This theory of a change of mobility with the concentration had been previously advanced by Jahn (*Zeitsch. physikal. Chem.*, 1900, **33**, 545; **35**, 8) as applying to the ions of all strong electrolytes, and affording an explanation of the breakdown of the dilution law of Ostwald. The assumption of a varying mobility in dilute solution has, however, been vigorously criticised on many sides, and may be regarded as not yet confirmed (Wegscheider, *Zeitsch. physikal. Chem.*, 1909, **69**, 503).

From migration ratios obtained with dilute solutions of hydrochloric acid, Drucker and Krsnjavi (*Zeitsch. physikal. Chem.*, 1908, **62**, 731) have concluded that 313 at 18° (that is, 346 at 25°) is the maximum possible value for the velocity of the hydrogen ion.

In the above summary of investigations it will be seen that the values obtained range from a minimum of 338 to a maximum of 365; the general results of the more recent experiments are, however, within the much narrower limits of 345 to 348. The value must be determined more definitely than this before the problem regarding the dissociation of strong acids can be solved by the substantiation of any formula from the figures of experiment.

The failure to obtain satisfactory conductivity measurements with very dilute solutions of strong acids has been attributed to the influence of the impurities in the water used, namely, carbonic acid and ammonia from the atmosphere, and alkali from the glass vessels employed. No satisfactory correction can be applied, since the mutual influence of the substances in solution on their dissociation is quite uncertain (Kohlrausch, "Leitvermögen der Electrolyte," 1898, p. 92). The figures are, in general, given without any correction, and the degree of error is unknown. Any deductions from the results cannot, therefore, unless supported by other evidence, be regarded as conclusive; thus Kohlrausch (*Zeitsch. Elektrochem.*, 1907, **13**, 646) states, after a criticism of conclusions drawn by Bogdan from experiments with dilute solutions of hydrochloric and nitric acids (*Zeitsch. Elektrochem.*, 1907, **13**, 596): "The last word upon the subject of dilute acids and bases will certainly not be spoken until we have succeeded in investigating the solutions in pure water."

The water used in the following conductivity experiments was obtained by distillation, in the open air, from water to which a little Nessler's solution has been added. Jena-glass flasks and a bent tube of pure tin, fitted with a condenser, were used, and spirting-over was prevented by a series of constrictions in the upright portion of the tube. The first distillation gave water with a specific conductivity of $1{\cdot}20 \times 10^{-6}$ at 25°; by a second distillation this was reduced to $0{\cdot}90 \times 10^{-6}$. This value did not increase appreciably on exposure to outside air. Water of specific conductivity $0{\cdot}70 \times 10^{-6}$ was obtained by distillation in silica vessels, but on transference to a glass cell the value quickly rose to $0{\cdot}90 \times 10^{-6}$ at 25°.

With the water available for use in conductivity measurements possessing a specific conductivity of at least $0{\cdot}90 \times 10^{-6}$ at 25°, it did not seem probable that the results obtained from dilute acid solutions could be of sufficient accuracy to prove of service in the determination of the velocity of the hydrogen ion. Nevertheless, it was found possible, by a modification of the method for determining the value of the equivalent conductivity at infinite dilution, to obtain with acids of a certain strength very satisfactory results.

It has been observed previously by Drucker (*Zeitsch. physikal. Chem.*, 1904, **49**, 563) that the dissociation constants obtained for weak acids are more or less satisfactory according to the value for the velocity of the hydrogen ion that is employed in the calculation of the equivalent conductivity at infinite dilution. The fact that lower values than Kohlrausch's figure of 352 give more satisfactory dissociation constants for weak acids than does the latter, was considered by Drucker as a strong argument for the assumption that the value of Kohlrausch was too high. The point, however, seems to have escaped observation that with acids of a certain strength a satisfactory dissociation constant at high dilutions is to be obtained with the use of one particular value for the velocity of the hydrogen ion, and not with the use of any other value.

As an illustration of this point, the results obtained from one series of conductivity measurements of cyanoacetic acid at 25° are given below in table I. The method of experiment is described in full subsequently; the water employed possessed a specific conductivity of $0·90 \times 10^{-6}$ at 25°.

The first column gives the dilution v, the second the equivalent conductivity μ. The dissociation constants $100k_1$ and $100k_2$ are calculated with the use of the values of Ostwald and of Kohlrausch, $H^{\cdot} = 347·0$ and $H^{\cdot} = 352·0$ respectively. In the third column the percentage dissociation, using the value $H^{\cdot} = 347·0$, is shown. The mobility of the anion is taken as 38·9 (see table IX below).

TABLE I.

Cyanoacetic Acid. Water, $0·9 \times 10^{-6}$.

v.	μ.	100 m.	100 k_1 ($H^{\cdot} = 347·0$).	100 k_2 ($H^{\cdot} = 352·0$).
20·80	96·2	24·93	0·398	0·386
41·60	127·1	32·93	0·389	0·376
83·20	164·5	42·63	0·381	0·368
166·4	207·3	53·71	0·375	0·360
332·8	252·4	65·40	0·372	0·354
665·6	294·9	76·40	0·372	0·348
1331·0	329·2	85·32	0·372	0·338
2662·0	353·2	91·52	0·371	0·318
5324·0	368·3	95·44	0·375	0·288

For the above series it is evident that the value $H^{\cdot} = 347·0$ gives a far more satisfactory constant than the value $H^{\cdot} = 352·0$. Indeed, a satisfactory dissociation constant for the dilute solutions of the series can be obtained only within a very limited region about $H^{\cdot} = 347·0$. Values only a few tenths of a unit removed from this produce appreciable divergences in the constant.

With acids of this type it is possible, therefore, after the measurement of a number of conductivity series, carried to high dilutions, to obtain from each series that value for the velocity of the hydrogen ion that is required to give a satisfactory dissociation constant, and, by comparison of the values obtained, to ascertain to what degree of accuracy the determination can be carried. This has been done in the experiments described below.

The acids that can be employed are of a very limited range of strength, namely, those which possess a dissociation constant between the limits of 0·001 and 0·01. Acids of this type pass from slight to almost complete dissociation within the ordinary range of dilutions. With acids possessing a smaller dissociation constant, the constant obtained is fairly satisfactory through a large variation in the value taken for the velocity of the hydrogen ion, and no definite value for the latter can be deduced. With stronger acids, dissociation is so nearly complete in dilute solution that the errors of experiment exert sufficient influence, since they are greatly magnified in the calculation of the dissociation constant, to prevent any value taken giving a satisfactory constant. In the more concentrated solutions of these stronger acids, where the degree of dissociation is not so great, the dilution law of Ostwald is not exactly obeyed, as will be shown later.

The above difficulties exist even within the narrow limits indicated, and acids possessing dissociation constants near the centre of the range were found to be far more useful than those having constants near the upper or lower limit. Suitable acids are, however, very few in number. Acids of as simple a constitution as possible must be chosen, in order to avoid the presence of any group likely to cause complications at high dilutions. The acids employed were all, in fact, simple substituted acetic and benzoic acids:

Cyanoacetic acid...........................	$k=0{\cdot}00368$
o-Nitrobenzoic acid	$k=0{\cdot}00620$
o-Chlorobenzoic acid	$k=0{\cdot}00128$
3 : 5-Dinitrobenzoic acid	$k=0{\cdot}00157$

Of these, cyanoacetic acid was the most suitable. *o*-Nitrobenzoic acid, owing to its larger dissociation constant, gives results which are appreciably affected by the errors of experiment, whilst the remaining acids, which possess smaller constants, give results from which the value deduced is rather indeterminate.

It is obviously essential that the acids should be quite pure; they were therefore repeatedly crystallised until constant conductivity values at high dilutions were obtained. *o*-Chlorobenzoic and 3:5-dinitrobenzoic acids were specially prepared.

o-Chlorobenzoic acid was prepared by the distillation of salicylic acid with phosphorus pentachloride, as described by Hübner (*Annalen*, 1884, **222**, 19 The mixed chlorides obtained were decomposed by water, and steam was passed through the solution for several hours until all salicylic acid was removed. *o*-Chlorobenzoic acid was then obtained pure by recrystallisation from water.

3:5-Dinitrobenzoic acid was prepared by the nitration of benzoic acid, as described by Shukoff (*Ber.*, 1895, **28**, 1800), and purified by several crystallisations from water.

Cyanoacetic acid, being extremely soluble in water, was recrystallised from benzene until pure. Owing to the deliquescent nature of the acid, all solutions were made up volumetrically. *o*-Nitrobenzoic acid was obtained pure by repeated crystallisations from water.

The conductivity measurements were carried out with the greatest possible accuracy. The cells used were of the type described by Cantor (*Zeitsch. Elektrochem.*, 1903, **9**, 922). The cell constants were determined by means of $N/50$- and $N/100$-potassium chloride (Kahlbaum's 100·00 per cent.). With solutions made up independently, values were obtained all agreeing within 1 in 2000.

The dilutions were carried out in the cell itself by means of 30 c.c. and 60 c.c. graduations. The accuracy of these was tested by weighing the water run out at a known temperature. Correct volumes of 30 c.c. are not necessary; all that is required for accurate dilution is that the two volumes shall be equal. The correct graduations for doubling the volume were determined for each cell within an error of 0·01 c.c. in 30 c.c.

The conductivities of the solutions were measured by means of a rotating commutator and a galvanometer. By this method the results obtained at high dilutions are much more accurate than with the usual induction coil and telephone. The bridge employed was a three-metre platinum wire, divided into one thousand parts; readings could easily be obtained within one-tenth of a division, the galvanometer being used as a zero instrument, at all dilutions.

The cells were immersed in a small thermostat, heated beneath, and regulated to 25°. The copper sides of the bath were not protected in any way, and convection was sufficient, without any stirring at all, to keep the temperature constant. The cells were suspended away from the sides, and the temperature in their neighbourhood was never found to vary more than 0·03° from 25°.

The acid solutions used were standardised either volumetrically or gravimetrically. In the former case a known volume was titrated with barium hydroxide solution, phenolphthalein (except where otherwise stated) being used as indicator. The barium hydroxide solution (approximately $N/100$) was standardised against $N/10$-hydrochloric acid, and also against certain of the acids used—the results obtained were in agreement within 1 in 1000.

In the latter case a weighed quantity of acid was dissolved in water and made up to a known volume. All weights were reduced, with sufficient accuracy, to true weights in vacuum by addition of one-thousandth part. This is the correction for substances with a specific gravity slightly greater than unity, and is accurate for the acids used well within the limits of error in weighing. All volumes were reduced to volumes occupied at 25°.

The results obtained by the above methods were, on comparison, usually in agreement within 1 in 1000; the greatest divergence was 1 in 600. This may be taken as the maximum degree of error in the estimation of the concentration of a solution.

The graduation of the cells is accurate within 0·01 c.c. of 30 c.c., as described above; the various dilutions in a conductivity series were not carried out, however, within a greater accuracy than 0·03 c.c. in 30 c.c. This is due to considerations of time, since for more exact dilutions it is necessary to allow the cell to remain for a long period, in order to drain completely, before each reading. A series must be completed as quickly as possible, and with the above apparatus the measurements are already protracted, since the large glass surface of the cell is slow in attaining the true temperature of the thermostat, from which the cell must be removed during the mixing of the solutions. Greater accuracy than the above (1 in 1000) was therefore not aimed at in the dilutions. The error is not so important as may at first sight appear, since it is not (as is the initial error in the graduation) doubled at each step, but is equally likely to be positive or negative at each dilution. Indeed, as has often been pointed out, the most important error incurred in conductivity determinations is in the estimation of the initial concentration of a solution. Two series, differing slightly in their first values, will usually run parallel throughout their whole length.

There remains the question of the influence of the impurities in the water on the values of the equivalent conductivity obtained for very dilute solutions. In the series for cyanoacetic acid given above, no correction has been made for this. From the figures obtained it seems that the impurities in the water used do not affect the value appreciably until a high dilution is reached. Here a small increase is observable, still, however, within the limits of experimental error. A small difference in the value taken for the velocity of the hydrogen ion produces a much greater effect on the dissociation constant; the influence of the water impurities cannot therefore be directly measured.

We can determine, however, to what dilutions the experiments can be carried without taking the influence of the water into account, by examination of the results obtained with dilute solutions of a much weaker acid. In such solutions any small error in the value taken for the velocity of the hydrogen ion does not influence the dissociation constant, owing to the less complete dissociation;

at the same time the specific conductivity of the solutions is small, and the influence of the water on the value obtained is more readily perceived.

With this object preliminary experiments were carried out with acetic acid. Two series of conductivity measurements were performed; the water used for dilution possessed a specific conductivity of $0·90 \times 10^{-6}$ in the first series, and of $1·20 \times 10^{-6}$ in the second. The results obtained are given in tables II and III; the value of the equivalent conductivity at infinite dilution is taken as 387·7 ($H^{\cdot} = 347·0$; $Ac' = 40·7$) (Bredig, *Zeitsch. physikal. Chem.*, 1894, **13**, 218).

TABLE II.

Acetic Acid. Water, $0·90 \times 10^{-6}$.

v.	*μ.*	100*m.*	100*k.*
13·57	6·086	1·570	0·001845
27·14	8·591	2·216	0·001851
54·28	12·09	3·118	0·001849
108·56	16·98	4·380	0·001849
217·1	23·81	6·141	0·001851
434·2	33·22	8·568	0·001849
868·4	46·13	11·90	0·001850
1737·0	63·60	16·41	0·001854
3474·0	86·71	22·36	0·001855
6948·0	116·8	30·13	0·001870
∞	387·7	—	—

TABLE III.

Acetic Acid. Water, $1·20 \times 10^{-6}$.

v.	*μ.*	100*m.*	100*k.*
15·816	6·561	1·692	0·001842
31·63	9·260	2·388	0·001848
63·26	13·03	3·361	0·001847
126·52	18·30	4·721	0·001848
253·04	25·60	6·603	0·001846
506·1	35·67	9·200	0·001843
1012·2	49·50	12·77	0·001846
2024·4	68·22	17·60	0·001856
4049·0	93·5	24·12	0·001893
8098·0	125·8	32·45	0·001924
∞	387·7	—	—

In the first series a very satisfactory dissociation constant is obtained, without the application of any correction, up to $v = 3500$; with water of a slightly higher specific conductivity, in the second table, the constant has already begun to show an increase at $v = 2000$.

It seems reasonable to suppose, therefore, that with the use of water of a specific conductivity $0·90 \times 10^{-6}$ at 25°, the measurements with stronger acids can be relied on, without any correction, up to high dilutions, as in table I. To test this further, however, and to find by experiment what effect the specific conductivity of the water used has on the value for the velocity of the hydrogen ion deduced from the measurements with these acids, the following plan was adopted. A conductivity series of each acid was carried out with four different samples of water, possessing the following specific conductivities at 25°:

$$(a)\ 0{\cdot}90\times10^{-6};\ (b)\ 1{\cdot}20\times10^{-6};\ (c)\ 1{\cdot}80\times10^{-6};\ (d)\ 2{\cdot}50\times10^{-6}.$$

The first two samples were obtained as described above; (*c*) is an earlier fraction of the first distillation; (*d*) is the ordinary distilled water of the laboratory.

The conductivity results obtained are expressed in tables V to XII. It is necessary, however, first of all to determine the equivalent conductivities of dilute solutions of the sodium salts of the acids employed, in order to obtain accurate values for the velocities of their respective anions.

The measurement of these conductivities was carried out as has been already described. The solutions were made up to known concentration by the exact neutralisation of known solutions of the acid and of sodium hydroxide. The latter was freshly made up from metallic sodium, and standardised with $N/10$-hydrochloric acid, using methyl-orange as indicator. In certain cases the results obtained were checked by preparing a small sample of the salt, and making up a solution gravimetrically.

The dilutions were made with water of a specific conductivity $1{\cdot}20\times10^{-6}$ at 25°; this value is subtracted from the conductivity obtained at each dilution (Kohlrausch, "Leitvermögen der Electrolyte," 1898, p. 91). The value of the equivalent conductivity at infinite dilution is obtained by graphical extrapolation, according to the empirical formula of Kohlrausch (*Zeitsch. Elektrochem.*, 1907, **13**, 337). From this value the velocity of the anion of each acid is found by subtracting 51·0, the value for the sodium ion.

The figures obtained agree closely, where comparison is available, with the results of Ostwald (*Zeitsch. physikal. Chem.*, 1888, **2**, 847); the greatest divergence obtained with independent series of the same salt was 0·3. Results are shown in table IV below, interpolated to the ordinary dilutions.

TABLE IV.

Equivalent Conductivity of Sodium Salts.

v.	Cyanoacetate.	*o*-Nitrobenzoate.	*o*-Chloro-benzoate.	3 : 5-Dinitro-benzoate.
16	73·6	66·9	—	—
32	77·3	70·6	71·5	68·8
64	80·3	73·6	74·3	71·3
128	82·7	76·0	76·6	73·2
256	84·4	77·9	78·4	75·0
512	85·8	79·3	79·8	76·3
1024	87·0	80·4	80·9	77·3
2048	87·9	81·2	81·8	78·1
∞	89·9	83·2	83·8	80·1
Mobility of anion	38·9	32·2	32·8	29·1

The conductivity measurements with the acids themselves are given in tables V to XI; the columns are arranged as in table I. The dissociation constant $100k_1$ is calculated with the use of that value for the equivalent conductivity at infinite dilution that gives the most satisfactory constant at high dilutions; $100m$ is the percentage dissociation obtained with this value. The constant $100k_2$ is calculated with the use of the mean value 347·2 finally taken (see p. 1293) for the velocity of the hydrogen ion.

The results obtained with each sample of water are shown in full only for cyanoacetic acid; for the other acids the figures for one sample are given in full, and the values obtained in the other cases are summarised in table XII. The effect of the different samples of water on the results was found to be the same for all the acids used, and is discussed later.

TABLE V.

Cyanoacetic Acid. Water, $0{\cdot}9 \times 10^{-6}$.

v.	μ.	$100m$.	$100k_1$. $(\mathrm{H}^{\cdot} = 347{\cdot}1)$.	$100k_2$. $(\mathrm{H}^{\cdot} = 347{\cdot}2)$.
16·82	88·0	22·80	0·400	0·400
33·64	117·0	30·31	0·392	0·392
67·28	152·5	39·50	0·383	0·383
134·56	193·9	50·23	0·378	0·378
269·1	238·7	61·84	0·372	0·372
538·2	282·6	73·20	0·372	0·371
1076·4	320·0	82·89	0·373	0·372
2153·0	347·1	89·90	0·373	0·371
4306·0	364·8	94·52	0·378	0·376
∞	386·0	—	—	—

TABLE VI.

Cyanoacetic Acid. Water, $1{\cdot}2 \times 10^{-6}$.

v.	μ.	$100m$.	$100k_1$ ($\mathrm{H}^{\cdot}=347{\cdot}0$).	$100k_2$ ($\mathrm{H}^{\cdot}=347{\cdot}2$)
17·404	89·4	23·16	0·401	0·401
34·81	118·8	30·79	0·393	0·393
69·62	154·8	40·12	0·386	0·385
139·24	196·3	50·86	0·378	0·378
278·5	241·4	62·54	0·375	0·375
557·0	285·0	73·83	0·374	0·373
1114·0	321·6	83·34	0·374	0·373
2228·0	348·1	90·20	0·372	0·371
4456·0	365·3	94·67	0·377	0·373
∞	385·9	—	—	—

TABLE VII.

Cyanoacetic Acid. Water, $1{\cdot}8 \times 10^{-6}$.

v.	μ.	$100m$.	$100k_1$ ($\mathrm{H}^{\cdot}=346{\cdot}8$).	$100k_2$ ($\mathrm{H}^{\cdot}=347{\cdot}2$).
17·350	89·3	23·15	0·402	0·401
34·70	118·8	30·80	0·395	0·394
69·40	154·7	40·11	0·387	0·386
138·8	196·1	50·83	0·379	0·378
277·6	241·2	62·53	0·376	0·375
555·2	284·8	73·82	0·375	0·373
1110·4	321·5	83·35	0·376	0·373
2221·0	347·9	90·19	0·374	0·369
∞	385·7	—	—	—

TABLE VIII.

Cyanoacetic Acid. Water, $2{\cdot}5 \times 10^{-6}$.

v.	μ.	$100m$.	$100k_1$ ($\mathrm{H}^{\cdot}=347{\cdot}0$).	$100k_2$ ($\mathrm{H}^{\cdot}=347{\cdot}2$).
21·05	96·5	25·00	0·396	0·396
42·10	127·7	33·09	0·389	0·388
84·20	165·2	42·81	0·381	0·380
168·4	208·0	53·90	0·374	0·374
336·8	253·0	65·56	0·370	0·370
673·6	295·6	76·60	0·372	0·371
1347·0	330·4	85·60	0·378	0·377
2694·0	354·8	91·94	0·389	0·387
∞	385·9	—	—	—

TABLE IX.

c-*Nitrobenzoic Acid.* Water, $0{\cdot}9 \times 10^{-6}$.

v.	μ.	$100m$.	$100k_1$ ($\mathrm{H}^{\cdot}=347{\cdot}0$).	$100k_2$ ($\mathrm{H}^{\cdot}=347{\cdot}2$).
32	139·7	36·85	0·672	0·671
64	179·0	47·22	0·660	0·659
128	221·9	58·52	0·645	0·644
256	265·0	69·88	0·633	0·632
512	303·6	80·07	0·628	0·626
1024	333·5	87·94	0·627	0·623
2048	353·6	93·26	0·629	0·624
4096	365·3	96·36	0·618	0·609
∞	379·2	—	—	—

TABLE X.

o-*Chlorobenzoic Acid.* Water, $0{\cdot}9 \times 10^{-6}$.

v.	μ.	$100m$.	$100k_1$. ($\mathrm{H}^{\cdot} = 347{\cdot}4$).	$100k_2$. ($\mathrm{H}^{\cdot} = 347{\cdot}2$).
150·1	134·6	35·41	0·1293	0·1294
300·2	174·0	45·76	0·1286	0·1288
600·4	218·0	57·34	0·1284	0·1286
1201·0	262·6	69·08	0·1284	0·1287
2402·0	302·1	79·45	0·1279	0·1283
4804·0	333·0	87·58	0·1286	0·1292
9608·0	353·7	93·05	0·1288	0·1298
∞	380·2	—	—	—

TABLE XI.

3 : 5-*Dinitrobenzoic Acid.* Water, $0{\cdot}9 \times 10^{-6}$.

v.	μ.	$100m$.	$100k_1$. ($\mathrm{H}^{\cdot} = 346{\cdot}7$).	$100k_2$. ($\mathrm{H}^{\cdot} = 347{\cdot}2$).
254·5	175·7	46·76	0·1614	0·1607
509·0	219·0	58·28	0·1599	0·1591
1018·0	262·7	69·90	0·1594	0·1585
2036·0	301·5	80·23	0·1599	0·1586
4072·0	330·9	88·06	0·1594	0·1574
8144·0	350·7	93·34	0·1602	0·1569
∞	375·8	—	—	—

The results of the above tables, together with those obtained from the remaining experiments for *o*-nitrobenzoic acid, *o*-chlorobenzoic acid, and 3 : 5-dinitrobenzoic acid, are summarised in table XII. The figures shown are those values for the velocity of the hydrogen ion that give, for each particular series, the most satisfactory dissociation constant at high dilutions, as found under $100k_1$ in the above tables.

TABLE XII.

Velocity of the Hydrogen Ion.

	Water, $0{\cdot}9 \times 10^{-6}$.	Water, $1{\cdot}2 \times 10^{-6}$.	Water, $1{\cdot}8 \times 10^{-6}$.
Cyanoacetic acid	347·1	347·0	346·8
o-Nitrobenzoic acid	347·0	346·7	346·6
o-Chlorobenzoic acid	347·4	347·4	347·2
3 : 5-Dinitrobenzoic acid	346·7	346·9	346·7
Mean value..	347·0	347·0	346·8

It will be seen that the values in the above table are all in agreement within a unit; the mean value obtained from all experiments is $\mathrm{H}^{\cdot} = 347{\cdot}0$. A modification in this figure, however, to the slightly higher value $\mathrm{H}^{\cdot} = 347{\cdot}2$ will be shown to be necessary in a later section of the paper.

The variation in the values obtained with the use of the three different samples of water given in the table is negligible. With the first sample, which is the purest, the results obtained are more trustworthy than in the other cases, since the agreement of the values of the dissociation constant at high dilutions was here found to be more satisfactory. With the second and third samples the agreement is still good, but with the fourth sample, the ordinary distilled water of the laboratory, no agreement at all could be obtained, as will be seen in table VIII for cyanoacetic acid. The influence of the impurities in the water on the conductivity measurements is here appreciably affecting the results; the use of the fourth sample was therefore discontinued. The constant $100k_1$ in table VIII is calculated with the use of the mean value obtained from other experiments with the same acid.

From the above results it would appear that the influence of the water on the conductivity measurements obtained may be neglected, up to very high dilutions, if its specific conductivity is not greater than $1{\cdot}8 \times 10^{-6}$ at 25°. Such a general conclusion, however, cannot be drawn, for it was found that with a sample of specific conductivity only $1{\cdot}1 \times 10^{-6}$ at 25° (obtained by "rushing" a current of outside air for some time through the laboratory distilled water) no satisfactory results could be obtained in the above experiments, since the dissociation constant showed an appreciable increase at high dilutions. It seems that the nature of the impurities in the water is of importance, as well as the amount. The amount is so small that we can only, in most cases, speculate as to its nature.

We cannot be certain that the measurements obtained with dilute acid solutions are the true values unless, as stated by Kohlrausch, the water used is absolutely pure. Nevertheless, it is possible that in certain cases water with a fairly large specific conductivity will not affect the values obtained, and this would appear to be so with the water obtained by distillation from water containing Nessler's solution.

Whilst, owing to the uncertainty as to the nature of the minute trace of impurities present, we are unable to assume this with certainty, yet the satisfactory results obtained at high dilutions support the view that such is here the case.

Limits of Ostwald's Dilution Law.

It will be found on an examination of tables VI to XI that the dissociation constant $100k_1$ obtained in each case is not a true constant at the higher concentrations. The value falls steadily with dilution, and only at very high dilutions does it approach a limit. The acids employed belong, therefore, to the class of transition acids, which obey the dilution law of Ostwald only in very dilute solution.

The divergence from the law is seen to be greater as the strength of the acid increases. The difference with *o*-nitrobenzoic acid is greater than with cyanoacetic acid at the same dilution; *o*-chlorobenzoic acid and 3:5-dinitrobenzoic acid give very small divergences, and acetic acid (table II) obeys the law exactly.

The dilution law of Ostwald, which is not applicable at all to solutions of strong electrolytes, is thus applicable for weak electrolytes only within certain limits. These limits have been fully discussed by Wegscheider (*Zeitsch. physikal. Chem.*, 1909, **69**, 603); the conclusions there drawn are summarised below.

In the first place, the law holds exactly only for dilute solutions; as solutions become more concentrated the dissociation constant obtained decreases, owing to the diminished fluidity of the solution. This effect begins to be appreciable, for the majority of organic acids, between $v=16$ and $v=32$; more dilute solutions obey the dilution law exactly.

The second disturbing influence, of greater theoretical importance, is in the opposite direction, increasing the dissociation constant, and depends on the ionic concentration. The dilution law holds approximately only for solutions where the ionic concentration is less than $N/60$; if it exceeds this limit, an increasing constant is obtained; thus, for binary electrolytes, the law is approximately obeyed if $2v/m$ is greater than 120 (m being the degree of dissociation at the dilution v), and breaks down for more concentrated solutions.

In order to determine the particular point at which the law ceases to hold exactly, it is evident that accurate conductivity measurements must be made for a series of dilutions. Such experiments have been carried out by Wegscheider and Lux (*Monatsh.*, 1909, **30**, 411) in the cases of several sulphonic acids. The result obtained is that Ostwald's dilution law gives perfect agreement for solutions in which $2v/m$ exceeds 320, and approximate agreement for solutions up to $2v/m=120$.

In the conductivity measurements given above in tables I to XI, the point at which the law ceases to be applicable in each case is of interest, for comparison with the results of Wegscheider. Tables I and V to VIII (cyanoacetic acid) and table IX (*o*-nitrobenzoic acid) show clearly the divergence in the values obtained for the dissociation constant at the higher concentrations. With *o*-chlorobenzoic acid and 3:5-dinitrobenzoic acid a slight increase in the value obtained at the highest concentration is suggested, but the acids employed are so slightly soluble that solutions of a concentration at which the effect would be appreciable cannot be prepared.

The results from the above tables are given in table XIII below. v indicates the dilution at which the divergence from the law of Ostwald becomes inconsiderable, m is the degree of dissociation at that dilution, and $2v/m$ the ionic concentration.

TABLE XIII.

Limits of Ostwald's Dilution Law.

Table.	v.	m.	$2v/m$.
1. Cyanoacetic acid	166	0·537	618
5. ,, ,, ...	135	0·502	538
6. ,, ,, ...	139	0·509	546
7. ,, ,, ...	139	0·508	547
8. ,, ,, ...	168	0·539	623
9. *o*-Nitrobenzoic acid	256	0·699	733

The limit is evidently higher than that obtained by Wegscheider, and the law is seen to be applicable only for solutions with an ionic concentration of less than $2v/m=600$ (approximately). This is one dilution further than the limit given by Wegscheider, but it is by no means certain that the law is exactly applicable for solutions still more dilute, although any divergence will naturally diminish with the concentration; for we have, in the above tables, arbitrarily fixed the value for the equivalent conductivity at infinite dilution so as to obtain a satisfactory dissociation constant at high dilutions. We have no proof that a value, higher by a few tenths of a unit, which would give at these dilutions a still slowly decreasing constant, may not be nearer to the truth.

A modification of Ostwald's dilution law, so that it will apply to the more concentrated solutions, would enable us to calculate what effect this second disturbing influence exerts on the constant at high dilutions. Such a formula is developed below.

The Dissociation of Transition Electrolytes.

In dilute solution (v greater than 16) very weak electrolytes are found to follow exactly the dilution law of Ostwald, $m^2/(1-m)v=k$, as will be seen for acetic acid in tables II to III. Strong electrolytes obey approximately the empirical formula of van't Hoff, $m^3/(1-m)^2v=C$, which may be written in the form $m^2/(1-m)v=c(1-m)/m$. It is therefore to be expected that the intermediate or transition electrolytes will obey an intermediate formula, for example,

$$m^2/(1-m)v=k+c(1-m)/m;$$

and the agreement of this with the experimental data is shown in the tables which follow.

The values for $m^2/(1-m)v$ that are obtained for solutions of an acid by the above formula decrease with the concentration of the solution, and ultimately attain a limiting value k_∞ at infinite dilution. The value of k_∞ is found from the conductivity results of a series of dilutions by the use of that particular value for the velocity of the hydrogen ion that gives values, for $m^2/(1-m)v$, slowly falling as dilution increases, and ultimately approaching (so far as can be perceived within experimental error) a limiting value. The value of c is obtained by trial from the experimental results.

In the results shown previously in table XII, that velocity for the hydrogen ion was taken in each series that gave constant values for $m^2/(1-m)v$ at high dilutions. The mean value deduced was $H^\cdot = 347{\cdot}0$. The value required to give slowly-falling figures for $m^2/(1-m)v$ at high dilutions is very slightly higher in each series; the mean value required is $H^\cdot = 347{\cdot}2$. In the following tables, therefore, k_∞ is obtained with the use of this value, $H^\cdot = 347{\cdot}2$.

Table XIV gives the results for cyanoacetic acid obtained from table V. The first column shows the dilution, the second the ratio of the non-ionised to the ionised part. In the third column the values calculated from the formula for the dissociation constant at each dilution are given. These are compared with the experimental values, $100m^2/(1-m)v$, obtained with the use of the two different values for the velocity of the hydrogen ion referred to above. These experimental figures are the same as were expressed by $100k_1$ and $100k_2$ in table V. Finally, the figures under $100k$ show the value obtained at each dilution from the experimental results in the preceding column ($H^\cdot = 347{\cdot}2$) by subtracting the value of $c(1-m)/m$. The constancy of the values obtained in the last column therefore shows the agreement of the formula with the experimental results.

TABLE XIV.

Cyanoacetic Acid (see table V). $k_\infty = 0{\cdot}00368$; $c = 0{\cdot}00010$.

v.	$(1-m)/m$.	$100(k_\infty + c(1-m)/m$.	$100m^2/(1-m)v$ ($H^\cdot = 347{\cdot}1$).	$100m^2/(1-m)v$ ($H^\cdot = 347{\cdot}2$).	$100k$.
16·82	3·39	0·402	0·400	0·400	0·366
33·64	2·30	0·391	0·392	0·392	0·369
67·28	1·53	0·383	0·383	0·383	0·368
134·56	0·99	0·378	0·378	0·378	0·368
269·1	0·62	0·374	0·372	0·372	0·366
538·2	0·37	0·372	0·372	0·371	0·367
1076·4	0·21	0·370	0·373	0·371	0·369
2153·0	0·11	0·369	0·373	0·371	0·370
4306·0	0·06	0·369	0·378	0·376	0·375
∞	0·00	0·368	—	—	—

The agreement between the calculated and experimental values is seen to be very satisfactory throughout the whole range of dilutions. Further examples of the agreement of the formula with the previous results are shown in its application to *o*-nitrobenzoic acid and 3:5-dinitrobenzoic acid in tables XV and XVI below.

TABLE XV.

o-*Nitrobenzoic Acid* (see table IX). $k_\infty = 0{\cdot}00620$; $c = 0{\cdot}00032$.

v.	$(1-m)/m$.	$100(k_\infty + c(1-m)/m$.	$100m^2/(1-m)v$ ($H^\cdot = 347{\cdot}0$).	$100m^2/(1-m)v$ ($H^\cdot = 347{\cdot}2$).	$100k$.
32	1·71	0·675	0·672	0·671	0·616
64	1·12	0·656	0·660	0·659	0·623
128	0·71	0·643	0·645	0·644	0·621
256	0·43	0·634	0·633	0·632	0·618
512	0·25	0·628	0·628	0·626	0·618
1024	0·14	0·624	0·627	0·623	0·619
2048	0·07	0·622	0·629	0·624	0·622
4096	0·04	0·621	0·618	0·609	0·608
∞	0·00	0·620	—	—	—

TABLE XVI.

3:5-*Dinitrobenzoic Acid* (see table XI). $k_\infty = 0{\cdot}001570$;
$c = 0{\cdot}000030$.

v.	$(1-m)/m$.	$100(k_\infty + c(1-m)/m$.	$100m^2/(1-m)v$ ($H^\cdot = 346{\cdot}7$).	$100m^2/(1-m)v$ ($H^\cdot = 347{\cdot}2$).	$100k$.
254·5	1·14	0·1604	0·1614	0·1607	0·1573
509·0	0·72	0·1592	0·1599	0·1591	0·1569
1018·0	0·43	0·1583	0·1594	0·1585	0·1572
2036·0	0·25	0·1577	0·1599	0·1586	0·1579
4072·0	0·14	0·1574	0·1594	0·1574	0·1570
8144·0	0·07	0·1572	0·1602	0·1569	0·1567
∞	0·00	0·1570	—	—	—

The agreement of the formula with the results of experiment is for both acids very satisfactory. With the very dilute solutions the values for $m^2/(1-m)v$ obtained with the use of $H^\cdot = 347{\cdot}2$ are seen to be in better agreement with the formula than those given in the preceding column. The results obtained in tables XIV to XVI, therefore, lead us to the conclusion that the value for the velocity of the hydrogen ion is not that required to give constant values for $m^2/(1-m)v$ at high dilutions, but that which gives values slowly decreasing and ultimately reaching a limit.

The method employed in the first part of the paper to obtain the velocity of the hydrogen ion is thus found to give results a little below this required value. The mean value $H^\cdot = 347{\cdot}0$ previously deduced has therefore been amended to the slightly higher figure of $H^\cdot = 347{\cdot}2$.

The values for the velocity of the hydrogen ion obtained in table XII are all in agreement within a unit. If the two purest samples of water only are considered, the agreement is slightly better; results are concordant within 0·2 to 0·4 for each acid, whilst the greatest divergence between those for different acids is 0·7. The value for the velocity of the hydrogen ion, amended from the above results, can therefore be stated as $347·2 \pm 0·4$ at 25°. At 18° the value becomes, with the use of the temperature-coefficient given by Kohlrausch (*Zeitsch. Elektrochem.*, 1902, **8**, 290), $\mathrm{H}^{\cdot} = 313·9$.

The General Application of the above Dissociation Formula.

It has been remarked that the divergence from the simple dilution law increases with the strength of the acid used, and in tables XIV to XVI it is seen that c does increase with k. With very weak acids, therefore, it will be impossible to notice any divergence from Ostwald's dilution law in dilute solutions; this is so in the case of acetic acid, as shown in table II. With stronger acids, however, the variation in the values of the dissociation constant with dilution will be much greater; an example—trichlorobutyric acid—is given in table XVII below.

The figures given in the table differ materially from those of Ostwald (*Zeitsch. physikal. Chem.*, 1888, **3**, 194). This is probably due to the removal of impurities in the method of purification adopted. The acid dissolves readily on treatment with a small quantity of water, but leaves a less soluble residue. This was collected, and the clear filtrate carefully evaporated to dryness. The acid was then dissolved in light petroleum, and recrystallised several times.

TABLE XVII.

Trichlorobutyric Acid. $k_\infty = 0·095$; $c = 0·35$.

v.	μ.	$(1-m)/m$.	$100(k_\infty + c(1-m)/m$.	$100m^2/(1-m)v$.	$100k$.
38·63	326·4	0·152	14·8	14·8	9·5
53·98	336·0	0·119	13·7	13·9	9·7
77·26	343·9	0·093	12·7	12·7	9·5
107·96	350·4	0·073	12·1	11·8	9·2
154·5	357·0	0·054	11·4	11·5	9·6
215·9	361·2	0·041	10·9	10·9	9·5
309·0	365·1	0·030	10·5	10·5	9·5
431·8	368·2	0·021	10·2	10·7	10·0
618·0	370·9	0·014	10·0	11·6	11·1
∞	(376·0)	0·000	9·5	—	—

The value for the equivalent conductivity at infinite dilution is only approximate, being obtained from the number of atoms in the molecule by Ostwald's method (*Zeitsch. physikal. Chem.*, 1888, **2**, 840). In view of the proximity of the measurements to this uncertain value, the agreement throughout the series between the calculated and experimental figures is very satisfactory.

A complete series of measurements with a still stronger acid, namely, *p*-toluenesulphonic acid, has been carried out by Wegscheider and Lux (*Monatsh.*, 1909, **30**, 436); the agreement of the formula with their results is shown in the following table. In the calculation of the results from the experimental data the value $H^{\cdot} = 347·2$ is employed.

TABLE XVIII.

p-*Toluenesulphonic Acid.* $k_\infty = 0·090$; $c = 5·6$.

v	25·00	32·66	44·44	51·02	59·17	69·44	82·64	100·0	123·4
$100(k_\infty + c(1-m)/m)$	50·4	45·4	39·8	37·0	34·8	32·0	29·7	28·0	25·8
$100m^2/(1-m)v$	50·6	44·3	38·7	37·2	35·2	34·0	31·8	28·7	26·5
$100k$	9·2	7·9	7·9	9·2	9·4	11·0	11·1	9·7	9·7

v	156·3	204·1	277·7	330·6	400·0	493·8	625·0	816·8	1111	1600	∞
$100(k_\infty + c(1-m)/m)$	24·1	21·9	19·6	18·5	17·4	16·2	15·2	14·0	12·9	11·8	9·0
$100m^2/(1-m)v$	22·6	21·0	18·3	17·4	16·8	16·0	14·9	13·9	13·0	13·1	—
$100k$	7·5	8·1	7·7	7·9	8·4	8·8	8·7	8·9	9·1	10·3	—

The acid is so highly dissociated that the differences between the calculated and experimental values are all within the limits of experimental error. The formula is found to hold throughout a five-fold change in the values obtained by experiment for $m^2/(1-m)v$.

The agreement of the formula for an acid of another type—phosphoric acid—is shown in table XIX. The results are calculated with the use of the value $H^{\cdot} = 347·2$ by interpolation from the figures given by Rothmund and Drucker for the experiments of Loomis (*Zeitsch. physikal. Chem.*, 1903, **46**, 850).

TABLE XIX.

Phosphoric Acid. $k_\infty = 0·0070$; $c = 0·0013$.

v	16	32	64	128	256	512	1024
$100(k_\infty + c(1-m)/m)$	0·97	0·89	0·83	0·78	0·75	0·73	0·72
$100m^2/(1-m)v$	0·96	0·87	0·82	0·81	0·76	0·77	0·69
$100k$	0·69	0·68	0·69	0·73	0·71	0·74	0·67

The agreement between the calculated and observed figures is again satisfactory. The second and third dissociations of the acid are evidently too weak to affect the results, even at the highest dilutions given.

The stronger inorganic acids, such as hydrochloric acid, are of a different type. The values obtained for $m^2/(1-m)v$ certainly do fall away, as dilution is increased, to a limiting value k_∞, but that limiting value is zero. The results for hydrochloric acid are given in table XX below. The measurements of Goodwin and Haskell at 18° (*Zeitsch. physikal. Chem.*, 1905, **52**, 630) are employed, the value $H^{\cdot} = 313·9$ being used in the calculation of the degree of dissociation at each dilution.

TABLE XX.

Hydrochloric Acid. $k_\infty = 0{\cdot}00$; $c = 13{\cdot}4$.

v	20	33·3	50	100	200	500	667	1000	1333	2000	4000	∞
$100(k_\infty + c(1-m)/m)$	78·5	62·4	50·9	36·4	24·5	14·8	13·5	12·4	11·4	8·5	6·3	0·0
$100m^2/(1-m)v$	80·6	61·5	50·6	35·6	26·9	18·1	14·7	10·6	8·7	7·8	5·2	—
$100k$	+2·1	−0·9	−0·3	−0·8	+2·4	+3·3	+1·2	−1·8	−2·7	−0·7	−1·3	—

The conductivity measurements are all so very near to the value at infinite dilution that the possible degree of error in the above calculations is considerable; the agreement in all cases is within the limits of experimental error.

In conclusion, the dissociation formulæ of a number of typical electrolytes, calculated from the available experimental data, are collected in table XXI.

TABLE XXI.

Dissociation of Electrolytes.

Dissociation formula: $m^2/(1-m)v = k + c\,.\,(1-m)/m$.

Acid.	Observer.	k.	c.
Acetic	Kendall	0·0000185	—
o-Bromobenzoic	Ostwald	0·00140	0·00004
p-Nitrophenylglycollic	,,	0·00149	0·00004
3 : 5-Dinitrobenzoic	Kendall	0·00157	0·00003
Aniline-*o*-sulphonic	Ostwald	0·00310	0·00015
Cyanoacetic	Kendall	0·00368	0·00010
Trichlorolactic	Ostwald	0·00440	0·00020
o-Nitrobenzoic	Kendall	0·00620	0·00032
Phosphoric	Loomis	0·0070	0·0013
5-Bromo-2-nitrobenzoic	Ostwald	0·012	0·007
4 : 6-Dibromoaniline-3-sulphonic	,,	0·019	0·030
Dichloroacetic	Walker	0·0316	0·080
β-Resorcylic	Ostwald	0·032	0·075
Trichlorobutyric	Kendall	0·095	0·35
p-Toluenesulphonic	Wegscheider and Lux	0·090	5·6
β-Naphthalenesulphonic	,, ,,	0·120	6·6
Hydrochloric	Goodwin and Haskell	—	13·4

It is evident from the above figures that c increases with k, and increases much more rapidly. Ostwald's dilution law is a limiting case of the formula, since with very weak electrolytes c is so nearly equal to zero that the dissociation constant is practically unaffected. Similarly, van't Hoff's empirical law for strong electrolytes is a special case of the above formula, where $k = 0$. The dissociation formula given above is therefore applicable to all acids. For salts, however, the divergences from the simple van't Hoff formula are beyond the limits of experimental error, even in dilute solution.

It does not seem possible to establish a connexion between the constants k and c. In the above table c is roughly proportional to k^2 for the weaker acids, but this relation cannot be general, since for strong electrolytes c is large whilst k is zero. Finally, it may be noted that the dissociation of transition acids can in no way be expressed by a formula intermediate between Ostwald's dilution law and Rudolphi's formula for strong electrolytes.

Summary of Results.

The following method has been employed for the determination of the velocity of the hydrogen ion, and has been found to give concordant results. If conductivity measurements are carried out with a series of very dilute solutions of a weak acid, the values obtained for the dissociation constant vary greatly according to the value for the velocity of the hydrogen ion used in the calculation of the equivalent conductivity at infinite dilution. With acids of a certain range of strength ($100k$ between 0·1 and 1·0) it has been found that a satisfactory dissociation constant at very high dilutions can only be obtained with the use of one particular value for the velocity of the hydrogen ion. The mean of the values deduced from a number of experiments with different acids was $H^{\cdot} = 347{\cdot}0$. A slight modification of this result was afterwards found necessary, the figure finally obtained being $H^{\cdot} = 347{\cdot}2$ at 25° (or 313·9 at 18°), with a maximum divergence of $\pm 0{\cdot}4$.

It has been found that the dilution law of Ostwald is not exactly obeyed by the acids employed in the above determination, even in very dilute solution. A formula for the dissociation of these acids, $m^2/(1-m)v = k + c(1-m)/m$, where k and c are constants for each acid, has been developed, and found to be in perfect agreement with the experimental data. For the transition acids in general, c increases with k.

This formula has been extended to acids of all types. Ostwald's dilution law for weak electrolytes is a limiting case, since as k decreases c approaches zero; van't Hoff's formula for strong electrolytes is a special case, where k is zero. The above dissociation holds, therefore, within the limits of experimental error for all acids.

I desire to express my thanks to Professor Walker for the interest he has taken in this research, and for advice during its progress.

CHEMISTRY DEPARTMENT,
UNIVERSITY OF EDINBURGH.

Richard Clay and Sons, Limited,
Brunswick St., Stamford St., S.E., and
Bungay, Suffolk.

3

THE PROBLEM OF STRONG ELECTROLYTES.
(PRELIMINARY NOTE.)

BY

JAMES KENDALL.

From the Proceedings of the Chemical Society, 1912. Vol. 28.

257. "The problem of strong electrolytes. (Preliminary note.)"

By James Kendall.

The dissociation formula $m^2/(1-m)v = k + c\,.\,(1-m)/m$ has been recently shown by the author from experimental results (*Trans.*, 1912, **101**, 1275) to hold for all acids. The above formula may be arrived at theoretically by the assumption of the presence of complex ions of the type $(R_2)^{\cdot\cdot}$ or $(X_2)''$ in the aqueous solution of an electrolyte RX. This is already known to be the case for mercurous chloride, which ionises as $(Hg_2)^{\cdot\cdot}(Cl')_2$.

The equations for equilibrium, under the assumption of one complex ion, are of the form:

$$RX \rightleftharpoons R^{\cdot} + X' \qquad (1)$$
$$2RX \rightleftharpoons (R_2)^{\cdot\cdot} + 2X' \qquad (2)$$

Let the undissociated ratio at dilution v be $1-m$; of the total dissociated part m let n, in the case of one ion, be complex.

Then, applying the law of mass action to the balanced equations (1) and (2) above, we obtain:

$$(m/v)\,.\,[(m-n)/v] = k\,.\,(1-m)/v \qquad (3)$$
$$(n/2v)\,.\,(m^2/v^2) = (c/2)\,.\,(1-m)^2/v^2 \qquad (4),$$

where k and $c/2$ are constants.

From equation (4) we have $n = cv(1-m)^2/m^2$; substituting for n in (3) we finally arrive at the equation:

$$m^2/(1-m)v = k + c\,.\,(1-m)/m \qquad (5),$$

already found by experiment to hold in the case of all acids.

By the assumption that the ions form complexes of the above type in aqueous solution, the above dissociation formula, first obtained experimentally for acids only, may be extended to cover all uni-univalent electrolytes.

R. CLAY AND SONS, LTD., BRUNSWICK ST., STAMFORD ST., S.E., AND BUNGAY, SUFFOLK.

MEDDELANDEN
FRÅN
K. VETENSKAPSAKADEMIENS NOBELINSTITUT
BAND 2. N:r 38.

THE DISSOCIATION CONSTANTS OF ORGANIC ACIDS

BY

JAMES KENDALL

◆

UPPSALA & STOCKHOLM
ALMQVIST & WIKSELLS BOKTRYCKERI-A.-B.
BERLIN
R. FRIEDLÄNDER & SOHN
11 CARLSTRASSE
LONDON
WILLIAM WESSLEY & SON
28 ESSEX STREET, STRAND
PARIS
LIBRAIRIE C. KLINCKSIECK
11 RUE DE LILLE
1913

MEDDELANDEN

FRÅN

K. VETENSKAPSAKADEMIENS NOBELINSTITUT

BAND 2. N:o 38.

The Dissociation Constants of Organic Acids.

By

JAMES KENDALL.

Communicated June 4th 1913 by S. ARRHENIUS and Å. G. EKSTRAND.

I. Introduction.

The well-known dilution law for weak electrolytes:

$$m^2/(1-m)v = k,$$

formulated by OSTWALD[1] in 1888 from the law of mass action and tested by him for a very large number of organic acids, was one of the earliest and strongest confirmations of the dissociation theory of ARRHENIUS. All normal members of the class of the so-called «weak acids» were shown by OSTWALD to obey the above law; a similar proof for the weak bases was given by BREDIG[2] in 1894. The remaining electrolytes, however, (strong acids and bases, and all salts) have not yet been brought into line with the law of mass action; the various formulae that have been proposed to express their dissociation equilibrium, such as the RUDOLPHI and VAN'T HOFF equations, are merely empirical.

---

[1] Zeitschr. phys. Chemie, **2**, 36, (1888).

[2] Zeitschr. phys. Chemie, **13**, 289, (1894).

Later investigations have shown that exact agreement with the dilution law of OSTWALD, in the case of weak acids and bases also, is only to be obtained within certain limits. There is no fixed line of demarcation between weak and strong electrolytes, the one class merges into the other through the «intermediate» or transition electrolytes. These deviate more and more appreciably from the dilution law according as their acidic or basic strength increases; the weaker of them approximate to the dilution law of OSTWALD, the stronger to the formula of VAN'T HOFF. The dilution law of OSTWALD must therefore be regarded as a limiting case, the divergences from which increase rapidly with the strength of the electrolyte.

In dilute solutions of weak electrolytes the divergences from the dilution law are wholly within the limits of experimental error, and exact agreement is obtained in the most accurate work. As the concentration of the solution is increased, however, the deviations become appreciable. The limits of the exact applicability of the dilution law have been critically discussed by WEGSCHEIDER.[1] The cause of the divergences is two-fold.

In the first place, the dilution law holds exactly only for dilute solutions; as the solutions examined become more concentrated the dissociation constant obtained *decreases,* owing (among other causes) to the diminished fluidity of the solution. This effect is first appreciable, for the majority of organic acids, between $v = 16$ and $v = 32$, and increases more and more rapidly with the concentration; more dilute solutions obey the dilution law exactly, provided that the second disturbing influence is not apparent.

This second disturbing influence works in the opposite direction to the first, and *increases* the value of the dissociation constant. Its magnitude depends upon the ionic concentration in the solution. The dilution law holds exactly only for solutions of electrolytes in which the total ionic concentration is less than one-hundredth normal (approximately); if the total ionic concentration exceeds this limit, an increasing dissociation constant is obtained.

It must be understood that the above-stated limits are merely approximate, since it is evident that the deviations will be

---

[1] Zeitschr. phys. Chemie, **69**, 503, (1909).

capable of observation at a greater dilution, the greater the accuracy with which the experiments are carried out. Also, since the two disturbing factors work against each other, their influence upon the dissociation constant will, in certain cases, be obscured.

Two difficulties have been encountered in the exact determination of the degree of dissociation of an acid by conductivity measurements, necessary for the evaluation of the dissociation constant. The first has lain in the fact that the velocity of the hydrogen ion was not accurately determined, the suggested values of the various investigations at 25° C. ranging from 338 (ROTHMUND and DRUCKER[1]) to 365 (NOYES and SAMMET[2]). The second has been the question of the influence of the impurities in the water used upon the values obtained for the equivalent conductivity of very dilute solutions, and the uncertainty of the validity of any correction applied for this influence.

In a recent paper,[3] I have determined by an indirect method (the determination of the dissociation constants of certain transition acids at very high dilutions) the velocity of the hydrogen ion, the value obtained being 347·2 at 25° C. (equivalent to 313·9 at 18° C.) with a maximum divergence of ± 0·4. In the course of the same research it was found that the disturbing influence of the impurities in the water employed in the dilution of the solutions could, in the case of the acids investigated, be neglected if the specific conductivity of the water were less than $1{\cdot}8 \times 10^{-6}$, and that the values obtained for the conductivities of the solutions up to very high dilutions could therefore be used in the calculation of the dissociation constant without the application of any correction.

It was shown, also, that the dissociation equilibrium of the intermediate or transition acids could be represented by the equation:

$$m^2/(1-m)\,v = k + c(1-m)/m, \qquad (1)$$

where k and c were constants for each particular acid. This equation holds for acids of all types; for the weak acids, c is

---

[1] Zeitschr. phys. Chemie, **46**, 827, (1903).

[2] Zeitschr. phys. Chemie, **43**, 49, (1903).

[3] Journ. Chem. Soc., **101**, 1275, (1912).

equal (or approximates to) zero; for the strong acids, *k* is equal (or approximates to) zero. In the transition acids themselves *c* increases extremely rapidly with acidic strength. The equation is intermediate between the dilution law of OSTWALD and the formula of VAN'T HOFF, both of which represent limiting cases.

In the following pages there are given the results of a number of conductivity determinations with various acids, which serve to illustrate the points mentioned above — the effect of the two disturbing influences on the dissociation constant, and the representation of the second disturbing influence in the above formula. The acids examined were of widely divergent strengths, in order that the magnitude and importance of the divergences in the various cases could be ascertained.

The first part of the experimental work recorded below consists of the conductivity measurements of the acids employed in the previous investigation for the determination of the velocity of the hydrogen ion (amplified in certain cases to include the more concentrated solutions) and of other simple acids of a normal type, the conductivities of which have been more accurately determined than was previously the case. The second part contains an investigation into the conductivities of dilute solutions of salicylic acid and some of its derivatives, which at first sight appeared to give results conflicting with those obtained from the remaining acids employed in the previous research. These results are here shown to be capable of a simple explanation.

The conductivities of the sodium (or potassium) salt of each acid through a range of dilutions were also determined in the majority of cases, in order to obtain directly the value for the equivalent conductivity of the acid at infinite dilution. For certain acids the value obtained for the velocity of the anion by previous observers was taken; in some cases also, where the direct determination of the specific conductivity of the salt at high dilutions presented special difficulties, an approximate value was obtained for the velocity of the anion by OSTWALD's[1] method of counting the number of atoms in the molecule.

The apparatus and the accurate experimental methods employed have already been fully described in the previous paper, to which reference must be made for the working details. The

---

[1] Zeitschr. phys. Chemie, **2**, 840, (1888).

water employed in the dilution of the solutions possessed a specific conductivity of $0{\cdot}9 - 1{\cdot}2 \times 10^{-6}$ at 25° C.; this is subtracted in the case of the sodium salts, but neglected in the case of the acids. All experiments were carried out at 25° C. In the tables below v indicates the dilution, μ the specific conductivity in terms of the reciprocal ohm, and m the degree of dissociation. k and c are constants having the significance expressed in equation (1) above; the expression $k + c(1 - m)/m$ represents the dissociation constant.

II. Experimental Results (Part I).

1. *Acetic Acid.* The sodium salt has been investigated by BREDIG,[1] and the value obtained for the velocity of the anion at 25° C. is 40·7. The equivalent conductivity of the acid at infinite dilution is therefore 387·9. (The value $H^{\cdot} = 347{\cdot}2$ is used troughout this paper.)

Table I. Acetic Acid.

v	μ	100 m.	$100\{k + c(1-m)/m\}$
0·989	1·443	0·372	0·001405
1·977	2·211	0·570	0·001652
3·954	3·221	0·833	0·001759
7·908	4·618	1·191	0·001814
15·816	6·561	1·692	0·001841
31·63	9·260	2·387	0·001846
63·26	13·03	3·359	0·001846
126·52	18·30	4·719	0·001847
253·04	25·60	6·600	0·001843
506·1	35·67	9·196	0·001841
1012·2	49·50	12·76	0·001844
2024·4	68·22	17·59	0·001853
∞	387·9	—	—

$k = 0{\cdot}00001845$; $c = 0{\cdot}0$.

---

[1] Zeitschr. phys. Chemie, **13**, 218, (1894).

It will be seen from the above figures that the dissociation constant is a true constant for solutions less than $v = 16$; for solutions of higher concentration the dissociation constant shows a decreasing value. Thus only the first disturbing influence is here evident; acetic acid is such a weak acid that the value of the constant c is equation (1) above is too small to exert any appreciable affect upon the dissociation constant.

The value for k obtained is slightly higher than that given by OSTWALD[1] (0·0000180) but is in accordance with the more recent work of WHITE and JONES[2] (0 0000184).

2. *Cyanacetic Acid.* The acid was obtained pure from a sample of KAHLBAUM by repeated crystallizations from benzene. Conductivity determinations of solutions of the sodium salt gave the following results.

Table II. Sodium Cyanacetate.

v	μ	100 m.
16	73·6	81·9
32	77·3	86·0
64	80·3	89·3
128	82·7	92·0
256	84·4	93·9
512	85.8	95.4
1024	87·0	96·7
2048	87·9	97·8
∞	89·9	—

By graphical extrapolation according to the formula of KOHLRAUSCH[3] the value of the equivalent conductivity of the sodium salt at infinite dilution is obtained as equal to 89·9. When the value for the velocity of the sodium ion, 51·0, is subtracted from this, the velocity of the anion is found to be 38·9. This gives the value 386·1 for the equivalent conductivity of the acid at infinite dilution, employed in Table III below.

---

[1] Zeitschr. phys. Chemie, **3**, 174, (1889).

[2] Amer. Chem. Journ., **44**, 165, (1910).

[3] Zeitschr. Elektrochem., **13**, 337, (1907).

Table III. Cyanacetic Acid.

v	μ	100 m.	$100\{k + c(1 - m)/m\}$	
			expt.	calc.
2·102	33·61	8·70	0·395	(0·473)
4·205	47·30	12·25	0·407	(0·440)
8·410	65·2	16·88	0·408	(0·417)
16·82	88·0	22·80	0·400	0·402
33·64	117·0	30·31	0·392	0·391
67.28	152.5	39·49	0·383	0·383
134·6	193·9	50·22	0·378	0·378
269·1	238·7	61·83	0.372	0·374
538·2	282·6	73·18	0·371	0·372
1076·4	320·0	82·87	0·371	0·370
2153	347·1	89·88	0·371	0·369
4306	364·8	94·50	0·376	0·369
∞	386·1	—	—	0·368

k = 0·00368; c = 0·00010.

Cyanacetic acid is a typical acid of the intermediate or transition class, and affords a good illustration of the applicability of the general formula (1) given above. The constants k and c in the general formula are here calculated as having the values 0·00368 and 0·00010 respectively, and the agreement between the experimental and calculated values obtained for the dissociation constant at each dilution is shown in the last two columns of the above table. It will be seen that the agreement is perfect, within the limits of experimental error, for solutions less concentrated than $v = 16$. At higher concentrations the first disturbing influence comes into play, and the decrease in the dissociation constant due to the concentration of the solution becomes appreciable, and finally preponderates.

The manner in which the two disturbing influences upon the dissociation constant act against each other is clearly illustrated in the above table. A maximum value in the dissociation constant exists between the dilutions $v = 4$ and $v = 8$. On one side of this maximum the first disturbing influence is the more important, on the other side the second.

3. *Dichloracetic Acid.* Conductivity determinations with solutions of the potassium salt gave the following results.

Table IV. Potassium Dichloracetate.

v	μ	100 m.
1	68.6	60·8
2	77·8	68·9
4	84·4	74·8
8	90·1	79·8
16	94·5	83·7
32	97·9	86·7
64	100·6	89·1
128	102·9	91·1
256	105·1	93·1
512	107·0	94·8
1024	108·9	96·4
∞	112·9	—

Subtracting the value for the velocity of the potassium ion, 74·5, from the value obtained at infinite dilution, we obtain the figure 38·4 for the velocity of the anion. This gives the value 385·6 for the equivalent conductivity of the acid at infinite dilution.

Table V. Dichloracetic Acid.

v	μ	100 m.	100 $\{k + c(1 - m)/m\}$	
			expt.	calc.
1	81·5	21·14	5·67	(9·33)
2	114·9	29·79	6·33	(7·68)
4	151·7	39·34	6·38	(6·70)
8	190·2	49·32	6·00	6·08
16	231·6	60·04	5·64	5·65

v	μ	$100\ m$	$100\{k + c(1 - m)/m\}$	
			expt.	calc.
32	273·1	70·83	5·38	5·34
64	309·7	80·32	5·12	5·14
128	338·7	87·82	4·96	5·02
256	359·2	93·14	4·94	4·94
512	371·5	96·34	4·96	4·90
∞	385·6	—	—	4·85

$k = 0·0485$; $c = 0·0120$.

The change in the value of the dissociation constant with the concentration is quite similar to that observed with cyanacetic acid, and the same remarks are applicable. Owing to the greater strength of dichloracetic acid, however, the second disturbing influence is here relatively more important, and the solution with maximum dissociation constant lies at a point of higher concentration, namely between $v = 2$ and $v = 4$. In general, it may be stated that the maximum of the dissociation constant will be more marked, and will lie at a higher concentration, the stronger the acid is.

4. *Trichloracetic Acid.* Conductivity determinations with solutions of the potassium salt gave the following results.

Table VI. Potassium Trichloracetate.

v	μ	$100\ m.$
2	74·7	67·2
4	81·2	73·0
8	86·3	77·6
16	90·7	81·5
32	94·4	84·9
64	97·5	87·7
128	100·1	90·0
256	102·6	92·3
512	104·9	94·3
1024	106·9	96·1
∞	111·2	—

From the figures we obtain the figure 383·9 for the value of the equivalent conductivity of the acid at infinite dilution.

Table VII. Trichloracetic Acid.

v	μ	$100\ m$.	$100\,\{k+c(1-m)/m\}$
1	181·3	47·23	42·3
2	236·2	61·53	49·2
4	275·7	71·82	45·7
8	306·1	79·72	39·2
16	327·9	85·40	31·3
32	346·0	90·14	25·7
64	356·1	92·75	18·6
128	362·1	94·32	12·2
256	369·6	96·28	9·7
512	376·0	97·95	9·1
∞	383·9	—	—

The acid is so strong that it is almost completely dissociated at the higher dilutions, and consequently the errors of experiment exert so great an influence upon the values calculated for the dissociation constant that it is impossible to determine exactly the values of the constants k and c in accordance with the general equation (1). Also, since the acid employed was not specially purified, the figures for the higher dilutions may be liable to error; they are probably rather low. It will be seen, however, that the run of the dissociation constant with dilution is precisely similar to that obtained with the two preceding acids. The point of the maximum is, as in the case of dichloracetic acid, between the dilutions $v = 2$ and $v = 4$. A comparison of the figures will show that the exact maximum point here is at a slightly higher concentration than for dichloracetic acid, a result which is in accordance with the relative strengths of the two acids.

5. *Trichlorbutyric Acid.* ($CH_3 . CHCl . CCl_2 . COOH$).) Conductivity measurements with solutions of the sodium salt gave the following results.

Table VIII. Sodium Trichlorbutyrate.

v	μ	100 m.
32	68·2	85·5
64	71·0	89·0
128	72·9	91·3
256	74·5	93·4
512	75·8	95·0
1024	76·9	96·4
∞	79·8	—

Hence we obtain the figure 376·0 for the value of the equivalent conductivity of the acid at infinite dilution.

Table IX. Trichlorbutyric Acid.

v	μ	100 m.	$100\{k + c(1 - m)/m\}$	
			expt.	calc.
5·90	237·3	63·11	18·3	(30·0)
11·80	276·8	73·62	17·4	(22·0)
23·59	308·5	82·13	15·9	(17·2)
38·63	326·4	86·80	14·8	14·8
47·18	331·8	88·22	14·0	14·2
53·98	336·0	89·35	13·9	13·7
77·26	343·9	91·46	12·7	12·7
107·96	350·4	93·20	11·8	12·1
154·5	357·0	94·95	11·5	11·4
215·9	361·2	96·05	10·9	10·9
309·0	365·1	97·10	10·5	10·5
431.8	368·2	97·90	10·7	10·2
618·0	370·9	98·62	(11·6)	10·0
∞	376·0	—	—	9·5

$k = 0{\cdot}095$; $c = 0{\cdot}35$.

The figures given in the above table differ materially from those obtained by OSTWALD.[1] This is probably due to the removal of impurities in the method of purification adopted. The acid (a sample from KAHLBAUM) dissolved readily on treatment with a small quantity of water, but left a less-soluble residue. This was filtered off, and the clear filtrate evaporated to dryness under a partial vacuum. The acid was then dissolved in ligroin, and recrystallized several times.

The excellent agreement of the general equation (1), in the case of this fairly-strong member of the transition acid type, is seen from a comparison of the experimental and calculated values for the degree of dissociation at each dilution, given in the last two columns of the above table. The figures are in accordance up to a concentration of $v = 32$ (approximately), after which the first disturbing influence begins to come into play. The experimental range does not include the point of maximum dissociation constant, but it is evident from the run of the figures that it will lie between $v = 2$ and $v = 4$, as in the case of dichloracetic and trichloracetic acids. Trichlorbutytic acid lies intermediate in acidic strength between these two.

In the above tables a series of the aliphatic acids of widely-divergent strengths, ranging from the «weak» acetic acid to the «strong» trichloracetic acid, has been examined. The remainder of this section is occupied with a consideration of a few members of the aromatic acid series.

6. *o-Chlorbenzoic Acid.* This acid was prepared by the distillation of salicylic acid with phosphorus pentachloride, as described by HÜBNER.[2] The mixed chlorides obtained were decomposed by water, and steam was passed through the solution for several hours until all salicylic acid was removed. The o-chlorbenzoic acid was then obtained pure by recrystallization from water.

Conductivity measurements with solutions of the sodium salt gave the following results.

---

[1] Zeitschr. phys. Chemie, **3**, 194, (1888).

[2] Annalen, **222**, 192, (1884)

Table X. Sodium o-Chlorbenzoate.

v	μ	100 m.
32	71·5	85·3
64	74·3	88·7
128	76·6	91·4
256	78·4	93·6
512	79·8	95·2
1024	80·9	96·5
2048	81·8	97·6
∞	83·8	—

From the above figures we deduce the value 380·0 for the equivalent conductivity of the acid at infinite dilution.

Table XI. o-Chlorbenzoic Acid.

v	μ	100 m.	$100\{k + c(1-m)/m\}$	
			expt.	calc.
150·1	134·6	35·42	0·1294	0·1293
300·2	174·0	45·78	0·1288	0·1288
600·4	218·0	57·36	0·1286	0·1285
1201	262·6	69·10	0·1287	0·1283
2402	302·1	79·48	0·1283	0·1282
4804	333·0	87·62	0·1292	0·1281
∞	380·0	—	—	0·1280

$k = 0·001280$; $c = 0·000007$.

The acid is so nearly a typical weak acid, owing to its small dissociation constant, that the increase in the value of the constant with increasing concentration can be proved only by very careful determinations. The run of the figures in the above table, however, shows conclusively that such an increase does exist. The small solubility of the acid in water prevents the extension of the series to the higher concentrations.

7. *o-Nitrobenzoic Acid.* The acid was purified by repeated crystallizations from water. Conductivity determinations with solutions of the sodium salt gave the following results.

Table XII. Sodium o-Nitrobenzoate.

v	μ	$100\ m$.
16	66·9	80·4
32	70·6	84·9
64	73·6	88·5
128	76·0	91·3
256	77·9	93·6
512	79.3	95·3
1024	80·4	96·6
2048	81·2	97·6
∞	83·2	—

From these figures we obtain the value 379·4 for the equivalent conductivity of the acid at infinite dilution.

Table XIII. o-Nitrobenzoic Acid.

v	μ	$100\ m$.	$100\{k + c(1 - m)/m\}$	
			expt.	calc.
32	139·7	36·83	0·671	0·675
64	179·0	47·20	0·659	0·656
128	221·9	58·50	0·644	0·643
256	265·0	69·85	0·632	0·634
512	303·6	80·04	0·626	0·628
1024	333·5	87·90	0·623	0·624
2048	353·6	93·22	0·624	0·622
4096	365·3	96·32	0·609	0·621
∞	379·4	—	—	0·620

$k = 0{\cdot}00620$; $c = 0{\cdot}00032$.

The increased strength of the acid, in comparison with o-chlorbenzoic acid, is marked by a large increase in the value of the constant c, and consequently a large variation in the dissociation constant with dilution.

8. *meta-meta-Dinitrobenzoic Acid.* The acid was prepared by the nitration of benzoic acid, as described by SHUKOFF,[1] and purified by several crystallizations from water. Conductivity measurements with solutions of the sodium salt gave the following results.

Table XIV. Sodium m-m-Dinitrobenzoate

v	μ	100 m.
64	71·3	89·0
128	73·2	91·4
256	75·0	93·6
512	76·3	95·3
1024	77·3	96·7
2048	78·1	97·5
∞	80·1	—

Hence we obtain the figure 376·3 for the value of the equivalent conductivity of the acid at infinite dilution.

Table XV. m-m-Dinitrobenzoic Acid.

v	μ	100 m.	$100\{k + c(1 - m)/m\}$	
			expt.	calc.
254·5	175·7	46·70	0·1607	0·1604
509·0	219·0	58·20	0·1591	0·1592
1018	262·7	69·80	0·1585	0·1583
2036	301·5	80·13	0·1586	0·1577
4072	330·9	87·94	0·1574	0·1574
8144	350·7	93·22	0·1569	0·1572
∞	376·3	—	—	0·1570

$k = 0·001570$; $c = 0·000030$.

---

[1] Berichte, **28**, 1800, (1895).

The acid is only slightly stronger than o-chlorbenzoic acid, but the variation of the dissociation constant with dilution is much greater, owing to the rapid increase in the value of c with the acidic strength.

9. *m-Chlor-m-Nitrobenzoic Acid.* The following method of preparation was adopted. m-m-Dinitrobenzoic acid was first reduced to m-nitro-m-aminobenzoic acid, as described by HÜBNER,[1] and then chlorinated by the SANDMEYER method. An almost theoretical yield of the crude acid was obtained, and was purified by several recrystallizations from water, in which the acid is very sparingly soluble.

The conductivity of the sodium salt was not investigated, the approximate value 378·0 being obtained for the equivalent conductivity of the acid at infinite dilution by the method of OSTWALD.

Table XVI. m-Chlor-m-nitrobenzoic Acid.

v	μ	$100\ m.$	$100\{k + c(1 - m)/m\}$
456·4	165·6	43·8	0·0748
912·8	208·8	55·3	0·0747
1825·6	253·4	67·0	0·0747
3651	294·5	77·9	0·0752
∞	(378·0)	—	—

$k = 0·000748.$

Owing to the uncertainty of the infinite value, the agreement of the dissociation constant with the general formula (1) cannot be tested. In any case, the acid is so weak that it is very unlikely that any variation in the dissociation constant could be observed in the high dilutions available for experiment.

III. General Conclusions (Part I).

In the above pages the variation in the dissociation constant with the dilution, throughout a series of acids of widely-

---

[1] Annalen, **222**, 81, (1884).

livergent strengths, has been examined. The separate effects f the two disturbing influences upon the dissociation constant – the total concentration influence causing a decreasing value vith increasing concentration, and the ionic concentration inluence causing an increasing value with increasing concentration – have been considered. The relative importance of the two listurbing influences, at different dilutions and for different acidic trengths, has been investigated.

At dilute solutions (v greater than 32) the ionic concenration influence is alone important, and the dissociation constant ises with the concentration, more or less rapidly according to he acidic strength. At more concentrated solutions (v less than 2) the total concentration influence begins to come into play, nd soon becomes the more important factor, the dissociation onstant sinking rapidly with increasing concentration. There s thus an intermediate point of «maximum dissociation constant». his maximum was found to be more marked, and to lie at a igher concentration, the stronger the acid under examination.

The applicability of the general formula:

$$m^2/(1-m)v = k + c(1-m)/m \tag{1}$$

or the expression of the dissociation equilibrium of the various cids examined has been tested, and in all cases good agreement etween the experimental and calculated values for the dissocition constant at the higher dilutions (v greater than 32) has een obtained. The values of the constants k and c for the ifferent acids are collected in the following table.

Table XVII. Dissociation Constants of Organic Acids.

	k	c
Acetic acid	0·00001845	—
Cyanacetic acid	0·00368	0·00010
Dichloracetic acid	0.0485	0·0120
Trichlorbutyric acid	0·095	0·35
o-Chlorbenzoic acid	0·001280	0·000007
o-Nitrobenzoic acid	0·00620	0·00032
m-m-Dinitrobenzoic acid	0·001570	0·000030
m-Chlor-m-nitrobenzoic acid	0·000748	—

It will be seen that the value of the constant c increases regularly with the acidic strength, but far more rapidly. In other words, the deviations from the dilution law of OSTWALD in dilute solutions, which are negligible in the case of weak acids like acetic acid, increase extremely rapidly with the acidic strength.

The general dissociation formula given above was deduced empirically from the results of conductivity determinations. Almost simultaneously two other general dissociation formulae, differing but slightly from the above, were brought forward. BRAY and KRAUS,[1] using results obtained mainly from non-aqueous solutions of electrolytes, have deduced the relation:

$$(Cy)^2/C(1-y) = K + D(Cy)^m,$$

where C is the concentration of the electrolyte in the solution, y the degree of ionization, and K, D, and m are constants. MACDOUGALL[2] has shown that the dissociation of aqueous solutions of strong electrolytes can be represented by the formula:

$$K = Cy^2/(1-y)\{1 + m(Cy)^n\}$$

where K, m, and n are constants. n is found to approximate to the value 2/3, for which a theoretical explanation is attempted. The same equation has previously been proposed by LIEBENOW,[3] under the form:

$$m^2/(1-m)v = k + c(m/v)^{\frac{2}{3}}$$

on different theoretical grounds. It is evidently a special form of BRAY's and KRAUS's general equation, with one constant fixed.

That the general equation (1) is identical with the formula of BRAY and KRAUS may be shown by the application of STORCH's[4] law:

$$(Cy)^n/C(1-y) = \text{constant}.$$

---

[1] Trans. Amer. Electrochem. Soc., **21**, 143, (1912).

[2] Journ. Amer. Chem. Soc., **34**, 855, (1912).

[3] Zeitschr. Elektrochem., **8**, 933, (1902).

[4] Zeitschr. phys. Chemie, **19**, 13, (1896); **26**, 545, (1900).

It must be noticed, however, that the general formula (1) contains only two constants, whereas the equation of BRAY and KRAUS contains three; the former can therefore not be expected to show the same level of agreement as the latter with the results of experiment. Thus is does not apply to certain cases of the non-aqueous solutions investigated by BRAY and KRAUS.[1] For aqueous solutions, however, the above tables show that the agreement is extremely satisfactory.

The exact theoretical significance of the general equation:

$$m^2/(1-m)v = k + c(1-m)/m \qquad (1)$$

does not seem to be apparent. The equation has been deduced by the author[2] from a theoretical basis under the assumption of the existence of complex ions in the solution, but such an assumption introduces the difficulty of reconciling the freezing-point and conductivity data for solutions of strong electrolytes, and does not appear to rest upon a sufficiently firm foundation.

The presence of the expression $(1-m)$ as a factor in the right hand side of the equation, directly influencing the dissociation constant, seems to point to the fact that the activity of the undissociated molecule is the final cause of the variation in the constant. When the analogous case of neutral salt action in catalysis is considered, this view receives some confirmation.

The catalytic activity of an acid is not reduced, by the addition of a salt containing a common ion, in the ratio demanded by the reduction of the hydrogen ion concentration; in some cases it is considerably increased. This increase is now ascribed to the catalytic activity of the undissociated portion of the acid, which may even surpass the catalytic activity of the hydrogen ion itself. SNETHLAGE,[3] employing the experimental results of BRAUNE[4] and of ARRHENIUS,[5] has drawn the conclusion that the ratio of the catalytic activity of the undissociated molecule as compared with the activity of the hydrogen ion is greater, the greater the strength of the acid. This conclusion has recently been confirmed by TAYLOR.[6]

---

[1] Private communication from D:r BRAY, April 1913.

[2] Proc. Chem. Soc. **28**, 255, (1912).

[3] Zeitschr. Elektrochem., **18**, 539, (1912).

[4] See BREDIG, Zeitschr. Elektrochem., **18**, 535, (1912).

[5] Zeitschr. phys. Chemie, **31**, 197, (1899).

[6] Meddel. från K. Vet.-Akad:s Nobelinstitut. Bd 2. N:o 34, (1913).

The analogy between the increase in acidic strength by addition of a neutral salt, and by concentration of the solution, has been clearly pointed out by ARRHENIUS:[1]

»Diese Erhöhung (nämlich der Dissociationskonstante von schwachen Säuren durch Salzzusatz) entspricht gänzlich der Zunahme der Dissociationskonstante von Salzen bei weiterem Salzzusatz, d. h. bei zunehmender Konzentration.» Also, »Diese Salzwirkung auf die Dissociationskonstante ist am stärksten für ein Salz, und grösser für die untersuchten Säuren, je stärker sie dissociiert sind. Wahrscheinlicherweise ist demnach das OSTWALD'sche Verdünnungsgesetz für keinen Körper streng gültig; bei den schwächsten Säuren und Basen trifft es sehr nahe (innerhalb der Versuchsfehler) zu, die Abweichungen davon steigen mit der Dissociationskonstante der Säure (oder Basis) und werden am grössten für die am stärksten dissociierten Körper (Salze, starke Säuren und Basen).»

It will be seen that the views of SNETHLAGE — that the activity of the undissociated molecule increases with the acidic strength — and of ARRHENIUS — that the divergences from the dilution law increase with the acidic strength — are in perfect agreement with the conclusions drawn from the figures in the above tables. In fact, the parallelism between the variation in the ratio of the activity of the undissociated molecule to that of the hydrogen ion with the acidic strength, as given by SNETHLAGE, and the variation in the constant c in the general equation (1) with the acidic strength (see Table XVII above), is most striking. Both quantities increase with the strength of the acid under consideration, and both far more rapidly.

The study of the activity of the undissociated portion of an electrolyte in solution is probably destined to throw considerable light upon the problem of strong electrolytes, and this activity is a factor which finds expression (though only empirically) in the general equation for the dissociation equilibrium of electrolytes given above.

---

[1] Zeitschr. phys. Chemie, **31**, 228—9, (1899).

IV. **Experimental Results (Part II).**

The following section is occupied with conductivity determinations of solutions of salicylic acid and some of its derivatives, and with a discussion of the results.

The tables are arranged as in Section II of the paper, with the exception that here, for the sake of simplicity, the dissociation constant is denoted by k, in accordance with the OSTWALD dilution law.

10. *Salicylic Acid.* Conductivity determinations with solutions of the sodium salt give the following results. (The figures of BREDIG,[1] reduced to the modern units, are appended for comparison.)

Table XVIII. Sodium Salicylate.

v	μ	μ (BREDIG)
32	72·2	72·6
64	75·4	75·9
128	77·8	78·2
256	79·7	80·2
512	81·9	82·2
1024	84·4	84·7
2048	87·1	—
∞	—	86·5

The two series are in good agreement with each other, but it will be seen that in each, at high dilutions, the differences between the values for two succeeding dilutions instead of decreasing in the normal way, show an increase. It does not seem possible therefore to deduce with any degree of certainty a value for the equivalent conductivity at infinite dilution, indeed the figure deduced by BREDIG, (86·5), is already surpassed at dilution 2048, (87·1). It is evident that sodium salicylate, at high dilutions, does not behave like a normal salt.

The value for the equivalent conductivity of the acid at infinite dilution must be obtained indirectly, by the method of

---

[1] Zeitschr. phys. Chemie, **13**, 219, (1894).

OSTWALD. As a good approximation the velocity of the anion may be placed midway between the values for the anions of benzoic and chlorbenzoic acids, as given by BREDIG;[1] hence we obtain the value 33·0. This gives the fignre 380·2 for the equivalent conductivity of the acid at infinite dilution.

Table XIX. Salicylic Acid.

v	μ	100 m	100 k
100	105·3	27·70	0·1061
200	139·5	36·69	0·1064
400	179·7	47·28	0·1059
800	224·4	59·01	0·1063
1600	268·9	70·73	0·1068
3200	307·9	80·99	0·1078
6400	337·6	88·80	0·1100
—	380·2	—	—

$k = 0·00106.$

It will be seen that the dissociation constant is not constant at the more dilute solutions, but shows a slight increase. A careful repetition of the experiments confirmed this. It is true that if a higher figure is taken for the value of the equivalent conductivity of the acid at infinite dilution (about 1·5 units are required) a fairly constant value for the dissociation constant is obtained, but subsequent experiments indicate that there is another cause for the increase.

A rising dissociation constant at high dilutions is a characteristic property of dibasic acids, and appears as soon as the second stage of their dissociation becomes appreciable. Now salicylic acid contains, in addition to a carboxyl group, a phenol group. Phenol itself is such an exceedingly weak acid, as determined by WALKER and CORMACK,[2] that its acidic strength must be greatly increased before it can influence appreciably the conductivity measurements of salicylic acid, even at very high dilutions, since the hydrogen ion concentration already

---

[1] loc. cit.

[2] Journ. Chem. Soc., **77**, 18, (1900).

present depresses the ionisation of the phenol almost to zero. We have several reasons, however, for believing that the proximity of the carboxyl group is sufficient to produce such an increase in the acidic strength of the phenol, and that salicylic acid is weakly dibasic. The acid does not titrate at all sharply, with phenolphthalein as an indicator, as has been noticed by several other investigators, e. g. WALKER and WOOD.[1] The equivalent conductivity of the sodium salt shows an abnormal increase at high dilutions, as is seen in Table XVIII above. Finally, the introduction of other groups into the benzene nucleus is found to increase the dibasic characteristics still more, as will be seen in the following tables.

11. *5-Bromsalicylic acid.* This acid was prepared from salicylic acid, as described by HEWITT, KENNER and SILK,[2] and purified by repeated crystallisations from water. The sodium salt was also prepared, but as no satisfactory values could be obtained for its equivalent conductivity at high dilutions, the value for the equivalent conductivity of the acid at infinite dilution was deduced (approximately) from the number of atoms in the molecule, by the method of OSTWALD. This remark applies also to the other derivatives of salicylic acid examined below.

Table XX. 5-Bromsalicylic Acid.

v	μ	100 m	100 k
256	203·4	53·5	0·241
512	248·1	65·3	0·240
1024	290·4	76·4	0·242
2048	324·8	85·5	0·245
4096	349·2	91·9	0·254
∞	380·0	—	—

$k = 0·00241.$

Here it will be seen that the rise in the dissociation constant at high dilutions is more marked than is the case with salicylic acid. It is very improbable that this increase is due

---

[1] Journ. Chem. Soc., **73**, 620, (1898).

[2] Journ. Chem. Soc., **85**, 1228, (1904).

to the value taken for the equivalent conductivity of the acid at infinite dilution being too low, since this number was intentionally taken at its maximum possible figure, the value for benzoic acid being only 0·5 units higher. The acid is evidently weakly dibasic; it titrates extremely badly against phenolphtalein, the end-point being very indefinite.

12. *1-2-4-Oxysalicylic Acid.* A sample from KAHLBAUM was purified by several recrystallizations from water.

Table XXI. 1-2-4-Oxysalicylic Acid.

v	μ	$100\, m$	$100\, k$
64	63·2	16·6	0·0518
128	85·8	22·6	0·0514
256	115·2	30·3	0·0515
512	151·6	39·9	0·0517
1024	194·1	51·1	0·0521
2048	239·9	63·1	0·0528
∞	380·0	—	—

$k = 0·000516$.

The dissociation constant of this acid also shows a steady rise at high dilutions.

13. *?-1-2-4-Bromoxysalicylic Acid.* A brominated derivative of the above acid was prepared from it by the method of ZEHENTER,[1] and purified by recrystallizations from water. The position of the bromine atom in the benzene nucleus is unknown.

Table XXII. ?-1-2-4-Bromoxysalicylic Acid.

v	μ	$100\, m$	$100\, k$
512	193·0	50·8	0·102
1024	238·1	62·7	0·103
2048	282·3	74·3	0·105
4096	319·6	84·1	0·109
∞	380·0	—	—

$k = 0·00102$.

---

[1] Monatsh., **8**, 293, 1887).

The dibasic characteristic of the acid is again marked by a rise in the dissociation constant at high dilutions. In this case an additional proof of the strength of the second acidic group can be obtained, for the acid, by titration against phenolphthalein, is a dibasic acid. The phenol group is therefore, in this acid, more strongly acidic than phenolphtalein. By titration against methyl orange the acid is monobasic.

14. *1-2-5-Oxysalicylic Acid.* A sample from KAHLBAUM was purified by several recrystallizations from water.

Table XXIII. 1-2-5.Oxysalicylic Acid.

v	μ	100 m	100 k
64	86·6	22·8	0·105
128	116·3	30·6	0·105
256	153.5	40·4	0·107
512	196·8	51·8	0·109
1024	242·8	63·9	0·110
2048	287·0	75·5	0·114
∞	380·0	—	—

$k = 0{\cdot}00105$.

A steady increase in the value of the dissociation constant at high dilutions is again evident.

15. *?-1-2-5-Bromoxysalicylic Acid.* A brominated derivative of the above acid was prepared from it by the method of v. HEMMELMAYR,[1] and purified by recrystallizations from water. The position of the bromine atom in the benzene nucleus is unknown.

Table XXIV. ?-1-2-5-Bromoxysalicylic Acid.

v	μ	100 m	100 k
128	189·4	49·8	0·387
256	234·6	61·7	0·389
512	278·5	73·3	0·393

---

[1] Monatsh., **30**, 258, (1909).

v	μ	100 m	100 k
1024	315·4	83·0	0·396
2048	342·5	90·1	0.402
4096	360·2	94·8	0·411
∞	380·0	—	—

$k = 0{\cdot}00387$.

Here again there is a steady increase in the value of the dissociation constant at high dilutions. From the above tables (XVIII—XXIV) it will be evident that the effect of the phenolic group upon the dissociation constant of salicylic acid and its derivatives is appreciable in very dilute solutions. The acids all behave as dibasic acids, in which the degree of secondary dissociation is extremely small. In one case, however, (the brominated derivative of 1-2-4-oxysalicylic acid) the second acidic group is more strongly acid than phenolphthalein.

V. Summary.

From the conductivity results of a series of acids of widely-divergent strengths, the limits within which OSTWALD's dilution law for weak electrolytes is exactly obeyed have been discussed. The relative importance of the two disturbing influences — the total concentration influence and the ionic concentration influence — upon the dissociation constants has been considered in the various acids, and the applicability of the general dissociation formula:

$$m^2 / (1 - m)\, v = k + c\, (1 - m) / m$$

has been examined.

The analogy between the results of this investigation and those obtained by SNETHLAGE and ARRHENIUS in the question of neutral salt action in catalysis has been pointed out.

An examination of salicylic acid and some of its derivatives has shown that the effect of the phenolic group upon the dissociation constant is appreciable at high dilutions, and that these acids are weakly dibasic.

The above investigation has been completed at the Nobel Institute of Physical Chemistry, after having been commenced at the University of Edinburgh and repeated (in part) at the Technological Institute, St. Petersburg. I have much pleasure in expressing here to Professor SVANTE ARRHENIUS, to Professor JAMES WALKER, and to Dr. DANIEL GARDNER, of the above institutions respectively, my sincere thanks for the facilities afforded me in the execution of the research.

Nobel Institutet, Experimentalfältet, June 1913.

◆

Tryckt den 11 november 1913.

Uppsala 1913. Almqvist & Wiksells Boktryckeri-A.-B.

[Reprinted from the Journal of the American Chemical Society.
Vol. XXXVI. No. 6. June, 1914.]

The Extension of the Dilution Law to Concentrated Solutions

By James Kendall

[Reprinted from the Journal of the American Chemical Society.
Vol. XXXVI. No. 6. June, 1914.]

[CONTRIBUTIONS FROM THE DEPARTMENT OF CHEMISTRY OF COLUMBIA UNIVERSITY,
No. 233.]

THE EXTENSION OF THE DILUTION LAW TO CONCENTRATED SOLUTIONS.

BY JAMES KENDALL.

Received January 23, 1914.

The dilution law of Ostwald:

$$\gamma^2/(1 - \gamma).v = K; \quad \text{or} \quad c_i^2/c_u = K, \qquad (1)$$

(γ = fraction ionized, v = dilution, c_i = ionic concentration, c_u = concentration of un-ionized part, K = dissociation constant), is apparently securely based upon the principle of mass action, and yet has definite limits in its *exact* applicability to aqueous solutions of electrolytes. The law is found, on examination,[1] to break down in two directions.

In the first place, it is followed exactly only if the *ionic concentration* is small. When a certain limiting ionic concentration (approximately $0.01\ N$) is exceeded, K begins to increase, and increases steadily with c_i. Divergences from the dilution law in this direction are, therefore, met with in all strong electrolytes, and also in many of the transition electrolytes[2] at the higher concentrations. (Anomaly of strong electrolytes.)

In the second place, the law is followed exactly only if the *total concentration* of the electrolyte is small. The limit of exact applicability is

[1] Wegscheider, *Z. physik. Chem.*, **69**, 603 (1909).

[2] Kendall, *J. Chem. Soc.*, **101**, 1275 (1912).

TABLE II.—ACETIC ACID, 25° (RIVETT AND SIDGWICK).

$1/v$.	Λ/v.	100 K.	η.	100 K_1.	d.	100 K_2.
2.9771	1.854	0.00077	1.347	0.00139	1.0235	0.00165
2.0060	1.789	0.00106	1.230	0.00161	1.0162	0.00180
1.4886	1.671	0.00125	1.169	0.00172	1.0122	0.00186
1.3374	1.620	0.00131	1.150	0.00173	1.0109	0.00186
1.0029	1.474	0.00144	1.112	0.00179	1.0084	0.00189
0.8917	1.415	0.00150	1.098	0.00181	1.0074	0.00190
0.6687	1.264	0.00160	1.073	0.00184	1.0036	0.00191
0.3722	0.9722	0.00170	1.041	0.00184	1.0032	0.00188
0.1861	0.7079	0.00181	1.021	0.00188	1.0017	0.00190
0.0930	0.4986	0.00180	1.010	0.00184	1.0009	(0.00185)
0.0402	0.3372	0.00192	1.004	0.00195	1.0004	(0.00195)

The experimental data in Table II are selected from a series of determinations by Rivett and Sidgwick;[1] the density and viscosity results in both tables are also obtained from the same paper, by interpolation from the figures there given. (Λ = equivalent conductivity, η = relative viscosity (water unity), d = relative density.)

It will be seen, from the third column of these tables, that the dissociation constant 100 K is a true constant for solutions less concentrated than $v = 16$, but that for higher concentrations the value obtained decreases, first slowly and afterwards more rapidly. (In Table II the constancy of the values at high dilutions is rather obscured by the relatively greater experimental error.)

There is, however, a viscosity correction to be applied to these results. The exact relation between conductivity and viscosity has been investigated and established by the researches of Green,[2] Johnston,[3] Washburn,[4] and Noyes and Falk.[5] The general conclusion drawn is that the simple equation,

$$\Lambda\eta/\Lambda_\circ\eta_\circ = \text{constant}, \tag{4}$$

($\Lambda_\circ$ = equivalent conductivity and $\eta_\circ$ = viscosity at zero concentration of solute) is not exactly followed; but rather the equation,

$$\Lambda/\Lambda_\circ = \text{constant } (\eta_\circ/\eta)^n, \tag{5}$$

(n is a constant varying with the electrolyte.) Nevertheless, n is in most cases so nearly equal to unity, and its exact determination is a matter of such difficulty, that we may assume, with Noyes, that the safest correction we can make is by the use of equation (4) above. In any case, the residual error will be small, unless very high concentrations (above normal) are considered.

Hence we obtain the corrected values for the dissociation constant by

---

[1] Rivett and Sidgwick, *J. Chem. Soc.*, **97**, 734 (1910).

[2] Green, *J. Chem. Soc.*, **93**, 2049 (1908).

[3] Johnston, THIS JOURNAL, **31**, 1010 (1909).

[4] Washburn, *Ibid.*, **33**, 1461 (1911).

[5] Noyes and Falk, *Ibid.*, **34**, 454 (1912).

employing the expression $\Lambda\eta$ instead of the experimental value Λ for the equivalent conductivity in the above tables. These corrected values are given under the heading $100 K_1$. The application of the viscosity correction has not destroyed the divergences at the highest concentrations, where a steady decrease in the dissociation constant is still evident. Further examination into the cause of these divergences is therefore necessary.

In the following section, the dilution law itself is critically examined and its exact theoretical basis tested. A modified form of the dilution law is tentatively proposed, which is subsequently applied to the above experimental data and found to account for the divergences up to very high concentrations.

A Modification of the Dilution Law.—The exact significance of the Ostwald dilution law will first be studied from the simple kinetic standpoint.

We have, for a uni-univalent electrolyte of the type RX, the dissociation equation,

$$RX \rightleftharpoons R^+ + X^-, \qquad (6)$$

from which, by the application of the law of mass action, the dilution law is immediately obtained in the form

$$c_i^2/c_u = K. \qquad (7)$$

The right-hand side of equation (6) presents no difficulty from the kinetic standpoint.[1] The concentration of each ion is c_i, and by the impact of two ions of opposite charge the undissociated salt is formed, with the mutual neutralization of the charges. The mechanism of the equilibrium reaction on the other side of the equation, however, is by no means so clear. *A definite conception of the nature of the reaction on the left-hand side of the equation has not yet been obtained, and, in spite of the importance of the question, it does not seem to have attracted any great attention, or to have been answered in any but the vaguest manner.*

The above statement may be further emphasized by an extract from a recent communication by Walden:[2] "The greater the dielectric constant of the interposed solvent, the less is the electrostatic attractive force [be-

---

[1] That is, so long as the ionic concentration is small. If c_i exceed a certain limit, then the electrostatic forces existing between the charged ions become of importance in the equilibrium, and we have the "anomaly of strong electrolytes."

[2] Walden, THIS JOURNAL, 35, 1649 (1913). This communication first reached the author's notice after the present investigation was practically completed. Walden has attacked the subject from precisely the opposite direction to that here followed, namely, by a consideration of the "anomaly of strong electrolytes" from the increase in the dielectric constant of the solvent due to the dissolved salt. The view is expressed that "the process of disaggregation of the polymerized salt molecules also causes and induces the process of ionic cleavage." The conclusions drawn in the present paper are not necessarily in opposition to those advanced by Walden, but may rather be considered as confirming and supplementing them, as will be shown later.

tween ions of unlike charge], and with the greater difficulty does the recombination to electrically neutral molecules take place. Nevertheless, the neutral molecules will be formed in the solution. Why then do they again break up into ions? *For what reason does the neutral salt molecule break up into ions at all, as soon as it enters into solution?* This fundamental question has, up to the present, not been answered. Strangely enough, we do not even make a serious attempt at its solution."

In the dilution law, as it stands, it is tacitly assumed that the undissociated molecules RX break up *quite spontaneously* into the separate ions R^+ and X^-. The whole equilibrium is taken to be exactly analogous to that existing in gaseous dissociation, and the analogy is indeed sufficiently striking. Nevertheless, there are fundamental differences between the two phenomena of gaseous and ionic dissociation, and one is the influence of the solvent medium upon the equilibrium in the latter case. *The nature of the solvent plays an important part in determining the degree of dissociation of the dissolved electrolyte.*

The rôle of the solvent in the dissociation equilibrium (except from the point of view of the dielectric constant) has been strangely neglected by the followers of the dissociation theory of Arrhenius.[1] The tendency has been to treat the solvent simply as so much "dead space." The upholders of the solvate theory, on the other hand, have referred all dissociation phenomena to interaction between solvent and solute.

A general, but indefinite, feeling of dissatisfaction with the present position (as is indicated above by Walden) has certainly existed among the followers of the dissociation theory, and this feeling has occasionally found its way into print in well-known text-books, where definitions of electrolytic dissociation may be found, which undoubtedly do not agree with the hypothesis of spontaneous dissociation of the undissociated molecule tacitly assumed above. For example, Stieglitz[2] states: "When an ionogen is dissolved in water, its molecules are immediately, more or less completely, *dissociated by the water* into smaller fragments or molecules of unlike composition." Similarly, Alexander Smith[3] writes: "The conducting power of the solution is indissolubly connected with the fact that the original molecules of the solute have been broken up by the solvent into smaller molecules containing one or more atoms." Nernst[4]

---

[1] Compare Lowry, *Science Progress* (1908).

[2] Stieglitz, "Qualitative Chemical Analysis," Part I, page 41. The italics are in the original. See also pages 61–66, where the ionizing power of solvents (as related to their dielectric behavior, the unsaturated condition of their simple molecules, and their power of association) is critically examined, and the above idea is repeatedly expressed.

[3] Alexander Smith, "Introduction to Inorganic Chemistry," page 317.

[4] Nernst, *Theoretische Chemie, Sechste Auflage* (1909), page 534. See also repeated statements on pages 378–80.

states: "Der Umstand, dass gerade das Wasser die ganz besondere Fähigkeit besitzt, gelözte Stoffe electrolytisch zu spalten, legt die Vermutung nahe, dass bei der Ionenspaltung chemische Verbindungen mit dem Wasser eine Rolle spielen." Here there is not only the statement that *the solvent* splits up the undissociated molecules into the separate ions, but the possibility also is noted that, in so doing, the solvent actually combines with the solute to form hydrates and hydrated ions.[1] Ostwald[2] himself goes so far as to say: "Das Wasser nimmt, in Bezug auf seine Fähigkeit elektrolytische Lösungen zu bilden, oder Stoffe in Ionen zu spalten, eine ausgezeichnete Stellung ein." Arrhenius[3] also speaks of "die Fähigkeit der Lösungsmittel, Elektrolyte in Ionen zu zerlegen."

Now, if the molecules of the undissociated salt in the solution are indeed broken up *by the molecules of the solvent* into the separate ions, then the concentration of the solvent in the solution should appear in the equation of equilibrium, and the simple dilution law is not valid. The equation is modified into the form:

$$c_i^2/c_u.c_s = K, \qquad (7)$$

(c_s = concentration of solvent in the solution.) At moderately high dilutions c_s becomes practically constant, and the equation reduces to the simple dilution law. At higher concentrations of solute, c_s begins to diminish, since molecules of solvent are being replaced in the solution by molecules of solute.

We may write equation (7) in the form:

$$c_i^2/c_u = Kc_s,$$

from which it is at once evident that the equation is *qualitatively* in accordance with the fact, shown by the results of experiment, that c_i^2/c_u is not constant at high concentration of solute, but exhibits a *decreasing* value. The validity of the equation at high concentrations may be tested *quantitatively* with the help of the density data.

This is done for acetic acid in the last columns of Tables I and II above. The values under 100 K are corrected by means of the ratio:

weight of solvent in one liter of pure solvent/weight of solvent in one liter of solution

and the results are given under 100 K_2, which therefore represents 100 K in equation (7) above.

---

[1] The subject of the hydration of ions has recently attracted much attention; for a summary of the bearing of the subject on the present discussion see Wegscheider, *Z. physik. Chem.*, 69, 605–6 (1909). Ciamician, reviewing the results obtained, makes the significant statement: "Alles scheint darauf hinzuweisen dass die Annahme, nach welcher die Dissociation in Lösungen durch das Lösungsmittel vermittelt und bedingt wird, heute an Berechtigung gewonnen hat und den bekannten Tatsachen am besten entspricht," *Z. physik. Chem.*, 69, 100 (1909).

[2] Ostwald, *Lehrbuch der Allgemeinen Chemie*, Band 2, Teil 1 (1893), page 705.

[3] Arrhenius, *Lehrbuch der Elektrochemie* (1901), page 55. Also "Theories of Chemistry" (1907), page 83.

It will be seen that the values for the dissociation constant are now *really constant*, up to concentrations of solute well above normal. (In very highly concentrated solutions there is still a slight decrease; this is considered in a later section.) Equation (7) is therefore valid for the expression of the dissociation constant of acetic acid *in concentrated solutions*. In subsequent tables it is shown that it is similarly applicable to other weak electrolytes. Meanwhile, some theoretical consequences of the hypothesis put forward above will be considered and its legitimacy tested.

In one respect it will, at first sight, appear that the dilution law of Ostwald claims preference over the modified law advanced above, namely in its simplicity. In equation (7) a variable factor, c_s, has been brought into the equation for the dissociation equilibrium, and this factor varies with the concentration in the desired direction for improving the constancy of K at high concentrations. Hence it may seem that the introduction of the variable factor c_s into the equation is simply a mathematical trick, which improves the agreement with the experimental results only by destroying the original simplicity of the dilution law. If this were indeed so, then the generally accepted theoretical basis lying behind the dilution law of Ostwald (the assumption of spontaneous dissociation of the undissociated molecule) could not legitimately be called into question here.

In the following section, however, it will be demonstrated that the above objection is not valid. The equilibrium of ionic dissociation has, so far, been considered only from the simple kinetic standpoint. When an exact thermodynamic examination is made, it is found that the original simplicity of the dilution law is not sacrificed by the modified view taken of the nature of the dissociation equilibrium; but that the dilution law has, on the other hand, *actually become less complicated*, inasmuch as certain simplifying assumptions, necessary for the development of the equation in its original form, may now be dispensed with.

Thermodynamic Investigation of the Dissociation Equilibrium.—The dilution law is first developed below in its original form and examined from the thermodynamic view-point. The modified form of the law, as deduced from the theoretical considerations advanced above, is then similarly derived, and the results compared.

For the Ostwald dilution law, the line of argument followed is substantially that given by Partington[1] in an investigation on the ionic equilibrium in solutions of electrolytes.

"The thermodynamic investigations lead to the equilibrium isotherm:[2]

---

[1] Partington, *J. Chem. Soc.*, **97**, 1159 (1910).

[2] It has been pointed out to the author by D. A. MacInnes that this is not a *purely* thermodynamic equation. From the laws of thermodynamics alone we arrive at the

$$n' \log c' + n'' \log c'' + n''' \log c''' + \ldots\ldots\ldots = \log K,$$

where K is a function of the temperature and total pressure for given components, but is constant at constant temperature and pressure. K is independent of the molecular concentration (c) and numbers of molecular weights (n) of the components. Thus:

$$c'^{n'}.c''^{n''}.c'''^{n'''}\ldots\ldots\ldots = K \qquad \text{(A)}$$

For the ionization of a binary electrolyte:

$$\begin{array}{ccccc} \mathrm{RX} & \rightleftharpoons & \mathrm{R}^{+} & + & \mathrm{X}^{-} \\ (c_u) & & (c_i) & & (c_i) \end{array}$$

$$c_u/c_i^2 = K \qquad \text{(B)}$$

If n_u, n_i, n_i are the corresponding numbers of molecular weights of the components,

$$c_u = n_u/(n_u + 2n_i + n_s);$$

$$c_i = n_i/(n_u + 2n_i + n_s);$$

where n_s refers to the solvent.

Substituting in (B), we obtain:

$$n_u(n_u + 2n_i + n_s)/n_i^2 = \text{constant} \qquad \text{(C)}$$

This reduces, *when n_u and n_i are small compared with n_s*, to the form:

$$n_u.n_s/n_i^2 = \text{constant}$$

Let v be the volume of solution containing one molecular weight of total salt, then (*again only if n_u and n_i are small compared with n_s*), we have,

$$n_s = kv(n_u + n_i),$$

where k is a constant of proportionality.

Thus finally,

$$n_u(n_u + n_i)v/n_i^2 = \text{constant}. \qquad \text{(D)}$$

This equation is as far as thermodynamic theory will proceed; to bring the result into a region accessible to experimental test, a further assumption is necessary. The determination of n_i, the ionic concentration, is made possible if we accept Arrhenius' fundamental theorem that the ratio of the number of "active" (or ionized) molecules of the electrolyte to the total number, active and inactive, present in a given portion of solution is equal to the ratio of the molecular electrical conductivity of the solution to the limiting value of this when the dilution is very great:

$$n_i/(n_u + n_i) = \Lambda/\Lambda_o = \gamma \qquad \text{(E)}$$

Substituting in (D) the value of $n_i/(n_u + n_i)$ from (E), we obtain:

$$\Lambda^2/\Lambda_o(\Lambda_o - \Lambda)v = \text{constant} = K \qquad \text{(F)}$$

This is Ostwald's Dilution Law.

---

equation: $n'v'd\pi' + n''v''d\pi'' + n'''v'''d\pi''' + \ldots\ldots = 0$. (Compare Washburn, THIS JOURNAL, 32, 484 (1910).) The equation given above is obtained by the integration of this and with the use of the further assumption that the relation $c = k\pi$ holds. (π = osmotic pressure, c = molecular concentration, k = constant.)

The thermodynamic derivation shows that the formula can, in any case, represent the course of ionization only in solutions of such dilution that the regions of solvent influenced by each molecule of solute are independent.

From the above argument it will be evident that the apparent simplicity of the Ostwald dilution law is obtained only at the sacrifice of its applicability to concentrated solutions. The changes necessary in the above thermodynamic derivation of the equation for the dissociation equilibrium, under the modified theoretical basis advanced above, may now be investigated.

The equation representing the process of ionization becomes:

$$\mathrm{RX} + (\mathrm{H_2O}) \rightleftharpoons \mathrm{R}^+ + \mathrm{X}^-,$$

corresponding with the view, expressed above, that the dissociation of the undissociated molecule RX into its component ions R^+ and X^- is brought about by impact with molecules of the solvent.

It may appear at this point that the above equation is incorrectly stated, inasmuch as it does not balance. As a matter of fact, the corresponding equation for the original dilution law also does not balance, since the ionic charges appear only on one side. It will be shown, in a subsequent section, that the solvent is not to be considered as acting *chemically* in the ionization equation written above. The process of dissociation is regarded as entirely *physical* in its nature, the action of the solvent molecules being ascribed to their unsaturated character, *i. e.*, to the free valences or "neutrons" attached to them. Thus the above equation is more correctly to be written:

$$\mathrm{RX} + \oplus\ominus \rightleftharpoons \mathrm{R}^+ + \mathrm{X}^-,$$

where $\oplus\ominus$ represents a neutron. This equation balances exactly. Since, however, the ionic charges are supplied directly by the molecules of the solvent, the concentration of the latter is the factor that must appear in the equation. The matter is discussed more fully later, in connection with the results of Walden.

From the above equation we obtain:

$$c_u.c_s/c_i^2 = K \qquad \text{(B}'\text{)}$$

For c_s we have the relation:

$$c_s = n_s/(n_u + 2n_i + n_s),$$

c_u and c_i being transformed as before. We now obtain, in the next step, the equation:

$$n_u.n_s/n_i^2 = \text{constant}, \qquad \text{(C}'\text{)}$$

which is *valid exactly at all concentrations.*

Let us now define v' as the number of *unit weights of solvent* employed to dissolve one equivalent weight of total salt. The change is thus made from volume concentration of the solute (equivalent weights per fixed volume of solution) to weight or molecular concentration (equivalent weights per fixed weight of solvent). Then we have:

$$n_s = k'v'(n_u + n_i),$$

where k' is a constant of proportionality.[1] This equation is also *exactly true for all concentrations.*

We now obtain:

$$n_u(n_u + n_i)v'/n_i^2 = \text{constant}, \qquad (D')$$

and finally, employing equation (E) as before, we have the modified dilution law,

$$\Lambda^2/\Lambda_\circ(\Lambda_\circ - \Lambda).v' = \text{constant} = K, \qquad (F')$$

both of which equations are valid not only for small concentrations of solute, but *for all concentrations.*

Equation (F′)—which is, of course, identical with the previous equation (7) above— therefore has, when compared with the dilution law in its original form, the two advantages of *simplicity* and of *agreement with the experimental data at high concentrations.* Several points in the above thermodynamic investigation, however, require more extended consideration; these are taken up in order below.

We have, first of all, the fact that it appears, on a first inspection of equation (F′) above, that there are two units of concentration simultaneously employed, namely in the expression of Λ (the equivalent conductivity, *i. e.*, the specific conductivity divided by the *volume concentration* of the solute) and of v' (the reciprocal of the *weight or molecular concentration* of the solute). However, the equation can be expressed, in terms of weight concentration only, without change of form, since Λ has the same value for either unit of concentration.

This becomes evident from an examination of the experimental method followed in the determination of equivalent conductivity. The quantity directly measured in experimental work is the specific electrical resistance of the solution. The specific conductivity, κ, is the reciprocal of this, and is proportional to the number of dissociated molecules in *unit volume of the solution.*[2] The equivalent conductivity Λ is equal to κv, where v represents the dilution in volume units.

If now, we change from volume concentration units to weight concentration units, thereby altering the dilution v to v', we must also modify our definition of specific conductivity, and this will now be proportional to the number of dissociated molecules in *unit weight of the solvent.* Consequently, if the specific conductivity under weight concentration units is κ', we have the relation:

---

[1] k' represents the number of equivalent weights of the solvent contained in the fixed weight of solvent chosen as unit. The equation consequently represents both molecular and weight ratios between solute and solvent.

[2] Kohlrausch and Holborn, "Leitvermögen der Elektrolyte" (1898), pages 102–3.

$$\kappa' = \kappa.(v/v').$$

Hence the equivalent conductivity under weight units, $\kappa'v'$, is equal to κv. The equivalent conductivity Λ therefore has the same value, expressed in either unit of concentration.

A second point for examination is how far we are justified in considering the fundamental assumption of Arrhenius:

$$\Lambda/\Lambda_0 = \gamma, \text{ the degree of dissociation,}$$

as being applicable to concentrated solutions.

It is a much-debated question[1] whether this assumption is exactly true even at very high dilutions. In any case, it can be directly valid only if the ionic mobilities are not functions of the concentration. Now at high concentrations the ionic mobilities certainly are variable, since they are affected by the increased viscosity of the medium, and any correction (as for acetic acid in Tables I and II) can be only approximate. At high dilutions, however, the viscosity factor (that is, the change in the nature of the medium) may be neglected. Variation in ionic mobility at high dilutions, therefore, can occur only if mobility is a function of *ionic concentration*. That this is indeed the case was a view first advanced by Jahn,[2] in order to account for the "anomaly of strong electrolytes." Arrhenius,[3] however, showed that neither Jahn's theoretical work nor his experimental data were sufficiently reliable to warrant the conclusions drawn. The case of the hydrogen ion has been most frequently investigated, and here the majority of results[4] certainly point to the fact that the mobility is constant in dilute solutions.

The hypothesis of Jahn has recently been brought into prominence again by the work of Lewis.[5] The opposite view—that the ionic mobility is constant, and that the abnormality of strong electrolytes must be attributed to the change in the dissociating power of the solvent, due to the addition of solute—first advanced by Arrhenius,[6] has also been supported by the extended researches of Walden.[7]

Here a choice must be made between the two views, and since the assumption of varying ionic mobility in dilute solution must be regarded as not yet confirmed,[8] the simple hypothesis of Arrhenius and Walden

---

[1] For a review of the subject and a list of references see Wegscheider (*Z. physik. Chem.*, **69,** 603 (1909)) and Partington (*J. Chem. Soc.*, **97,** 1162 (1910)).

[2] Jahn, *Z. physik. Chem.*, **33,** 545 (1900); **35,** 8 (1900).

[3] Arrhenius, *Ibid.*, **36,** 28 (1901).

[4] For references see Kendall, *J. Chem. Soc.*, **101,** 1275 (1912).

[5] Lewis, THIS JOURNAL, **34,** 1631 (1912).

[6] Arrhenius, *Z. physik. Chem.*, **31,** 197 (1899). See also Franklin and Kraus, THIS JOURNAL, **27,** 216 (1905); Lewis and Wheeler, *Z. physik. Chem.*, **56,** 179 (1906).

[7] Walden, THIS JOURNAL, **35,** 1649 (1913).

[8] Wegscheider, *Z. physik. Chem.*, **69,** 605 (1909).

will be followed in the present paper. It will be assumed that ionic mobility is not a function of ionic concentration.

When we consider higher concentrations, the mobilities of the ions undoubtedly vary. Also the different ions of an electrolyte are not equally affected by the change in the nature of the medium, since the transport numbers may vary appreciably with the concentration.[1] This variation is clearly connected with the phenomena of ionic hydration, and is important only in the case of electrolytes containing highly hydrated ions, where the variation in the degree of ionic hydration with the concentration will be greatest. For more normal electrolytes the change in the transport numbers of the ions, for solutions of less than normal concentration, may be regarded as of secondary importance.[2]

From the point of view taken above—that the ionic mobility is, in normal cases,[3] not a function of the ionic concentration—it follows that the degree of accuracy obtained in the determination of γ, as calculated from the experimental value for Λ, will be dependent primarily only upon the accuracy of the viscosity correction applied. This correction has already been discussed in an earlier section.

The fundamental assumption of Arrhenius, even if it does not lead us directly to conclusive results, yet enables us to attack problems which we should otherwise have to leave untouched. It has consequently been in general use in the investigation of concentrated solutions as our only means, until considerable advances have been made, of interpreting and using experimental results.[4]

The Change from Volume to Weight Units of Concentration.—From a purely thermodynamic and theoretical view point, there is no question as to the desirability of the change from volume to weight concentration units,[5] here as in other branches of physical chemistry. From the experimental side the use of the volume unit undoubtedly offers many advantages in simplicity and convenience of procedure, and these suffice to account for its general adoption for the expression of experimental data. However, since Λ has the same value expressed in either unit, the change

---

[1] Kohlrausch and Holborn, "Leitvermögen der Elektrolyte" (1898), page 201. In the case of two only of the simple uni-univalent electrolytes given is the variation in the transport number of the anion, between zero and half-normal concentration, greater than 0.01. These two electrolytes are the chlorides of lithium and sodium, the component ions of which are known to be highly hydrated.

[2] The accurate determination of transport numbers is extremely difficult, and in most cases a large variation in the transport number represents a relatively small change in the calculated value of γ.

[3] *i. e.*, where the variation in the degree of ionic hydration with concentration exercises no disturbing influence.

[4] Compare Lewis, *Z. physik. Chem.*, **70**, 217–8 (1910).

[5] Planck, *Wied. Ann.*, **32**, 489 (1887); Washburn, THIS JOURNAL, **32**, 668 (1910).

of units here involves no experimental difficulties to counterbalance its advantage for the expression and derivation of theoretical relations.

In several branches of physical chemistry, closely related to equivalent conductivity, the change to weight units has already furnished important results. A prominent example is afforded by the work of Morse and Frazer[1] on the osmotic pressures of solutions of sucrose. Results of experiments on the lowering of the freezing point, the raising of the boiling point, and the lowering of the vapor pressure of the solvent by dissolved salts have always been expressed in weight units of concentration.[2] In the application of the solubility-product principle, the concentrations of the dissolved electrolyes must be reduced to weight units to obtain comparable results.[3] Similarly, the viscosity of binary mixtures[4] (including solutions) has been shown to be a function of the molecular and not of the volume concentration of the two components. This is important in view of the close relation existing between viscosity and equivalent conductivity.

Experimental Data.—In the preceding section the modified form of the dilution law has been shown to be fundamentally more simple than the original dilution law, and to cover a more extended range, since it is exactly applicable to concentrated solutions. Hence it is, at this point, legitimate to emphasize the theoretical basis assumed above, namely, that the dissociation of the undissociated molecule in the solution is brought about, not spontaneously, but by the action of the solvent.

It is not asserted here that the above theoretical basis is definitely established by the results obtained. Several factors have been left out of consideration, which become of importance in concentrated solutions, as is discussed later; also the amount of *exact* experimental data that can be brought forward is, at present, extremely meagre.[5]

---

[1] Morse and Frazer, *Am. Chem. J.*, **34,** 1 (1905); see also Bancroft, *J. Phys. Chem.*, **10,** 319 (1906), and Morse, Frazer and Dunbar, *Am. Chem. J.*, **38,** 212–26 (1907).

[2] For example, in the freezing point data, collected by Noyes, THIS JOURNAL, **32,** 1026 (1910). In comparing the results obtained with those derived from conductivity experiments, however, Noyes has transferred these figures to volume concentrations without correction (THIS JOURNAL, **34,** 485 (1912)). Washburn and MacInnes, in a similar comparison of the freezing point and conductivity data for solutions of caesium nitrate, have, on the other hand, expressed all quantities in molecular concentrations, THIS JOURNAL, **33,** 1711 (1911).

[3] Kendall, *Proc. Roy. Soc.*, (*A*) **85,** 200 (1911).

[4] Kendall, *Meddel. från K. Vet. Akads. Nobelinstitut,* Band **2,** No. 25 (1912).

[5] Only very weak acids and bases are of use for examination here, since even in acids a little stronger than acetic acid we shall have, in *concentrated* solutions, the "anomaly of strong electrolytes" beginning to appear. The substances examined must also be very soluble in water to give sufficiently concentrated solutions. These conditions cut out the majority of the ordinary organic acids, and only in a few of those remaining are all the necessary data available.

An extensive list of weak electrolytes has been tabulated by Wegscheider,[1] and the concentration fixed in each case at which divergence from the dilution law begin to become appreciable. For all these electrolytes, it may be asserted that the modified dilution law will give *qualitatively* better agreement with the experimental data at high concentrations, but the absence of reliable density and viscosity results precludes, at present, the possibility of establishing *quantitatively* exact agreement.

Experiments are already in progress to supplement the few instances given below.

For the series of normal fatty acids, the following results are available. The conductivity data are selected from the determination of White and Jones;[2] the results for viscosity and density are taken from the work of Reyher.[3] The various columns have the same significance as in Table I.

TABLE III.—FATTY ACIDS, 25° (WHITE AND JONES).

Acid.	v.	Λ.	η.	d.	100 K.	100 K_2.
Acetic....................	2	2.089	1.060	1.0042	0.00169	0.00194
	8	4.342	1.017	1.0013	0.00183	0.00191
	32	8.699	1.004	1.0003	0.00186	0.00188
Propionic................	2	1.700	1.099	1.0035	0.00116	0.00145
	8	3.704	1.026	1.0011	0.00138	0.00147
	32	7.436	1.007	1.0003	0.00141	0.00143
n-Butyric...............	2	1.730	1.132	1.0022	0.00120	0.00161
	8	3.891	1.031	1.0006	0.00153	0.00164
	32	7.902	1.008	1.0002	0.00159	0.00162
iso-Butyric..............	2	1.633	1.129	1.0016	0.00108	0.00152
	8	3.821	1.032	1.0004	0.00147	0.00158
	32	7.621	1.008	1.0001	0.00148	0.00150

Considering the accuracy of the data employed, the degree of concordance in the values shown under 100 K_2 in the above table is satisfactory throughout. Hence the modified dilution law may be held to apply, for the above acids, up to solutions of at least half-normal concentration.

In Table IV the figures for a typical weak base—ammonia— are given.

TABLE IV.—AMMONIA, 25° (OSTWALD).

v.	Λ.	η.	d.	100 K.	100 K_2.
2	1.56	1.012	0.995	0.00193	0.00203
4	2.24	1.006	0.997	0.00199	0.00204
8	3.21	1.003	0.998	0.00205	0.00208
16	4.55	1.001	0.999	0.00207	0.00208
∞	(252)	...	...	.....	.....

---

[1] Wegscheider, *Z. physik. Chem.*, 69, 611–13 (1909).

[2] White and Jones, *Am. Chem. J.*, 44, 159 (1910).

[3] Reyher, *Z. physik. Chem.*, 2, 749 (1888). The viscosity results are liable to (relatively) considerable error, as will be evident by inspection of the original.

The conductivity results are those of Ostwald,[1] the viscosity and density data are interpolated from the figures given in Landolt-Börnstein.

The agreement of the values given under 100 K_2 is again satisfactory, in view of the nature of the experimental data. For example, an error of 0.01 in the value of Λ, at the first concentration given, corresponds to a difference of 3 units in 100 K_2.

The above tables may be amplified by extending the modified form of the dilution law to the author's equation for transition electrolytes, shown in equation (3), (which also fails in concentrated solutions) and testing its applicability there also. Equation (3) is modified to the form:

$$\gamma^2/(1-\gamma)v' = K + c\,(1-\gamma)/\gamma. \qquad (9)$$

The results for a typical transition electrolyte—dichloroacetic acid— are given in Table V. The viscosity and density figures are taken from the determinations of Kanitz.[2]

TABLE V.—DICHLOROACETIC ACID, 25° (KENDALL).

				$100\{K+c(1-\gamma)/\gamma\}$		$100\{K+c_2(1-\gamma)/\gamma\}$	
v.	Λ.	η.	d.	Expt.	Calc.	Expt.	Calc.
2	114.9	1.1318	1.0263	6.33	7.68	8.92	8.93
4	151.7	1.0640	1.0139	6.38	6.70	7.57	7.52
8	190.2	1.0287	1.0067	6.00	6.08	6.60	6.62
16	231.6	1.0143	1.0033	5.64	5.65	5.96	6.00
32	273.1	1.0071	1.0016	5.38	5.34	5.57	5.55
64	309.7	1.0035	1.0008	5.12	5.14	5.23	5.26
128	338.7	1.0018	1.0004	4.96	5.02	5.04	5.09
256	359.2	1.0009	1.0002	4.94	4.94	5.02	4.99
∞	385.6	....	....	..	4.85	..	4.85

$K = 0.0485$, $c = 0.0120$, $c_2 = 0.0173$.

The agreement of equation (3) in its original form with the experimental results is shown by the figures under $100\{K + c.(1-\gamma)/\gamma\}$ in Table V, the agreement of the equation in its modified form (9) is given by the figures under $100\{K + c_2(1-\gamma)/\gamma\}$. It will be seen that the equation holds exactly, in its original form, only for dilute solutions; while the modified form gives agreement throughout the entire series.

Additional experimental results will be given in a future communication, where the application of the above changes to solutions of strong electrolytes will also be considered. In conclusion here, the limits of the applicability of the modified dilution law proposed are briefly examined, and the results obtained in this paper compared with those of Walden.

Limits of Applicability of the Modified Dilution Law.—It has been shown that the dilution law, in its modified form, is exactly applicable up

---

[1] As transposed to the modern units in Kohlrausch and Holborn, "Leitvermögen der Elektrolyte" (1898), page 167.

[2] Kanitz, *Z. physik. Chem.*, **22**, 336 (1897).

to concentrations of at least half-normal for typical weak electrolytes. In the case of acetic acid, the values obtained for K with the aid of the modified law are constant up to concentrations well above normal, then follows a decrease when still higher concentrations are considered.

It will be evident, on examination, that the modified law *must* break down at these very high concentrations of solute, since many complicating factors arise which have not been taken into account. The chief of these are enumerated below.

In the first place, the viscosity correction to Λ becomes larger, and the probable error of its application greater, with increase of concentration. Also the likelihood that the fundamental assumption of Arrhenius, discussed previously, will be true even if an exact viscosity correction could be applied, decreases as the concentration of solute is increased.

At high concentrations, further, the hydration of the solute—both in its undissociated and in its dissociated state—complicates the equilibrium in the solution. The undissociated solute, if hydrated, will withdraw a considerable quantity of solvent from the equilibrium, and the concentration of "free" solvent in the solution will be greatly reduced. If the ions are hydrated, their mobilities may vary considerably in concentrated solutions, owing to the variations in the degree of hydration with the concentration of the solvent.

More important still, the change in the *nature* of the solvent at high concentrations of solute will be considerable. A highly associated solvent, such as water, will tend to dissociate more and more into simpler molecules as its concentration in the solution decreases.[1] Also the change in the dielectric constant of the medium, for high concentrations of solute, is of importance.

Finally the variation in the heat of dilution with the concentration (which affects the constancy of K) has not been taken into consideration.

The modified form of the dilution law, as expressed in the simple equations (7) and (F′), cannot be expected to hold in general, therefore, for *highly concentrated* solutions. Only up to (approximately) normal concentration of solute is it exactly valid. Even so, this represents a con-

---

[1] The ionizing power of a solvent is intimately connected with its *power of association* into large molecules. The best ionizing solvents are unsaturated, *e. g.*, water contains an unsaturated oxygen atom with two free valencies, and the simple molecule may be written $H_2O\overset{+}{-}$. Hence, by the loss of two free valences (the positive charge on one oxygen atom being neutralized by the negative charge on another) two simple molecules can combine to form a complex molecule, $+OH_2.H_2O-$. Such association can evidently continue further, each step being accompanied by the loss of two free valences. "One can readily see that such molecules would be electrically polarized, and their charges might easily have the power to cause electrolytic dissociation or ionization." Stieglitz, "Qualitative Chemical Analysis" (1912), Part 1, page 65. Compare also Arrhenius, "Theories of Chemistry" (1907), page 83.

siderable advance upon the previous limit of $v = 32$ (approximately) for the dilution law in its original form.

Comparison with the Results of Walden.—It is of interest at this point to compare the conclusions of the present investigation with those drawn by Walden from the study of the dielectric constants of dissolved salts, and to examine how far the results may be combined.

The hypothesis advanced here as an explanation of the immediate cause of the dissociation of the undissociated molecule in the solution of an electrolyte is that the simple undissociated molecules are broken up into their component ions by impact with the molecules of the solvent.

Walden,[1] on the other hand, concludes that "the process of disaggregation of the polymerized salt molecules also causes, and induces, the process of ionic cleavage." The following processes are assumed.[2]

$$(\mathrm{MeX})_x \rightleftharpoons (\mathrm{MeX})_{x-1} + \mathrm{MeX} + \oplus\ominus. \quad \text{(I) Depolymerization.}$$

$$\mathrm{MeX} + \oplus\ominus \longrightarrow \mathrm{Me}\oplus + \mathrm{X}\ominus. \quad \text{(II) Ionization.}$$

$(\mathrm{MeX})_x$ is the polymerized salt, x the extent of association, MeX the simple salt molecule. $\oplus$ and $\ominus$ represent a positive and a negative electron, respectively, $\oplus\ominus$ a neutral electron (neutron),[3] Me $\oplus$ a cation, X $\ominus$ an anion.

Now the depolymerization of the solid salt $(\mathrm{MeX})_x$, which takes place in its solution, must be regarded as due to the bombardment of the complex and unstable molecules of the salt by the molecules of the solvent. The reaction is specific in each case, and the natures of both solute and solvent are factors in the degree of depolymerization. That this is so is shown by the two facts that different substances are depolymerized to different degrees in the same solvent, and that the same substance is depolymerized to different degrees in different solvents.

In this depolymerization of the solute, neutrons are formed in the solution, as is indicated by the first equation of Walden above. These neutrons will attach themselves to molecules of the solvent,[4] and the dielectric constant of the medium will be changed.

The process can be studied from another point of view with similar re-

---

[1] Walden, This Journal, 35, 1661 (1913).

[2] The depolymerization process (Equation I) consists, of course, of successive stages from $(\mathrm{MeX})_x$ to MeX, of which one only is given above.

[3] Walden's conception of "neutral electrons" is retained in the discussion merely for convenience in the comparison of results. It will become evident below that the argument could be more logically expressed in terms of *free valences,* without the use of the indefinite expression "neutron."

[4] This statement is, of course, an assumption, since the neutrons might attach themselves directly to the simple undissociated molecule MeX. (Compare A. A. Noyes, *Carnegie Institute Publication,* No. 63, 351 (1907).) The change in the degree of association of the solvent with the concentration of solute necessitates, however, at least *some* transfer of neutrons to the solvent.

sults. After the addition of the salt, the concentration of the solvent in the solution will have been diminished, hence its degree of association will also have diminished. That is, some complex molecules of the solvent will have broken down into simpler molecules, and this process is essentially *the taking-up of neutrons.*[1] For example, in water,

$$(H_2O)_n^{\pm} \rightleftharpoons (H_2O)_{n-1}^{\pm} + (H_2O)^{\pm}. \qquad (10)$$

We may therefore rewrite the first equation of Walden in the form:

$$(MeX)_x + (H_2O)_n^{\pm} \rightleftharpoons (MeX)_{x-1} + MeX + (H_2O)_{n-1}^{\pm} + (H_2O)^{\pm}.$$

It is evident from this equation that *the process of depolymerization is common to both solvent and solute,*[2] and is accompanied by an increase in the number of neutrons in the solution and by a change in the dielectric constant. The change in the dielectric constant will be greater, the more neutrons the solvent has taken up, that is, the greater the degree of depolymerization.[3] This is in accordance with the results of Walden, and is of importance in the consideration of the "anomaly of strong electrolytes."

It is now evident that the second equation of Walden, for the expression of the ionization equilibrium, can be at once made identical with the equation given on page 1078 of the present paper by transformation as below:

$$MeX + [H_2O]^{\pm} \rightleftharpoons Me\oplus + X\ominus,$$

the solvent acting *simply as the carrier of the "neutron."* Hence also the equation

$$c_u.c_s/c_i^2 = K \qquad (7)$$

for the dissociation process can hold only so long as the concentration of neutrons in the solution is proportional to the concentration of the solvent. At high concentrations this can no longer be assumed to be the case, and the modified dilution law consequently cannot apply exactly, as has already been pointed out in the previous section.

We have now a simple means of expressing the mechanism of electrolytic dissociation. By impact of an undissociated molecule of the solute, MeX, with a molecule of the solvent, a neutron is transferred from the latter to the former, and the undissociated salt breaks up into its separate ions $Me\oplus$ and $X\ominus$. Similarly, by impact between ions of unlike

---

[1] See note on page 1085. A neutron is equivalent to *two free valences,* and is used in this sense throughout the present discussion.

[2] Hence, also, non-associated solvents do not depolymerize dissolved salts. Consequently salts are highly ionized only by associated liquids; for example, hydrochloric acid, which is almost entirely dissociated in water, gives practically a non-conducting solution in benzene (Kablukoff, *Z. physik. Chem.*, **4**, 430 (1889)).

[3] It is possible that the dielectric constant is *directly* a function of the concentration of neutrons on the solution. This will account for the low dielectric constants of non-associated liquids, and for the great increase in the dielectric constant of a feebly ionizing solvent on the addition of an electrolyte.

charge, Me ⊕ and X ⊖, a molecule of the undissociated salt MeX is formed, with the liberation of a neutron, which attaches itself to a molecule of the solvent. The solvent molecules thus lose and gain neutrons alternately, as expressed by equation (10). The above view is evidently consistent with the fact that ionizing solvents possess the two characteristic properties of *unsaturation* (presence of neutrons) and *association.*

By comparison of the results of Walden with those of the present paper and by combination of the conclusions drawn we are able to obtain, therefore, a simple view of the whole mechanism of the dissociation equilibrium in the solution of an electrolyte.

Summary.

A modified form of the dilution law has been proposed, which is found to be in accordance with the data of experiment throughout a region in which the dilution law, in its original form, fails to apply, namely in concentrated solutions of weak electrolytes.

The theoretical basis underlying this modification of the dilution law is that the dissociation of the undissociated molecule RX in the solution of a binary electrolyte, into its component ions R^+ and X^-, takes place not spontaneously but by impact with the molecules of the solvent.

With the use of this hypothesis the dilution law, as derived thermodynamically, is found to be fundamentally simpler in form than previously, since it is applicable exactly not only to dilute but also to concentrated solutions without any simplifying assumptions.

The advantage of a change from volume units of concentration to weight or molecular units, for the expression of equivalent conductivities and the calculation of dissociation constants, has been pointed out.

The conclusions of the present investigation have been compared and combined with those of Walden, with the result that a simple view of the mechanism of the ionization equilibrium is obtained. It is shown that the dissociating power of the solvent molecules is to be ascribed to their unsaturated character, *i. e.*, to the presence of free valences.

Additional experimental results will be given, and the case of strong electrolytes examined, in a future communication.

The above investigation was commenced at the Nobel Institute of Physical Chemistry, Experimentalfältet, Sweden. It is a pleasant duty to me to express here my gratitude to Professor Svante Arrhenius for his hospitality, and for his helpful criticism of the initial stages of the research.

NICHOLS LABORATORIES OF INORGANIC CHEMISTRY,
COLUMBIA UNIVERSITY, NEW YORK CITY.

From the PHILOSOPHICAL MAGAZINE *for June* 1912.

THE SOLUBILITY OF CALCIUM CARBONATE IN WATER.

BY

JAMES KENDALL, M.A., B.Sc.,
VANS DUNLOP SCHOLAR IN CHEMISTRY, UNIVERSITY OF EDINBURGH.

The Solubility of Calcium Carbonate in Water. *By* James Kendall, *M.A., B.Sc., Vans Dunlop Scholar in Chemistry, University of Edinburgh*[*].

THE determination of the solubility of calcium carbonate in water is evidently, apart from its purely chemical interest, a very important problem, owing to the application of the values obtained to the results of water analysis, and to their bearing upon the study of geological formations. Although much work has been done upon the subject, no satisfactory measurements have been made. The main difficulty in the determination of exact results lies in the fact that, in consequence of the extremely small degree of solubility, it has been necessary to adopt indirect methods for its estimation. Thus Kohlrausch and Rose (*Zeit. phys. Chem.* xii. p. 234 (1893)) included calcium carbonate in their investigations on the solubility of difficultly-soluble substances in water by means of the electrical conductivities of the saturated solutions. Calcite, arragonite, and the amorphous form of the carbonate were examined at temperatures ranging from 2° C. to 34° C., and provisional figures for the solubilities and temperature coefficients were given. The method and its application were further elaborated in a second paper published ten years later (*Zeit. phys. Chem.* xliv. p. 197 (1903)); but in the final paper (*Zeit. phys. Chem.* lxiv. p. 129 (1908)), giving the calculation of the actual solubilities of the substances examined from the observed conductivities, the figures for all carbonates were omitted. This was because the errors introduced by the correction necessary for the conductivity of the water itself may be greatly augmented owing to our lack of knowledge of the influence of the CO_3'' ion. Any values obtained could therefore only be regarded as rough approximations. The provisional figures of the first paper were consequently retained.

Holleman also, simultaneously with Kohlrausch and Rose (*Zeit. phys. Chem.* xii. p. 125 (1893)), applied conductivity measurements to the determination of the solubility of calcium carbonate, and obtained similar results.

Foote (*Zeit. phys. Chem.* xxxiii. p. 740 (1900)), using other indirect methods to determine the ratio of the solubilities of the two crystalline forms, confirmed the provisional figures of Kohlrausch in this respect, but made no actual solubility measurements.

In water analysis, the determination of the amount of calcium bicarbonate present in a given sample (*i. e.*, the

---

[*] Communicated by Prof. J. Walker, F.R.S

degree of the temporary hardness) is a matter of great importance. If the sample is boiled for some time the dissolved carbon dioxide is expelled, and the greater part of the temporary hardness is destroyed by precipitation of the calcium carbonate, but some will still remain in solution. The amount of this must be known before the values of the temporary and permanent hardness of the water can be calculated; it has been roughly estimated at ·02 gr. per litre. Measurements of the solubility of calcium carbonate at other temperatures and under ordinary conditions are altogether lacking.

At the suggestion of Professor Walker, I have attempted the direct estimation of the solubility of calcium carbonate in water. Experiments have been made, at temperatures between 25° C. and the boiling-point, upon all three varieties of the substance—calcite, arragonite, and the amorphous form; also upon solutions of the bicarbonate, in equilibrium with air free from carbon dioxide and with atmospheric air.

The method of procedure was, briefly, as follows:—a large volume—2 to 3 litres—of the saturated solution was prepared in a large silica flask, and filtered off into a second silica flask containing a small excess of acid; the liquid was evaporated to small bulk—50 to 100 c.c.—and titrated against a known solution of baryta.

It is the use of silica vessels that renders this direct determination possible; with glass or porcelain vessels the solution would dissolve out alkali, during concentration, sufficient to vitiate the results entirely. The silica flasks used were of three to four litres capacity; their resistance to neutral, acid, and alkaline solutions of the concentrations existing in the subsequent experiments was first tested as below.

Neutral Solution.—Water of specific conductivity $1{\cdot}25 \times 10^{-6}$ can be obtained by one distillation from tap-water by the addition of 10 c.c. Nessler's solution to two litres of water. Jena glass vessels and a tube of pure tin, fitted with a condenser, are employed; the distillation is carried out in the open air, and the first third of the distillate rejected. On redistillation of this water from one silica vessel to another, by means of a silica hood carefully ground on the neck of the first vessel, water of a specific conductivity $\cdot 85 \times 10^{-6}$ was obtained. If half of this distillate be boiled away, the residue possesses a specific conductivity of $\cdot 70 \times 10^{-6}$, which is the conductivity value for the purest water that can be obtained in contact with air. This shows conclusively that pure water dissolves no conducting material from a silica vessel.

Acid Solution.—10 c.c. of decinormal sulphuric acid were added to about two litres of water in one of the vessels, and the solution evaporated down to 50 c.c. On titration against baryta, with phenolphthalein as indicator, the existence of the original amount of acid in the solution (within limits of experimental error) was established.

Alkaline Solution.—Two litres of calcium hydroxide solution of concentration ·001 N were boiled in the silica vessel for some time, and then, after a known excess of sulphuric acid had been added, evaporated to small bulk. On titration against baryta, with phenolphthalein as indicator, the required excess of acid was found to exist in the solution.

The silica flasks are therefore not attacked, to any appreciable extent, by solutions of the above concentrations, and these were never exceeded in subsequent experiments.

The sulphuric acid used throughout was of approximately decinormal concentration, the baryta solution of approximately centinormal. Phenolphthalein was employed as indicator. All water used was freshly distilled, and collected directly into one of the silica flasks.

Mineral Calcite and Arragonite.

The calcite used consisted of large, transparent crystals of iceland-spar (density 2·72); the arragonite was a fine museum specimen (density 2·90), which showed no traces of strontium when tested by the spectroscope. Both minerals were finely powdered in an agate mortar. Successive experiments with the same sample of solid led to constant solubility results—a most rigorous test of purity. Experiments were carried out at three temperatures: 25° C., 50° C., and 100° C.

For the determinations at 100° C. a small quantity of the powdered substance was added to water at the boiling-point, and after the boiling had been continued for periods varying from 40 to 200 minutes, the solution was filtered off from the remaining solid. For those at 50° C. and 25° C. the silica vessel was immersed in a thermostat at the particular temperature, and fitted with a rubber cork, through which passed two silica tubes, one short and the other reaching to the bottom of the flask. The solution could thus be kept agitated by a current of pure air drawn through the apparatus; the air being led, from outside the building, through a long tube packed with cotton-wool, a wash-bottle containing Nessler's solution, two soda-lime towers, and finally a wash-bottle containing pure water, before entering the solution. Equilibrium was established much more slowly at these lower temperatures; the solutions were tested at different periods until a steady solubility value was reached.

The manner of filtration at the boiling-point occasioned a great deal of difficulty. Simple filtration through a double-walled porcelain funnel, fitted with a hardened fluted filter-paper, and heated without by a water-jacket, was first attempted; but no satisfactory results could be obtained. Although the filtration was carried out as rapidly as possible, the amount of evaporation from the filtrate was necessarily considerable, and further, the solution exerted an appreciable solvent action on the funnel itself, as was found by testing with solutions of prior known concentration. At the lower temperature also, open filtration could not be employed, since the short exposure of the solution during filtration to the carbon dioxide of the atmosphere led to a remarkable increase in the solubility value obtained.

The method of upright filtration was therefore adopted. The solution was drawn by suction from the first to the second silica vessel through a tube of pure tin, in the shape of an inverted U, one arm of which was longer than the other. The longer arm dipped into the solution, and was closed at the end by means of a double layer of hardened filter-paper, protected on both sides by squares of muslin, the whole being tied tightly to the tin tube by means of linen thread upon a rubber band. The shorter arm was fitted to the second vessel with a rubber cork, through which passed a silica tube leading to the pump. A glass flask, immersed in ice-cold water, was interposed as a condenser to intercept water vapour coming over from the hot filtrate.

By this method, using a tube of one-inch diameter, two litres of solution could be filtered over in a quarter of an hour. Loss of water from the filtrate by evaporation, and exposure to the air during filtration, were both avoided, and for a short time concordant results were obtained. After a few experiments, however, the hot solution began to attack the tin tube, and once the surface of this was worn away, the action increased rapidly. In the case of experiments at the boiling-point, the filtrate, instead of being clear, was quite cloudy on concentration, and, when tested, showed a decided trace of tin.

The tin tube was therefore discarded for a similar tube of silica, and with this satisfactory results at 100° C. were obtained. At the lower temperatures no noticeable action was exerted by the solution upon the tin tube, and this was therefore used at these temperatures on account of its greater convenience. A rubber cork, through which passed a short silica tube, being fitted to each arm of the tube, pure air was drawn through the solution during the whole period of filtration.

Immediately after filtration, and before cooling, the amount of liquid filtered over was ascertained by direct weighing. It was found by experiment that the difference in weight obtained by weighing when hot, and by weighing after closing the mouth of the vessel and allowing to cool, was between 1 and 2 grammes. This, with a filtrate of 2 litres, introduces an error of less than ·1 per cent., which is negligible. The saving of time is very great, as the solution requires at least two hours to cool to the ordinary temperature, and another half-hour to be brought to the boiling-point again. The actual evaporating down of the solution takes two to three hours, being conducted rapidly at first and more slowly as the volume decreases. When 50 to 100 c.c. remain, the vessel is allowed to cool, and the amount of the residue found to within ·1 gramme by weighing.

The silica vessels remained practically constant in weight throughout the whole series of experiments.

The calculation of results is very simple, since all the solutions are so dilute that their densities may be taken as equal to that of water at the same temperature. Thus, if 2000 grammes of solution be added to 10 c.c. $\frac{N}{10}$ acid, and evaporated down to 50 grammes, and it is found that 1·53 c.c. $\frac{N}{100}$ baryta solution are required to neutralize 25 c.c. of the residue, we have

$$\frac{10(\cdot 1)-2000\,x\,.\,a}{50\,b}=\frac{\cdot 01\times 1\cdot 53}{25},$$

where x is the normality of the solution, and a and b the number of cubic centimetres occupied by one gramme of water at temperature of filtration and at the ordinary temperature respectively.

The results thus obtained in normalities are transformed in the tables given below into grammes per litre, and the figures of Kohlrausch are appended for comparison.

All experiments were performed at least in duplicate, in some cases they were repeated many times. This was necessary since, on several occasions, single results were not confirmed on repetition; indeed, the general experience throughout was that, at any time, and for no apparent reason, a false result was liable to be obtained. Further, when results in agreement were obtained, the degree of accuracy was usually not closer than within 2 per cent., whereas the limits of error should not amount in all to 1 per cent.

The causes of this are, I think, as follows. Firstly, there is the extreme difficulty of keeping the silica vessels and filtering apparatus chemically clean. The amount of surface is necessarily very large, a great deal of handling has to be done in the course of an experiment, and the slightest trace of acid or alkali introduced on the tube or the interior of the vessels would be sufficient to spoil a result. The surface of the silica vessels is very rough, and particles of solid are washed out only with great difficulty. Thus, in using a vessel for arragonite which has been employed for calcite, it is not sufficient to wash out, or even to boil out, with water; the vessel must be boiled out first with dilute acid for a long time, and then with successive quantities of water.

As an illustration of the reality of danger of error from this source, it may be pointed out that the introduction of ·001 gr. of alkali (calcium carbonate) is sufficient to cause an error of from 5 to 10 per cent.

The silica vessels were therefore most scrupulously cleaned out before each set of experiments, the filtering apparatus before each single experiment. The filter-paper and muslin squares were changed after each determination.

A second source of error is the presence of a trace of carbon dioxide in the water used. As this reappears, however, in a much greater degree, in the course of subsequent experiments, it will be discussed later.

The results for calcite and arragonite at 25° C., 50° C., and 100° C. are given below, both in tabular and in graphic form. At the two lower temperatures the thermostat was kept constant within 0°·1 C.; the figures given for 100° C. are those obtained at the boiling-point, the barometric pressure being observed at the time of the experiment. The true temperature was usually a few tenths of a degree lower than 100° C., but, as will be seen from the diagram, the temperature coefficient is so small that the results are substantially correct for that temperature. The diagram also shows the solubility curve for calcite under ordinary atmospheric conditions (see page 973).

Calcite.

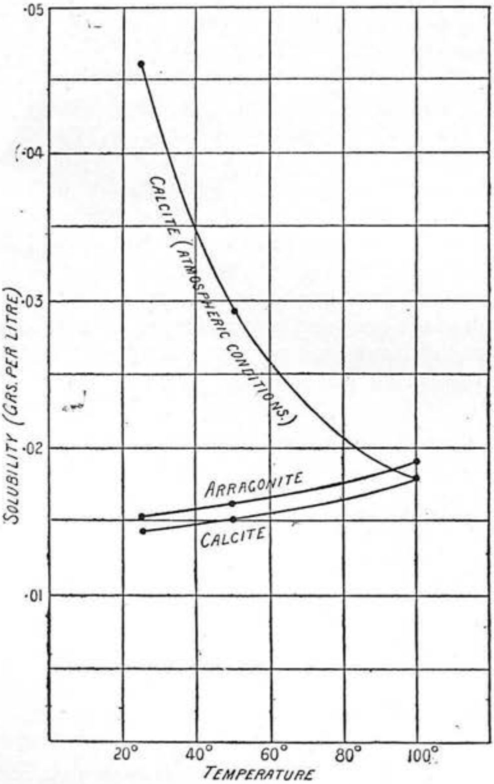
Temperature.	Time before filtration.	Grs. per litre dissolved.			Mean result.	Kohlrausch.
25° C.	1 day	·01428	·01440		·01433	·014
	2 days	—	·01433			
	3 days	·01431	—			
50° C.	1 day	·01507	·01506		·01504	·016
	2 days	·01491	—			
	3 days	—	·01513			
100° C.	40 mins.	(·01816)	·01785	—	·01779	—
	60 mins.	(·01819)	·01770	·01777		
	80 mins.	(·01810)	·01776	—		
	120 mins.	(·01804)	·01785	·01780		

Arragonite.

Temperature.	Time before filtration.	Grs. per litre dissolved.		Mean result.	Kohlrausch.
25° C.	6 days.	(·01075)	—	·01528	·016
	10 days.	(·01286)	—		
	6 days.*	(·01511)	—		
	10 days.*	·01524	·01530		
	12 days.*	·01522	·01536		
50° C.	3 days.	(·01206)	—	·01617	·018
	6 days.	(·01572)	—		
	3 days.*	(·01608)	—		
	6 days.*	·01616	·01611		
	8 days.*	·01616	·01624		
100° C.	60 mins.	(·01178)	—	·01902	—
	120 mins.	(·01660)	—		
	180 mins.	·01926	—		
	60 mins.*	·01901	·01890		
	120 mins.*	·01919	·01898		
	180 mins.*	·01902	·01879		

The results for calcite at 100° C. that are placed between brackets are those obtained with the tin tube; although they agree well together, they are slightly higher than those found when using the silica tube, and are not employed in the calculation of the mean value. The results which are bracketed together are those obtained from experiments with successive portions of the same solution at different times; by this means it could be ascertained when the final solubility value had been reached, in the case of solutions only slowly attaining equilibrium.

It will be seen that arragonite is far slower in attaining equilibrium in solution than calcite. Indeed, in order to obtain results in a reasonable time, arragonite was taken not with water but with a saturated calcite solution, carefully filtered free from solid. Thus, the solution being already almost saturated with regard to arragonite, the end point was reached much more quickly. Experiments performed in this manner are distinguished by a star in the table. Where it is evident that the true solubility value has not been reached, the result is placed between brackets and is not used in the calculation of the mean value.



The comparative slowness with which equilibrium is attained in the case of arragonite is not due to the larger size of the particles, for by observation with the microscope it was found that the two minerals were ground to equal degrees of fineness, but may rather be ascribed to the greater density of the arragonite, offering more resistance to the solvent action of the water.

The results for arragonite are, in general, less concordant than those for calcite ; this is due to the instability of the former. Observations with the microscope were made on slides of the solid residue from each experiment ; calcite was always unchanged, but arragonite at 100° C. always showed a few crystals of calcite, the rhombic crystals of the latter being easily distinguishable among the needle-shaped crystals of arragonite. The proportion of calcite present, although always very small, increased regularly with the time of boiling, and thus a true solubility value for arragonite was never attained, but an intermediate value between the solubilities of the two minerals. At 50° C. and 25° C., no change of arragonite to calcite was observed.

The values obtained are in good agreement with those of Kohlrausch at the ordinary temperature. The ratios of the two solubilities at different temperatures are also fairly concordant with the results of Foote (*Zeit. phys. Chem.* xxxiii. p. 740 (1900)). It will be seen from the diagram that the two curves run almost parallel ; any transition point is obviously either far above or far below the ordinary temperature, if it exists at all. The ratios of the solubilities are $\left(\frac{\text{arragonite}}{\text{calcite}}\right)$:—

	25° C.	50° C.	100° C.
Observed	1·064	1·075	1·069
Foote (by interpolation) ...	1·130	1·114	—

Foote has concluded, from the decrease of the ratio obtained with rise of temperature, that the inversion temperature is above the ordinary range ; the above results, however, show a constant ratio, and hence, since the solubility increases with the temperature, greater difference of solubility with rise of temperature.

It is an interesting point that the ratio of the specific gravities of the two forms is $\frac{2\cdot 90}{2\cdot 72}=1\cdot 066$. The ratio of concentration in the solid form to concentration in the solution thus appears to be constant for the two varieties.

Calcium Bicarbonate Solutions.

The presence of carbon dioxide increases the solubility of carbonates in water to a marked degree, owing to the formation of soluble bicarbonates. The equilibrium of the system is determined by the partial pressure of the carbon dioxide over the solution; and in the case of calcium carbonate here considered, a very small proportion of carbon dioxide corresponds to an enormous increase in the solubility. For this reason, it has been possible to investigate, by the ordinary methods, the equilibrium of the system even for very small partial pressures of carbon dioxide (Schloesing, *Compt. rend.* lxxiv. p. 1552 (1872); Treadwell and Reuter (*Zeit. anorg. Chem.* xvii. p. 170 (1898)). Beyond a certain limit, however, the results become too inaccurate, owing to the diminished solubility. The equilibrium under ordinary atmospheric conditions, for example, which is of importance in water analysis, cannot be determined by the usual volumetric methods.

If a current of air free from carbon dioxide be drawn through a bicarbonate solution, equilibrium is re-established by precipitation of carbonate, and this precipitation will continue until all bicarbonate disappears from the solution, *i. e.*, until all free carbon dioxide is removed. There will therefore remain a saturated solution of calcium carbonate.

Much confusion has always existed in regard to the state in which calcium carbonate falls out of solution. The precipitate obtained differs according to the concentration of the solution, the rate at which precipitation occurs, the temperature of experiment, the partial pressure of carbon dioxide above the solution, and the presence of other salts. The most complete experiments are those of Rose (*Jour. prak. Chem.* lxxxi. p. 383 (1860) ; lxxxii. p. 351 (1861)). From bicarbonate solutions above 90° C., arragonite is deposited ; between 90° C. and 30° C., a mixture of calcite and arragonite ; under 30° C. only calcite. The stability of the arragonite varies according to the conditions of formation.

By double decomposition between concentrated solutions of a calcium salt and a carbonate in the cold, amorphous calcium carbonate is said to be precipitated, transformation to calcite following. The formation of a third crystalline form, also unstable, has lately been described by Meigen (*Chemiker-Zeitung*, xxxiv. p. 1015 (1910)).

In the experiments described below the primary object was to determine the degree of solubility of the carbonate, by the complete withdrawal of the carbon dioxide from bicarbonate solutions, at the temperatures of 25° C., 50° C., and 100° C. The values obtained would, it was expected, give some indication of the form in which precipitation had occurred, and also check the figures for the solubility of calcite and arragonite previously obtained.

The direct preparation of the bicarbonate solutions, by bubbling carbonic acid gas through water containing finely powdered carbonate in suspension, could not be employed. The solution of the crystalline carbonate under these conditions is very slow, and it is essential, to ensure that the precipitate to be obtained afterwards shall be naturally deposited, that no trace of solid carbonate should be present in the liquid.

The solution was therefore prepared as follows. Finely-powdered calcite was converted into lime by roasting in a platinum crucible, and transferred to a flask of Jena glass, filled with water. A second flask was half filled with water through which carbon dioxide had been bubbled for about ten minutes. To this the lime water was added in a slow stream by filtration. A hardened filter-paper was used, supported in a funnel with a long stem, drawn out to a fine jet, dipping into the water. As the liquids met a fine, cloudy precipitate was produced, which immediately dissolved on shaking the flask. The solution could be kept clear only by means of constant agitation; if the precipitate was once allowed to settle, it assumed a hard, crystalline form and was most difficult to dissolve. The addition of the lime-water was stopped before the solution became saturated with bicarbonate, as soon as the precipitate began to be slow in disappearing.

The solution was now added to a large excess of water contained in one of the vessels. The water in the silica flask was maintained, during this addition, at the temperature of the subsequent experiment, and the bicarbonate solution was added slowly, so that any immediate precipitation of carbonate took place at the required temperature. This was of special importance in the case of solutions at the boiling-point. The experiments were now carried on exactly as previously described. At 25° C. and 50° C. the silica flask was suspended in a thermostat and air free from carbon dioxide drawn through the solution; at 100° C. the carbon dioxide was expelled by boiling. Supersaturation was very liable to occur at the lower temperatures, unless the solution was made concentrated enough to give a large excess of calcium carbonate on removal of the carbon dioxide.

The precipitates obtained were always tested by the microscope, and examination showed :—

at 25° C.	rhombic crystals only.
at 50° C.	an intimate mixture of rhombic and needle-shaped crystals.
at 100° C.	needle-shaped crystals, with a very few rhombic.

This is in agreement with the results of Rose—that, at 25° C., calcite is obtained; at 100° C. arragonite, slowly transforming into calcite; at 50° C. a mixture of the two forms.

Nevertheless the previous solubility values were not confirmed. At 25° C. and 50° C., equilibrium was established so slowly that the final value could not be determined, the fall in concentration being extremely slow; at 100° C., a fairly constant value was obtained; this, however, was much higher than the value found for arragonite at 100° C. Examples of the results obtained, with the times of experiment, are given below, expressed as before in grammes per litre.

	25° C.		50° C.	
3 days	·03444	·03097	·02861	—
5 ,,	·03421	—	·02635	·02692
9 ,,	—	·02962	—	·02480

	100° C.	
40 mins.	·02511	—
80 ,,	·02331	·02329
120 ,,	·02346	·02333
180 ,,	·02309	—

The explanation of the results at 100° C. was at first thought to lie in the fact that the needle-shaped crystals precipitated were not, as has been held, identical with mineral arragonite, but were another modification of the carbonate (compare Meigen on the formation of "Vaterite," *Chemiker-Zeitung*, xxxiv. p. 1015 (1910)). This view seemed to be confirmed by the action of cobalt nitrate upon the precipitate.

The differences of behaviour of the various forms of calcium carbonate with boiling cobalt nitrate solution have been examined, qualitatively and quantitatively, by Meigen (*Central-blatt*, ii. p. 1128 (1901); *Chemiker-Zeitung*, xxxiv. p. 1015 (1910)). When finely-powdered arragonite is boiled with a dilute solution of cobalt nitrate, a lilac-coloured precipitate is quickly produced; in the case of calcite, the action is much slower, and the precipitate is tinted blue. Presence of other metallic salts in the solution confuses those colour reactions.

The precipitated crystals gave, when the test was applied, an immediate flocculent lilac-coloured precipitate. Mineral calcite and arragonite, powdered to the same degree of fineness (as observed by the microscope), were only slightly tinted after boiling for some minutes, and no noticeable precipitate was formed.

The specific gravity of the precipitated crystals was found, however, by the Westphal balance to be identical with that of arragonite, 2·89.

The higher values obtained at the lower temperatures of 25° C. and 50° C. are clearly to be accounted for by the obstinate retention of the last trace of carbon dioxide by the solution, equilibrium never being attained in the time of experiment. This was found to be also the case at 100° C. When the experiments were conducted as before until a precipitate had formed, and then all the liquid decanted off, fresh water added to the crystals remaining, and the experiment continued as before, the following solubility values were obtained.

	25° C.	50° C.
4 days	·01879	·01958
6 days	·01868	·01976

	100° C.
60 mins.	·02271
120 mins.	·02238

These are still, it will be seen, much higher than those previously found for calcite and arragonite; the value at 100° C. is scarcely lowered at all. The curve of the solubility has now, however, become approximately parallel to those given by the two crystalline varieties.

Further investigation showed that decantation is insufficient to remove the final trace of carbon dioxide. It is necessary to shake up thoroughly the crystals that remain with successive quantities of water, before proceeding with the experiment; and by this means constant results were finally obtained, comparable with those previously found for the mineral calcite and arragonite.

	25° C.		Mean result.
2 days	·01450	—	
5 days	·01464	·01466	·01460
	50° C.		
2 days	·01554	·01549	
5 days	·01536	—	·01546
	100° C.		
60 mins.	·01909	·01917	
120 mins.	·01899	·01911	·01909

It will be seen that the results of the experiments at 25° C. are substantially the same as those for mineral calcite at that temperature; those at 50° C. lie between the values for calcite and arragonite; those at the boiling-point are identical with the value for arragonite at the boiling-point.

There is still a difference of 1 to 2 per cent. in the values obtained by the two methods; this must be attributed to a minute trace of carbon dioxide, not removed by the washing. It is probably the carbon dioxide that remains, as it were, adsorbed on the surface of the crystals that causes the different behaviour with cobalt nitrate solution.

From the above it will be evident that the accuracy of the method depends entirely upon the purity of the water used for experiment, a trace of carbon dioxide being sufficient to raise the solubility of the carbonate very appreciably. In all experiments the water used was freshly distilled into one of the siclia flasks, yet it would always contain a small amount of carbon dioxide, and small differences in this amount would be sufficient to affect the constancy of the results.

Amorphous Calcium Carbonate.

The conditions for the precipitation of calcium carbonate in its amorphous form have already been discussed. In the dilute solutions employed for the experiments with bicarbonate solutions, one or other of the crystalline forms was always obtained; only in the preparation of the solutions was the amorphous form obtained as a cloudy precipitate, which immediately, unless dissolved, transformed into a crystalline form, calcite.

The amorphous form is the most unstable of the three varieties of the carbonate, and its solubility is necessarily higher than those of the other forms. Nevertheless, the figures given by Kohlrausch (*Zeit. phys. Chem.* xii. p. 234 (1893)) are identical with those for calcite. It is evident that transformation of the amorphous form to calcite had occurred in the course of the experiment.

Similar results were obtained in the direct determinations given below. Experiments were carried out both with natural and prepared forms. The former consisted of ordinary soft chalk; the latter was obtained by heating finely-powdered calcite to lime in a platinum crucible, and reforming the carbonate by means of a current of carbon dioxide passed over the slowly-cooled oxide. The experiment was carried out quantitatively to ensure the absence of unchanged calcite—the heating being continued until the loss of weight was equal to the theoretical. The cooling in a current of carbon dioxide was also repeated until the original weight was restored, in order to remove all traces of quicklime. The experiments were carried out exactly as before, at the temperatures of 25° C., 50° C., and 100° C., and results are given below in grammes per litre.

Prepared Carbonate.

25° C.

			Mean result.
2 days	·01445	·01454	·01445
3 days	·01436	·01444	

50° C.

			Mean result.
2 days	·01510	·01526	·01515
3 days	·01521	·01503	

100° C.

			Mean result.
60 mins.	·01824	...	
100 mins.	·01809	·01816	·01816

Soft Chalk.

100° C.

			Mean result.
60 mins.	(·02117)	·01784	
100 mins.	·01769	...	·01777

It will be seen that the figures are the same as for calcite. The experiments with soft chalk were carried out by treating a quantity with successive portions of water—the first high value is due to the removal of impurities.

The amorphous form is hence seen to be extremely unstable, and no figures for its solubility can be obtained. Another method of preparation—heating the precipitated oxalate to oxide and converting to carbonate by slowly cooling in a current of carbon dioxide—led to the same solubility values being obtained. Conversion to calcite takes place either as soon as the carbonate is formed at the high temperature, or else as soon as it is brought in contact with water. The powdered substance shows, under the microscope, no signs of crystalline character; its density is, however, the same as that of calcite (2·70 by the Westphal balance). For this reason no change in volume could be observed when a dilatometer was packed with the powder and water drawn in to fill the bulb.

Solubility under Atmospheric Conditions.

The extremely small proportion of carbon dioxide in ordinary air is sufficient to raise the solubility of calcium carbonate at the ordinary temperature several hundred per cent. It is therefore necessary to know accurately the amount of carbon dioxide in the air at the time of experiment to render the results, which are of special importance for their applications to water analysis and geology, of any value.

The method of estimation employed was that of Pettenkofer, as improved by Walker (J. C. S. lxxvii. p. 1110 (1900)). By its use the proportion of carbon dioxide in the atmosphere could be determined accurately within ·1 part in 10,000; the determinations actually made varied from 3·56 to 3·88 parts in 10,000, with an average value of 3·69 parts in 10,000.

This value can be taken as the conditions for all experiments given below, for by observation it was found that the final equilibrium of the solution was established so slowly that constant results were obtained in spite of slight changes in the carbon dioxide values from day to day. For the same reason small changes in the barometric pressure had no effect on the solubility values obtained; the mean barometric height was 754 mm.

The experiments were performed at 25° C. and 50° C. as before; powdered calcite was taken in the silica flasks with freshly distilled water, and atmospheric air led through the solution, after being passed through a long tube filled with cotton-wool to remove all dust. The results are given below, in grammes per litre, and are also shown in graphic form upon the diagram on page 965.

	25° C.	Mean value.
3 days	(·04351)	
5 ,,	(·04545)	
18 ,,	·04607	·04608
19 ,,	·04592	
21 ,,	·04625	

	50° C.	
4 days	(·02911)	
7 ,,	·02930	·02925
9 ,,	·02935	

The solubility at 25° C. is hence seen to be more than three times as great as that in pure air (·04608 and ·01433 gr. per litre respectively); that at 50° C. is nearly twice as great (·02925 and ·01504 gr. per litre respectively). At 100° C. the two values should be identical (·01779 gr. per litre). A reference to the diagram (page 965) will show clearly the remarkable difference in the characters of the two solubility curves.

At the ordinary temperatures a bicarbonate solution would give the same values as calcite, since the precipitation takes place in that form. Mineral arragonite would be, as in pure air, slightly more soluble, but the exact determination of the value is of little importance, the results given above being all that are required for practical use.

Conductivity of Bicarbonate Solutions.

The importance of measurements of electrical conductivity in the determination of the purity of a sample of water, and especially in the discovery of any sudden change in the degree of hardness or in the salt content of a town supply, has only recently been recognized. An apparatus for the above purpose (the Dionic Water Tester) is already in the market.

The introduction of the measurement of electrical conductivities into water analysis has rendered necessary the accurate determination of the conductivities of bicarbonate solutions. The values for calcium bicarbonate are clearly of special importance.

The conductivity of solutions of sodium bicarbonate has been investigated by Walker and Cormack (J. C. S. lxxvii. p. 10 (1900)) for the purpose of determining the velocity of the HCO_3' ion. Experiments were carried out at 18° C. between dilutions of 32 and 512. Within this range no difference was observed between solutions diluted with pure water and with water saturated with carbon dioxide.

In the following experiments the dilution was carried further, solutions being used from $v=10$ to $v=10{,}000$, at a temperature of 25° C. The conductivities were determined in a Cantor cell, with the use of a rotating commutator and a galvanometer. Much more accurate values can be obtained by this method for dilute solutions than with the usual induction-coil and telephone.

Sodium bicarbonate solution was made up by bubbling excess of carbon dioxide through sodium hydroxide solution, freshly prepared from metallic sodium. The solution was standardized both volumetrically by neutralization with a known solution of hydrochloric acid, and gravimetrically, by neutralizing 100 c.c. with hydrochloric acid in a platinum basin, evaporating carefully to dryness, and weighing the residue.

Two series of dilutions were made, one with pure water, the other with water containing excess of carbon dioxide. The pure water was prepared by distillation, in the open air, of water to which a little Nessler's solution had been added, as described before; its specific conductivity was $1{\cdot}10 \times 10^{-6}$. The correction for the water conductivity is made as follows. The part due to carbonic acid is, at most, $\cdot 70 \times 10^{-6}$ (Walker and Cormack, J. C. S. lxxvii. p. 11 (1900)). The influence of this on the bicarbonate solutions is negligible up to very high dilutions. The remaining conductivity, $\cdot 40 \times 10^{-6}$, is directly subtracted from the observed values, as below. The values given are the equivalent conductivities of the solutions, expressed in reciprocal ohms.

Conductivity of $NaHCO_3$.
$v=10·07$ (volumetrically); 10·08 (gravimetrically).

V.	With pure Water.		With Water containing CO_2.
	Uncorrected.	Corrected.	
10·07	76·3	76·3	76·5
20·15	80·8	80·8	81·0
40·3	84·6	84·6	84·8
80·6	87·4	87·4	87·8
161·2	89·8	89·7	90·1
322·4	91·7	91·6	92·1
645	93·4	93·1	94·2
1290	94·6	94·1	98·3
2580	95·9	94·9	107·5
5160	98·2	(96·1)	137·3
10320	101·7	(97·6)	—
∞	—	97·0	—

It will be seen that the two series are practically identical up to the limits investigated by Walker and Cormack. At the higher dilutions, however, the presence of the excess of carbonic acid in the solution gives rise to a rapidly-increasing conductivity value. This is due to the ionization of the carbonic acid, which is quite appreciable in the more dilute solutions.

The corrected values for the first series lead to a conductivity value at infinite dilution of 97·0. At the two highest dilutions hydrolysis has evidently begun to be appreciable. The velocity of the HCO_3' ion is therefore found to be, taking the velocity of the sodium ion as 51·0, equal to 46·0.

Calcium bicarbonate solution was made up as previously described, the requisite volume of lime-water of known concentration being run into water containing carbon dioxide to give a solution of dilution 32. This was too unstable at 25° C. to permit of a conductivity value being obtained before precipitation of carbonate occurred. A series was obtained, however, from dilutions 50 to 8000; results are given below. The dilutions were with pure water, of conductivity $1·10 \times 10^{-6}$.

Conductivity. $\frac{1}{2}Ca(HCO_3)_2$.

V.	Uncorrected.	Corrected.
50	81·0	81·0
64	83·5	83·5
128	88·9	88·9
256	93·4	93·3
512	96·8	96·6
1024	100·0	99·6
2048	103·0	102·2
4096	106·7	(105·1)
8192	112·0	(108·7)
∞	—	108·0

As before, the values for the two highest dilutions show that hydrolysis is there appreciable. The value of the conductivity at infinite dilution may be taken as 108·0; taking the velocity of $\frac{1}{2}Ca^{\cdot}$ 61·5, we have the velocity of the HCO_3' ion equal to 46·5.

Finally, the conductivity of solutions of calcium sulphate, the values of which are also of importance in water analysis, was determined. (Compare Kohlrausch and Holborn, *Leitvermögen der Elektrolyte*, p. 161 (1898).) Calcium sulphate was precipitated by mixing dilute solutions of potassium sulphate and calcium chloride, filtered off from the solution, and thoroughly washed. A saturated solution at 25° C. was prepared by rotating a small quantity in a well-stoppered flask, half filled with water, in a thermostat for some days. The liquid was obtained free from excess of solid by means of a pipette fitted with a filter-cover; its concentration was determined gravimetrically by evaporating 100 c.c. carefully to dryness in a platinum basin. The water used for dilution had a specific conductivity of $1·20 \times 10^{-6}$, the whole of which is subtracted for correction, and the corrected results are as below. The figures are the mean of two determinations.

Conductivity. $\frac{1}{2}CaSO_4$.

(Saturated solution at 25° C. $v=32·50$.)

V.	Conductivity.
32·5	72·9
65	83·7
130	94·7
260	105·5
520	115·0
1040	123·3
2080	129·2
4160	134·1
8320	138·4

I desire, in conclusion, to express my thanks to Professor Walker, at whose suggestion the above investigations were carried out, for his advice and assistance during the progress of the research.

Chemistry Department,
University of Edinburgh.

4

MEDDELANDEN
FRÅN
K. VETENSKAPSAKADEMIENS NOBELINSTITUT
BAND 2. N:O 25.

THE
VISCOSITY OF BINARY MIXTURES

BY

JAMES KENDALL

◆

UPPSALA & STOCKHOLM
ALMQVIST & WIKSELLS BOKTRYCKERI-A.-B.

BERLIN
R. FRIEDLÄNDER & SOHN
11 CARLSTRASSE

LONDON
WILLIAM WESSLEY & SON
28 ESSEX STREET. STRAND

PARIS
LIBRAIRIE C. KLINCKSIECK
11 RUE DE LILLE

1913

MEDDELANDEN
FRÅN
K. VETENSKAPSAKADEMIENS NOBELINSTITUT
BAND 2. N:o 25.

The Viscosity of Binary Mixtures.

By

JAMES KENDALL.

Communicated October 9th 1912 by S. ARRHENIUS and Å. G. EKSTRAND.

The viscosity of binary liquid mixtures has been a subject of frequent investigation, but no satisfactory formula has been obtained by which the viscosity of a mixture can be calculated from the viscosities of its two components. In the first place, it is clear that a linear formula does not fit the case, for the variation in the viscosity of a mixture, as we pass from one component to the other, is not expressed by a straight line.

DUNSTAN[1] has shown that the viscosity curves of liquid mixtures may be divided into three classes. The first or normal class approximately obeys the law of mixtures, but the observed viscosities are always smaller than those calculated from the linear formula. In other words, the curves are not linear, but exhibit a certain amount of »sagging» towards the axis of percentage composition. The second class of curve possesses a maximum of viscosity, the third class a minimum; both classes are abnormal. Here it is certain either that chemical combination (such as the formation of hydrates) accompanies the mixing of the liquids, or that, one or both of the components being associated, the degree of association varies with the concentration in the mixture. With rise of temperature the tendency

---

[1] DUNSTAN, Journ. Chem. Soc. 91, 83, (1907).

to form complexes, as well as the degree of association, will decrease. FAUST[1] has investigated typical examples of the second and third types of curves at different temperatures, and has shown that in every case the maximum or minimum tends to vanish with increase of temperature.

It will be obvious that any formula for the viscosity of liquid mixtures can be applicable only to the first or normal class of curves, that is, to mixtures of non-associating and indifferent liquids. It is impossible to include mixtures, in which changes of state occur, in a general formula. Here it must be noted that, even where the curve of the viscosity appears to be of the normal type, changes of state may have occurred in the mixture which are not sufficient to bring about a maximum or minimum point. Small changes of volume and temperature almost invariably accompany mixture, even in the case of the so-called indifferent liquids. It is to be expected therefore that the agreement of any formula with the results of experiment will only be approximate, and that the divergences will be, in general, beyond the limits of experimental error.

The failure of the linear formula:

$$\eta = \nu_1 \eta_1 + \nu_2 \eta_2 \qquad \text{(I)}$$

(where η_1 and η_2 are the viscosities of the two components, ν_1 and ν_2 their percentage volume concentrations in the mixture) to meet the normal type of curve has already been mentioned. The logarithmic formula of ARRHENIUS:[2]

$$\eta = \eta_1^{\nu_1} \eta_2^{\nu_2}; \text{ or, } \log \eta = \nu_1 \log \eta_1 + \nu_2 \log \eta_2 \qquad \text{(II)}$$

is found to hold satisfactorily for mixtures of liquids, when one component is present to the extent of 90 % or more, but is not valid throughout the whole range of mixtures. LEES,[3] after an examination of the various formulae, has found that the mobility formula:

$$1/\eta = \nu_1/\eta_1 + \nu_2/\eta_2 \qquad \text{(III)}$$

---

[1] FAUST, Zeitschr. phys. Chemie, 79, 97, (1912).

[2] ARRHENIUS, Zeitschr. phys. Chemie, 1, 285, (1887).

[3] LEES, Phil. Mag. [VI], 1, 128, (1901).

is also unsatisfactory, and that exact agreement can only be obtained by the introduction of an additional constant depending on the particular mixture considered.

The experiments of JONES, BINGHAM, and MAC MASTER[1] have led them to the conclusions that the fluidity, and not the viscosity of a solution, is the characteristic additive property, and that, in the normal type of mixtures, the curve of the fluidity will be a straight line. The calculations of LEES[2] show that this is not the case if the concentrations of the two components are expressed in volume percentages. DRUCKER and KASSEL,[3] however, have recently restated the mobility formula, using not volume but weight percentages, i. e.,

$$1/\eta = \omega_1/\eta_1 + \omega_2/\eta_2. \qquad \text{(IV)}$$

The agreement of the calculated with the experimental results is, in general, closer than that obtained with the two viscosity formulae given above, but is not superior to that obtained from the volume mobility formula.

It will be seen that in the above equations the concentrations of the two components of the mixture are expressed either in volume or in weight percentages; a molecular percentage formula has not been proposed. This is certainly strange, since from first principles the viscosity is a function of the molecular concentration, «viscosity being essentially the frictional resistance encountered by molecules of the solution in moving over one another».[4]

I have therefore recalculated the values obtained with the various formulae, using molecular percentages of the two components, and now propose the following modified formula of ARRHENIUS:

$$\eta = \eta_1^{n_1}\eta_2^{n_2}; \text{ or, } \log \eta = n_1 \log \eta_1 + n_2 \log \eta_2 \qquad \text{(V)}$$

where n_1 and n_2 are the molecular percentage concentrations of the two components in the mixture. This formula has been

---

[1] JONES, BINGHAM, and MAC MASTER, Zeitschr. phys. Chemie, 57, 234, (1906).

[2] LEES, loc. cit.

[3] DRUCKER and KASSEL, Zeitschr. phys. Chemie, 76, 367, (1911).

[4] NOYES, Journ. Am. Chem. Soc. 34, 457, (1912).

tested over the whole of the available experimental data, notably the mixtures investigated by Thorpe and Rodger,[1] by Linebarger,[2] by Dunstan and Stubbs,[3] and by Getman.[4] Typical exemples are given below in Tables 1—6. The first column in the tables gives the molecular percentage concentration of one component of the mixture. the second shows the observed viscosity, the third the value calculated from the formula. The remaining columns give the percentage divergences between the experimental and calculated results, as obtained by the application of the formulae (I) to (V) respectively.

Table I. Carbon Tetrachloride and Benzene. 60° C.

(Thorpe and Rodger.)

% C_6H_6	Viscosity		Percentage Error				
	Observed	Calculated	I	III	III	IV	V
0·00	·00582	—	—	—	—	—	—
36·10	·00503	·00504	+ 3	+ 1	— 1	+ 4	0
60·42	·00456	·00457	+ 3	+ 2	— 1	+ 5	0
80·41	·00422	·00423	+ 2	+ 1	— 1	+ 4	0
100·00	·00391	—	—	—	—	—	—

Table II. Acetic Ether and Nitrobenzene. 25° C.

(Linebarger.)

% $C_6H_5 . NO_2$	Viscosity		Percentage Error				
	Observed	Calculated	I	II	III	IV	V
0·00	·00434	—	—	—	—	—	—
17·53	·00582	·00559	+ 18	— 3	— 13	— 10	— 4
47·76	·00889	·00864	+ 26	— 2	— 22	— 15	— 3
68·80	·01204	·01170	+ 17	— 2	— 15	— 15	— 3
100·00	·01834	—	—	—	—	—	—

---

[1] Thorpe and Rodger, Journ. Chem. Soc. 41, 360, (1897).

[2] Linebarger, Amer. Journ. Science, [iv], 2, 331, (1896).

[3] Dunstan and Stubbs, Journ. Chem. Soc. 93, 1919, (1908).

[4] Getman, Journ. Chem. Phys. 4, 398, (1906).

Table III. Carbon Bisulphide and Ether. 25° C.
(LINEBARGER.)

% $(C_2H_5)_2O$	Viscosity		Percentage Error				
	Observed	Calculated	I	II	III	IV	V
0·00	·00358	—	—	—	—	—	—
13·42	·00338	·00337	− 2	− 4	− 5	− 1	0
35·03	·00306	·00306	− 3	− 6	− 8	− 2	0
63·45	·00269	·00270	− 3	− 5	− 6	− 1	0
100·00	·00230	—	—	—	—	—	—

Table IV. Ethyl Acetoacetate and Pyridine. 25° C.
(DUNSTAN and STUBBS.)

% Ester	Viscosity		Percentage Error				
	Observed	Calculated	I	II	III	IV	V
0·00	·008805	—	—	—	—	—	—
11·14	·009297	·00934	+ 6	+ 3	+ 2	+ 2	0
22·30	·009918	·00992	+ 8	+ 5	+ 2	+ 2	0
38·76	·01090	·01085	+ 9	+ 6	+ 1	+ 3	0
59·88	·01233	·01215	+ 7	+ 4	+ 1	+ 1	− 1
100·00	·015081	—	—	—	—	—	—

Table V. Ethyl Diethylacetoacetate and Benzene. 25° C.
(DUNSTAN and STUBBS.)

% Ester	Viscosity		Percentage Error				
	Observed	Calculated	I	II	III	IV	V
0·00	·006145	—	—	—	—	—	—
1·57	·006240	·00629	+ 10	+ 4	+ 1	+ 1	+ 1
6·48	·006817	·00678	+ 33	+ 10	0	+ 2	− 1
29·14	·009876	·00956	+ 66	+ 27	− 2	+ 1	− 3
47·35	·01321	·01259	+ 55	+ 26	− 4	− 1	− 5
100·00	·02793	—	—	—	—	—	—

Table VI. Ether and Toluene. 25° C. (GETMAN.)

% $C_6H_5.CH_3$	Viscosity		Percentage Error				
	Observed	Calculated	I	II	III	IV	V
0·00	·00223	—	—	—	—	—	—
24·63	·00290	·00279	+ 5	− 3	− 10	− 7	− 4
49·48	·00360	·00350	+ 8	− 3	− 12	− 8	− 3
74·58	·00445	·00439	+ 6	− 1	− 9	− 6	− 1
100·00	·00553	—	—	—	—	—	—

It will be seen from the above tables that the agreement of the proposed formula with the results of experiment is, in general, closer than that obtained with the remaining formulae. In certain mixtures the divergence between the calculated and experimental values may be considerable, but this can be regarded as due to the fact that such mixtures do not fulfil the requirements of the normal type. The case of acetic ether and nitrobenzene (Table II above) may be instanced. Here there is a contraction of 0·8 per cent for a 50 per cent by volume mixture, which shows that some interaction has taken place, and the viscosity is greater than in a normal mixture.

The highest divergence between calculated and observed results in the whole series of mixtures investigated was 8 per cent. This compares favourably with the maximum differences obtained with the use of the other formulae, as will be seen from the tables above.

From the collected results of the above observers, the following figures are obtained for the average percentage divergences between calculated and experimental viscosities, as given by the various formulae. In all, 84 mixtures of liquids are included, representing the whole of the available data for mixtures of the normal type.

	Percentage Error
Linear Formula	11·1
Logarithmic Formula (Volume)	4·7
Mobility Formula (Volume)	3·4
Mobility Formula (Weight)	3·2
Logarithmic Formula (Molecular)	2·3

The superiority of the proposed formula over those previously brought forward is thus established. A molecular mobility formula has also been tested, but was found to give no better agreement than those cited above.

The results obtained appear to be in conflict with the general conclusions of recent investigations, that the fluidity and not the viscosity is the characteristic property of a solution. A logarithmic formula, however, is at the same time true both for fluidity and for viscosity, since $1/\eta$ may be substituted for η without affecting the result. The agreement of the above formula does, nevertheless, point to the fact that neither the viscosity nor the fluidity is the true characteristic property, but the logarithms of these quantities. From the above equation the logarithmic viscosity (or fluidity) of a mixture is found to be an additive property of the logarithmic viscosities (or fluidities) of its two components.

The Viscosity of Solutions.

The formulae that have been brought forward to express the viscosity of solutions are, in general, similar to those for binary liquid mixtures, and similarly unsatisfactory. Thus the linear formula:

$$\eta = (1 + Ax)\,\eta_0 \qquad (\text{I})$$

(where η_0 is the viscosity of the pure solvent, x the volume of solute per unit-volume of solution, and A a constant) is true only for very dilute solutions. The logarithmic formula of ARRHENIUS:[1]

$$\eta = A^x \eta_0;\ \text{or,}\ \log \eta/\eta_0 = x \log A \qquad (\text{II})$$

also becomes unsatisfactory as the concentration of the solution is increased. The mobility formula of LEES:[2]

$$1/\eta = \nu_1/\eta_1 + \nu_2/\eta_2 \qquad (\text{III})$$

---

[1] ARRHENIUS, Zeitschr. phys. Chemie, 1, 285, (1887).

[2] LEES, Phil. Mag. [VI]. 1, 139, (1901).

regards the most concentrated solution as one component, and treats the system as a binary liquid mixture, as in the former section. Here again agreement cannot be obtained without the introduction of an additional constant, depending or the particular mixture considered.

GREEN[1] has investigated the agreement of various formulae for aqueous solutions of sucrose over a wide range of concentration. No satisfactory results were obtained, but the best agreement was given by the expression:

$$\eta = A^{\nu/\omega} \eta_0 \tag{IV}$$

where ν is the volume of the sucrose, and ω the volume of the water, present per unit-volume.

The formula proposed here is again a modification of the ARRHENIUS formula, the molecular concentration of the solute being substituted for the volume concentration. The equation is therefore:

$$\eta = A^x \eta_0; \text{ or, } \log \eta/\eta_0 = x \log A, \tag{V}$$

where A is a constant, and x is the molecular concentration of the solute, not in a fixed volume of the solvent, but in a fixed weight.

The experimental data for testing the above formula with normal solvents (i. e., non-associated and indifferent liquids) are very scanty. In Table VII below, however, are collected the results of DUNSTAN and THOLE[2] for the viscosity of solutions of the octyl hydrogen phthalates in benzene. The three varieties of the solute — racemic, dextro, and laeso — are denoted by the letters r, d, l respectively. The concentrations of the solutions are re-calculated to molecules of solute per 100 molecules of solvent. In the second column the observed viscosities are given, the value for that of the pure solvent being interpolated from the figures of THORPE and RODGER.[3] The constancy of the values for log A given in the third column shows that the formula is valid within the limits of experimental error. From

---

[1] GREEN, Journ. Chem. Soc. 93, 2023, (1908).

[2] DUNSTAN and THOLE, Journ. Chem. Soc., 97, 1249, (1910).

[3] THORPE and RODGER, Phil. Trans. A 195, 397, (1894).

the mean value obtained for log A, ·0285, the viscosities given in the last column are calculated; the maximum divergence between calculated and observed values is only 1 per cent.

Table VII. Octyl Hydrogen Phthalates in Benzene. 25° C.

	Mols. solute in 100 mols. solvent	Viscosity (observed)	log A	Viscosity (calculated)
	0·000	·006030	—	—
r	1·805	·006767	·0278	·006787
r	2·597	·007189	·0294	·007150
r	3·363	·007520	·0285	·007520
r	5·097	·008432	·0286	·008424
r	5·228	·008604	·0295	·008498
r	6·490	·009190	·0282	·009230
d	1·910	.006844	·0289	·006835
d	3·478	·007575	·0285	·007575
d	3·642	·007631	·0281	·007657
d	6·996	·009525	·0284	·009544
l	6·928	·009418	·0280	·009499

The viscosity of aqueous solutions is of greater importance, and has been more frequently investigated. Here, however, the complicating effects of dissociation and hydration of the solvent come into play, and it is obviously impossible for the above formula to hold, as it stands, for solutions of electrolytes. Solutions of non-electrolytes may be expected to follow the formula provided that hydration or association of the solute does not occur to any marked extent.

In the following table are given the results of Green[1] for aqueous solutions of sucrose at 25° C. The concentrations are expressed as molecules of solute per 1000 grammes of water, as calculated from the concentration in normalities with the help of the density data.

---

[1] Green, loc. cit.

Table VIII. Sucrose in Water. 25° C.

Concentration of solute		Viscosity	A
Mols. per litre solution	Mols. per 1000 grs. water		
0	0	·008953	—
0·4	0.4382	·013083	2·38
0·8	0·9666	·02105	2·42
1·2	1·618	·03805	2·44
1·6	2·440	·07973	2·45
2·0	3·516	·2072	2·44
2·5	5·440	1·058	2·41

The constancy of the values for A in the last column shows that the formula holds satisfactorily thoughout the whole range of concentration, even for solutions containing 65 per cent by weight of sugar, where the viscosity is more than a hundred times as great as that of pure water. If the logarithmic volume formula is applied to the same solutions, the value of the constant is found to rise steadily, from 2·4 to 5·7, with increasing concentration.

A third example is given for aqueous solutions of carbamide, from the experiments of DUNSTAN and MUSSELL.[1] The agreement is again seen to be satisfactory throughout a large range of concentration.

Table IX. Carbamide in Water. 25° C.

Concentration of solute		Viscosity	A
% water in solution	Mols. per 1000 grs. water		
0	0	·00891	—
1·02	0·1715	·00895	(1·026)
8·13	1·473	·00939	1·036
11·89	2·247	·00969	1·038
15·47	3·040	·01005*	1·040
23·12	5·006	·01088	1·041
33·28	8·304	·01252	1·042
38·13	10·260	·01348	1·041
46·18	14·28	·01561	1·040

---

[1] DUNSTAN and MUSSELL, Journ. Chem. Soc. 97, 1935, (1910).

The divergence of the first value of A falls wholly within the limits of experimental error, owing to the small increase in the viscosity. The starred value is the table in given in the original paper as ·01035, interpolation shows that this must be a misprint for the value given above.

The viscosities of several amides in aqueous solution have been investigated by DUNSTAN and MUSSELL in the paper cited, and from the experimental results it is concluded that, while formamide and carbamide are not associated to any marked extent in aqueous solution, in the higher amides — such as acetamide and propionamide — the association increases with the molecular weight. It is therefore to be expected that, although formamide and carbamide obey the above formula, the higher amides will diverge more and more with increasing concentration. This is indeed the case, as will be shown later.

Connection of the Formulae for Mixtures and Solutions.

The formulae established in the preceding sections are:

(a) for liquid mixtures, $\eta = \eta_1^{n_1} \eta_2^{n_2}$;

(b) for solutions, $\eta = A^x \eta_0$.

It will be seen that both equations are of the same form, and the question therefore arises whether it is possible to obtain a connection between them, so as to possess one general formula applicable to all binary mixtures.

Since $n_1 + n_2 =$ unity, we may write the first formula as follows:

$$\eta = \eta_1^{\frac{n_1}{n_1 + n_2}} \eta_2^{\frac{n_2}{n_1 + n_2}}.$$

If now n_2 is small with respect to n_1, and we may neglect n_2 in the quantity $(n_1 + n_2)$, this becomes:

$$\eta = \eta_1 \eta_2^{\frac{n_2}{n_1}}; \text{ or } \eta = \eta_1 A^{n_2};$$

where A is a constant, and n_2 the molecular concentration of the second component in a fixed quantity of the first.

The formula for solutions is thus seen to be a first approximation to the formula for liquid mixtures, applicable exactly only for solutions of small molecular concentration. The exact formula for solutions in general will be of the same form as that for binary liquid mixtures;

$$\eta = \eta_1^{n_1} \cdot \eta_2^{n_2};$$

where η_1 represents the viscosity of the pure solvent, η_2 that of the solute in the «liquid state», and n_1 and n_2 the percentage molecular concentrations of the two components.

The unknown quantity here is η_2, the viscosity of the dissolved substance in the solution, which will obviously be very large. It may be found by throwing the equation into the form:

$$\log \eta - n_1 \log \eta_1 = n_2 \log \eta_2.$$

The validity of the formula can now be tested by the constancy of the values obtained for $\log \eta_2$ from solutions of varying concentration.

This is done for the case of the octyl hydrogen phthalates in benzene in Table X below. The first column shows the percentage molecular concentration of the solute, then follow the viscosity of the solution and the calculated value for $\log \eta_2$. These appear to be by no means constant, the variations are, however, irregular. The large divergences are due to the small concentration of the solute, and fall wholly within the limits of experimental error, as will be seen from the figures in the last column, where the viscosities of the solutions are re-calculated with the use of the mean value for $\log \eta_2$, ·754. The differences between the calculated and observed viscosities are seen to be within the errors of experiment.

Table X. Octyl Hydrogen Phthalates in Benzene. 25° C.

% solute (molecular)	Viscosity (observed)	$\log \eta_2$	Viscosity (calculated)
0	·006030	—	—
r 1·774	·006767	·602	·006810
r 2·532	·007189	·788	·007174
r 3·253	·007520	·728	·007535

% solute (molecular		Viscosity (observed)	$\log \eta_2$	Viscosity (calculated)
r	4·850	·008432	.782	·008404
r	4·970	·008604	·888	·008474
r	6·094	·009190	·782	·009157
d	1·874	·006844	·719	·006855
d	3·362	·007575	·725	·007591
d	3·618	·007631	·689	·007671
d	6·539	·009525	·816	·009434
l	6·479	·009418	·770	·009397

With aqueous solutions the problem again becomes more complicated, owing to the association of the solvent. Not only is the exact degree of association of water at a given temperature a matter of uncertainty, but we do not know what effect the introduction of a second substance as solute will have upon the degree of association. The true evaluation of n_1 and n_2 for any aqueous solution is therefore impossible. Where the molecular percentage concentration of the solute is small, however, it will be found on trial that, provided the solute does not change the degree of association of the water or itself associate in the solution, the course of the values obtained for $\log \eta_2$ with varying concentration is only slightly affected by the degree of association of the solvent. In applying the general formula obtained above to aqueous solutions, the molecular concentrations are therefore, in the following tables, calculated under the assumption that the solvent consists of simple molecules. From the constancy of the values obtained for $\log \eta_2$ at different concentrations the applicability of the formula can thus be tested; the absolute values for $\log \eta_2$ are, however, unknown. Table XI shows the results obtained for sucrose in aqueous solution.

Table XI. Sucrose in Water. 25° C.

% solute (molecular)	Viscosity	$\log \eta_2$
0·0	·008953	—
0·783	·013083	19·0
1·712	·02105	19·6

% solute (molecular)	Viscosity	log. η_2
2·83	·03805	20·2
4·21	·07973	20·5
5·96	·2072	20·8
8·93	1·058	21·1

It will be seen that, in the range of concentrations given above, log η_2 regularly increases from 19·0 to 21·1; that is, by 10 per cent. If the association of the solvent is taken into account, the run of the figures is unchanged, but the percentage divergence is slightly increased. Any explanation of this divergence from the general formula can only be tentative, owing to the various possible disturbing factors in the solution. In view of the very large range of concentration covered, however, it may be assumed that the formula is here also valid, though only approximately.

The same gradual increase with concentration in the values obtained for log η_2 will be seen in the table below, which shows the results for carbamide.

Table XII. Carbamide in Water. 25° C.

% solute (molecular)	Viscosity	log. η_2
0·0	·00891	—
0·308	·00894	($\bar{2}$·493)
2·585	·00939	$\bar{2}$·818
3·89	·00969	$\bar{2}$·890
5·19	·01005	$\bar{2}$·958
8·27	·01088	$\bar{2}$·997
13·02	·01252	$\bar{1}$·084
15·60	·01348	$\bar{1}$·102
20·46	·01561	$\bar{1}$·139

Exactly similar results are obtained with formamide, from the figures of DUNSTAN and MUSSELL.[1] It seems probable

---

[1] DUNSTAN and MUSSELL, Journ. Chem. Soc. 97, 1935, (1910).

therefore that the above gradual increase in the values obtained for log η_2 with increasing concentraion is the normal case for aqueous solutions of non-associating substances, when the molecular concentrations are calculated under the assumptions made above. When the solute associates in solution, however, a different course of the values is observed; an instance is given for propionamide below.

Table XIII. Propionamide in Water. 25° C.

% solute (molecular)	Viscosity	log. η_2
0·0	·00891	—
0·310	·00919	2·192
1·455	·01025	2·133
3·166	·01188	1·899
6·565	·01536	1·552
14·88	·03030	1·522
37·26	·05980	0·169

Here there is a considerable decrease in the values obtained for log η_2 with increasing concentration. The other higher amides investigated by Dunstan and Mussell[1] show the same course.

The general formula for binary mixtures in therefore found to be valid for non-associated solvents, and (approximately) for associated solvents when the solute is normal, but does not hold — as is only to be expected — when the solute is also associated in the solution.

Summary of Results.

The viscosity of binary liquid mixtures of the normal type has been shown to be represented by the formula:

$$\eta = \eta_1^{n_1} \eta_2^{n_2}; \qquad (1)$$

(where η_1 and η_2 are the viscosities of the two components, n_1 and n_2 their molecular percentage concentrations in the mixture)

---

[1] Dunstan and Mussell, loc. cit.

more exactly than by any of the formulae previously proposed. This formula has been tested over the whole of the available experimental data. By writing the equation in the form:

$$\log \eta = n_1 \log \eta_1 + n_2 \log \eta_2 \qquad \text{(II)}$$

it is seen that the logarithmic viscosity (or fluidity) of a solution is the characteristic additive property, and not these quantities themselves.

The viscosity of solutions has been found to follow the equation:

$$\eta = \eta_0 \, A^x. \qquad \text{(III)}$$

This formula has been tested both for non-aqueous and for aqueous solutions, and found to be valid throughout a wide range of concentration. Abnormal solutes such as electrolytes are naturally not included in the formula.

The connection between these two formulae has been established, and the second is found to be a simplification of the first, applicable exactly only to dilute solutions. The general formula for binary mixtures (equation (I) above) has been tested for solutions of various types, and has been found to give, in the more normal cases, satisfactory agreement.

The above investigation has been carried out at the Nobel Institute of Physical Chemistry, under the direction of Professor ARRHENIUS, and forms the first of a series of parallel researches on the variation of viscosity and molecular conductivity with temperature and concentration. I have great pleasure in expressing my thanks to Professor ARRHENIUS for the interest he has taken in the development of the above paper.

◆

Tryckt den 12 mars 1913.

Uppsala 1913. Almqvist & Wiksells Boktryckeri-A.-B.

MEDDELANDEN
FRÅN
K. VETENSKAPSAKADEMIENS NOBELINSTITUT
BAND 2. N:O 29.

THE PROPERTIES OF LIQUIDS
AS
FUNCTIONS OF THE CRITICAL CONSTANTS

BY

JAMES KENDALL

◆

UPPSALA & STOCKHOLM
ALMQVIST & WIKSELLS BOKTRYCKERI-A.-B.

BERLIN
R. FRIEDLÄNDER & SOHN
11 CARLSTRASSE

LONDON
WILLIAM WESSLEY & SON
28 ESSEX STREET. STRAND

PARIS
LIBRAIRIE C. KLINCKSIECK
11 RUE DE LILLE

1913

MEDDELANDEN
FRÅN
K. VETENSKAPSAKADEMIENS NOBELINSTITUT
BAND 2. N:o 29.

The Properties of Liquids as Functions of the Critical Constants.

By

JAMES KENDALL.

Communicated December 4th 1912 by S. ARRHENIUS and Å. G. EKSTRAND.

1. Introduction.

The critical constants of temperature, volume and pressure are characteristic fixed points for each liquid; it is therefore probable that the various properties of liquids may he capable of development as simple functions of these constants. Equations of such a type will possess theoretical significance, in view of the relations existing between the the critical constants and the equation of VAN DER WAALS:

$$\left(p + \frac{a}{v^2}\right)(v - b) = RT.$$

Any formulae obtained may thus be expected to prove of value in the elucidation of the laws governing matter in the liquid state.

The determination of the critical constants of a large number of pure liquids, and of certain properties of these liquids through temperatures ranging from zero Centigrade to the critical point, has formed the subject of very extended researches by YOUNG and his collaborators. The final complete results have recently been published in a paper, the scope of which is indicated by its title: «The Vapour Pressures, Specific Volumes, Heats of Vaporization, and Critical Constants of Thirty Pure Substances.»[1] The extreme accuracy of the measurements renders the results of the greatest utility for testing the validity of formulae involving the above quantities.

In the following pages it is shown from the results of YOUNG that two important properties of liquids — the heat of vaporization and the specific volume — can be expressed as simple functions of the critical constants. The first part of the paper is occupied with the development of the equations and the demonstration of their applicability through the ordinary range of temperatures; the second part deals with the results which follow when these equations are applied at the absolute zero of temperature, and with some theoretical considerations.

The following notation is employed throughout:

T absolute temperature. T_c critical temperature. T_b boiling-point (760 mm. pressure). T_0 absolute zero of temperature. t temperature Centigrade.

v volume of one gramme of liquid. v_0 volume at absolute zero.

V volume of one gramme of saturated vapour.

d density of the liquid (referred to water at 4° C. as unity). d_c density at critical point. d_0 density at absolute zero.

D density of the saturated vapour.

P vapour pressure in millimetres of mercury.

Q heat of vaporization of one gramme of liquid, expressed in calories. Q_b heat of vaporization at the boiling-point. Q_0 heat of vaporization at absolute zero.

M molecular weight of the liquid.

R the constant of the gas equation, $PV = RT$; equal to 1·988.

k, k_1, k_2, c, μ' constants for each particular liquid.

2. The Heat of Vaporization.

The direct experimental determination of the heat of vaporization of a liquid by the calorimetric method, through an extended temperature interval, is a matter of extreme difficulty, and the results obtained at high temperatures are liable to be considerably in error. The thermodynamical equation of CLAU-

---

[1] YOUNG, Proc. Roy. Soc. Dublin, 12, 374, (1910).

SIUS and CLAPEYRON, however, affords a method of obtaining the heat of vaporization indirectly by the measurement of other quantities, and has always been found to give satisfactory agreement, where comparison is available, with the values obtained by the calorimetric method.

With the notation given above, the thermodynamical equation is expressed as follows:

$$Q = 0{\cdot}0_4 31833 \left(\frac{dP}{dT} \cdot T\right)(V - v) \qquad (1)$$

The numerical factor is the reciprocal of the value of the mechanical equivalent of heat under the units employed. The heat of vaporization at any temperature is thus obtained in terms of T, V, v, and $\frac{dP}{dT}$, and the degree of accuracy of the calculated value will depend upon the limits of experimental error in the determination of these quantities, and upon the relative effect of such errors in the calculation of the equation. These points have been examined by MILLS,[1] in a valuable paper supplementing the work of YOUNG.

The conclusion drawn is that, except at zero Centigrade and in the neighbourhood of the critical temperature, the calculated values for the heat of vaporization are substantially true, the error caused by inaccurate measurements and the multiplication of such errors in the calculation never exceeding two per cent, and being usually less than one per cent. At zero Centigrade the calculated values are too high; near the critical temperature the difficulty in the determination of $\frac{dP}{dT}$ renders the results somewhat uncertain.

A second formula representing the heat of vaporization has been developed by MILLS, and has been shown to give results, in the case of normal substances, which are in excellent agreement with those obtained by the thermodynamical equation. The formula may be stated thus:

$$Q = 0{\cdot}0_4 31833\ P(V - v) + \mu'(\sqrt[3]{d} - \sqrt[3]{D}). \qquad (2)$$

---

[1] MILLS, Journ. Amer. Chem. Soc., 31, 1099, (1909).

The first half of this expression represents the external heat of vaporization, due to the change in volume; the second half gives the internal heat of vaporization, representing the work done against the force of molecular attraction in moving the molecules of the liquid further apart. μ' is a constant varying for each particular substance.

The significance of this equation is expressed as follows: The molecular attraction varies inversely as the square of the distance apart of the attracting molecules, and the total amount of attractive force possessed by a molecule is a constant. Therefore the internal heat given out as the molecules approach each other, multiplied by the distance apart of the molecules, is equal to a constant.

A third formula proposed by DIETERICI:[1]

$$(3) \qquad Q = 0{\cdot}0_4 31833\, P(V - v) + 4{\cdot}577\; c \left(\frac{T}{M}\right) \log \frac{d}{D}$$

is critically examined by MILLS and found to be inaccurate at low temperatures, although the agreement at higher temperatures is remarkably good.

Finally, the heat of vaporization at low temperatures, where the gas laws may be assumed to be obeyed, has been shown by ARRHENIUS[2] to be capable of representation by the formula:

$$(4) \qquad Q = A_0 - CT^2.$$

A_0 is the free energy at absolute zero of temperature, C is a constant varying for each particular liquid, but of the same order of magnitude for all liquids. The formula is an expansion in ascending powers of T, in which higher powers than the second are neglected. It is therefore only to be expected that the equation will become less accurate at high temperatures, and it is found indeed that at temperatures near the critical point the higher terms of T cannot be left out of consideration.

In all of the above equations, the heat of vaporization is obtained expressed in terms of several distinct quantities. The formula developed below attempts to express the heat of va-

---

[1] DIETERICI, Ann. der Physik, 12, 144, (1903).

[2] ARRHENIUS, Meddel. från K. Vet.-Akad:s Nobelinstitut. Band 2. N:o 8, (1911).

porization as a function of one quantity only — the critical temperature of the liquid.

At the critical temperature the heat of vaporization is zero, since liquid and vapour are identical. If the heat of vaporization is plotted against the temperature, it will be found that as the temperature falls the heat of vaporization increases at first extremely rapidly, but that the rate of increase soon falls off and at ordinary temperatures has become very small.

A curve of this type — a sharp increase followed by a slow one — is given by an equation of the form $y = kx^n$, where n is fractional. The agreement of the values obtained for the heat of vaporization with an equation of this form, i. e.,

$$Q = k(T_c - T)^n \qquad (5)$$

was therefore tested for some typical normal liquids.

As a result it was found that the agreement was extremely good, for normal non-associated substances, throughout the whole range of temperature, except for small deviations at zero Centigrade and in the neighbourhood of the critical point. Furthermore, while k was a constant which varied for each particular liquid, the value of the exponent n was found to be the same for all substances, and equal to 0·386. The discussion of the significance of this figure is left over to a later section of the paper. In Tables I to IV below are given examples of the agreement of the values obtained by the above formula, with those calculated from the thermodynamical equation and the formula of MILLS respectively, for liquids of diverse types — a hydrocarbon, carbon tetrachloride, an ester, and an alcohol.

Table I. Octane. $Q = 9{\cdot}72\ (569{\cdot}2 - T)^n$.

t	Q (calc.)	Ther.	MILLS
0	87·49	89·46	86·69
120	71·56	71·43	71·83
160	64·79	64·75	65·06
200	56·64	56·61	56·72
240	46·02	45·97	45·72
260	38·85	39·14	38·63
280	28·50	28·26	28·17
290	19·35	19·10	19·50

Table II. Carbon Tetrachloride. $Q = 5\cdot92\,(556\cdot15 - T)^n$.

t	Q (calc.)	Ther.	MILLS
0	52·36	51·87	52·40
80	46·03	46·00	46·44
120	42·30	42·08	42·54
160	37·95	37·95	38·08
200	32·62	32·61	32·52
240	25·33	25·56	25·10
260	19·90	20·07	19·70
280	9·22	10·43	10·45

Table III. Methyl Butyrate. $Q = 10\cdot47\,(554\cdot25 - T)^n$.

t	Q (calc.)	Ther.	MILLS
0	92·35	95·79	90·91
100	77·95	77·80	78·13
140	70·77	70·84	71·04
180	62·26	62·00	62·26
220	51·28	51·31	51·07
260	34·10	34·44	34·06
275	21·30	21·26	21·66
280	11·59	11·16	10·98

Table IV. Methyl Alcohol. $Q = 36\cdot50\,(513\cdot0 - T)^n$.

t	Q (calc.)	Ther.	MILLS
0	302·8	289·2	289·4
40	282·2	277·8	275·8
80	258·9	259·0	256·8
120	231·7	232·0	231·7
160	198·1	198·3	199·4
200	151·6	151·8	154·4
230	88·8	84·5	92·2
236	62·3	61·7	68·9
238·5	42·7	44·2	51·1

For the normal liquids represented in Tables I to III above, the agreement between the three formulae is seen to be very satisfactory throughout. At the lowest temperature, zero Centigrade, where the thormodynamical equation is liable to give values somewhat too high, the agreement of the calculated values with those given by the formula of MILLS is still good. In general, thoughout the whole series of twenty-six normal liquids available for examination, the agreement of the formula of MILLS with that developed above is better than that between either of these and the thermodynamical equation. This is probably due to the greater influence of errors of observation upon the values calculated by means of this last equation.

In the case of methyl alcohol, Table IV, concordant values are obtained only at the higher temperatures. The divergences at ordinary temperatures are evidently to be ascribed to the association of the liquid. With the remaining associated substances investigated by YOUNG, including water and acetic acid, these divergences are still more marked, and persist even at the higher temperatures.

The value of the constant k for each particular substance is shown in the general table (Table V) below; the critical temperatures and molecular weights of the liquids are also there included. The whole of the thirty-eight substances examined by MILLS are tabulated; for the last seven, however, the experimental data are not always trustworthy. Where the value obtained is uncertain, owing to association of the liquid or to errors of observation, it is enclosed within brackets.

Table V.

	M	T_c	k	Mk	$Mk/T_c^{\cdot 614}$
Ether	74·08	466·8	11·86	879	20·2
Di-isopropyl	86·112	500·4	10·46	901	19·8
Di-isobutyl	114·144	549·8	9·22	1052	21·9
Isopentane	72·10	460·8	11·48	828	19·2
Pentane	72·10	470·2	11·94	861	19·7
Hexane	86·112	507·8	11·00	947	20.7
Heptane	100·13	539·9	10·46	1047	22·0
Octane	114·144	569·2	9·72	1110	22·6

	M	T_c	k	Mk	$Mk/T_c^{\cdot 614}$
Hexamethylene . .	84·096	553·0	11·02	927	19·2
Benzene	78·05	561·5	12·10	944	19·4
Fluobenzene	96·09	559·55	10·04	964	19.8
Chlorobenzene . . .	112·49	632·1	9·32	1048	19·9
Bromobenzene . . .	156·99	670·0	6·81	1069	19·7
Iodobenzene	203·89	721·0	5·48	1118	19·7
Carbon tetrachloride	153·8	556·15	5·92	911	18·8
Stannic chloride . .	260·8	591·7	3·89	1015	20·1
Methyl formate . .	60·032	487·0	14·79	888	19·9
Ethyl formate . . .	74·05	508·3	12·83	950	20·7
Methyl acetate . . .	74·05	506·7	13·31	986	21·5
Propyl formate . . .	88·064	537·85	11·45	1009	21·2
Ethyl acetate . . .	88·064	523·1	11·67	1028	22·0
Methyl propionate .	88·064	530·4	11·66	1027	21·8
Propyl acetate . . .	102·08	549·2	10·74	1096	22·8
Ethyl propionate . .	102·08	545·9	10·48	1070	22·3
Methyl butyrate . .	102·08	554·25	10·47	1069	22·1
Methyl isobutyrate .	102·08	540·55	10·22	1043	21·9
Water	18·016	643·0	(65·30)	(1177)	(22·2)
Methyl alcohol . .	32·032	513·0	36·50	1169	25·3
Ethyl alcohol . . .	46·048	516·1	(27·50)	(1266)	(27·3)
Propyl alcohol . . .	60·064	536·7	(21·40)	(1285)	(27·1)
Acetic acid	60·032	594·6	(14·80)	(889)	(17·6)
Carbon disulphide .	76·14	546·05	10·38	811	16·9
Chloroform	119·358	533·0	7·87	940	19·9
Acetone	58·048	510·5	17·32	1005	21·9
Ammonia	17·064	404.0	45.80	780	19·6
Sulphur Dioxide . .	64·07	429·0	13·04	835	20·2
Carbon Dioxide . .	44·00	304·35	(15·13)	(666)	(18·8)
Nitrous Oxide . . .	44·08	311·8	(13·46)	(592)	(17·4)

It will be seen that, as a general rule, the constant k decreases as the molecular weight of the liquid increases, the maximum value obtained being 65·30 for water, and the minimum 3·89 for stannic chloride. If the molecular heat of vaporization is calculated, the constant becomes Mk, and the values for different liquids are more comparable. The fourth column in Table V shows the values obtained; the highest for normal liquids is 1118 for iodobenzene, the lowest 828 for isopentane. When the members of a homologous series are compared, however, it is evident that there is a steady increase in the value of the constant Mk with increasing molecular weight.

A more satisfactory constant for all substances can be obtained by the help of the rule of TROUTON. According to this rule, which is only approximately true, the molecular heat of vaporization at the boiling-point is proportional to the temperature of ebullition, i. e.,

$$MQ_b = c \,.\, T_b; \text{ where } c \text{ is a constant.}$$

But from equation (5) above we have:

$$MQ_b = Mk\,(T_c - T_b)^{\cdot 386}.$$

Combining these two expressions, and applying the principle of GULDBERG, that the temperature of ebullition is proportional to the critical temperature, i. e. $T_b = (1 - a)\,T_c$, we obtain:

$$Mk\,(a\,T_c)^{\cdot 386} = c\,.\,(1 - a)\ T_c$$

or

$$Mk\,/\,T_c^{\cdot 614} = \text{constant.} \tag{6}$$

The calculated values of $Mk\,/\,T_c^{\cdot 614}$ for each substance are given in the last column of Table V, and it will be seen that the constancy of the expression, for normal liquids, is fairly satisfactory. There is a slight increase with increasing molocular weight noticeable when members of a homologous series are compared, such a tendency, however, is also to be found both in TROUTON's rule and in the principle of GULDBERG. For the normal substances investigated by YOUNG, the divergence from the mean value 20·7 is in no case so great as ten per cent.

The relation thus obtained enables us to introduce a simplification into equation (5) given above, inasmuch as the variable factor k can be removed. We have, as an approximation for normal liquids,

$$Mk = 20{\cdot}7\ T_c^{\cdot 614}$$

Hence:

$$MQ = 20{\cdot}7\ T_c^{\cdot 614}\,.\,(T_c - T)^{\cdot 386}$$

Or:

$$MQ = 20{\cdot}7\ T_c\,(1 - T\,/\,T_c)^{\cdot 386} \tag{7}$$

The equation (7) above contains no variable except temperature, and is approximately valid for all normal liquids. Nevertheless, for the calculation of the exact value of the heat of vaporization for a particular liquid, it is necessary to substitute for the constant 20·7 in the above equation the specific constant for the liquid under consideration.

3. Some Necessary Consequences of the Equations.

In Tables I to IV it is seen that the three equations considered all give concordant values for the heat of vaporization. The expressions (1), (2), and (5) above may therefore be equated together, and by such conjunction many interesting relations between the quantities involved may be deduced. Those obtained by the combination of equations (1) and (2) have been examined by MILLS.[1]

By the conjunction of equations (1) and (5), we obtain:

$$0{\cdot}0_4 31833 \left(\frac{dP}{dT} . T\right)(V - v) = k\,(T_c - T)^n$$

Or:

$$\frac{dP}{dT} = \frac{k}{0{\cdot}0_4 31833} \cdot \frac{(T_c - T)^n}{T(V - v)} \tag{8}$$

By this equation P is obtained as a function of temperature and volume, and the equation may be utilized as a check upon the experimental values of $\frac{dP}{dT}$, which are the most liable to bring errors into the thermodynamical equation. At low temperatures, where the gas laws may be assumed to hold exactly, the equation reduces to the following:

$$\frac{d \log_e P}{dT} = \frac{k\,(T_c - T)^n}{T^2} \tag{9}$$

where P, for any particular liquid, is a function of temperature alone.

---

[1] MILLS, loc. cit.

Similarly, by the combination of equations (2) and (5) we have:

$$k(T_c - T)^n = 0{\cdot}0_4 31833\, P(V - v) + \mu'(\sqrt[3]{d} - \sqrt[3]{D}). \qquad (10)$$

A simple relationship is here not immediately obvious, but closer examination leads to results which are important in themselves, and which also throw light upon the significance of the value of the exponent $n = 0{\cdot}386$ in equation (5).

The second part of the formula of MILLS may be broken up as below:

$$\sqrt[3]{d} - \sqrt[3]{D} = (\sqrt[3]{d} - \sqrt[3]{d_c}) + (\sqrt[3]{d_c} - \sqrt[3]{D}).$$

Now the densities of both liquids and saturated vapours are extremely variable with temperature near the critical point, while the rate of variation rapidly falls off as we proceed away from the critical temperature. In other words, the curves representing the cube roots of the densities of a liquid and of its saturated vapour, plotted against the temperature, are of the same general type as that representing the heat of vaporization.

It therefore seems probable that the quantities $\sqrt[3]{d} - \sqrt[3]{d_c}$ and $\sqrt[3]{d_c} - \sqrt[3]{D}$ may be found capable of representation as functions of the critical temperature of the same type as in equation (5) above. This is shown to be the case in the following section, after which the question of the connection between equations (2) and (5), as expressed in equation (9) above, is again taken up.

4. **The Specific Volumes.**

The variation in the specific volume with temperature will first be examined for the case of liquids.

It is found on trial, with the help of the results of YOUNG, that, as before, a formula of the type:

$$\sqrt[3]{d} - \sqrt[3]{d_c} = k_1(T_c - T)^n \qquad (11)$$

holds satisfactorily for all normal substances. As in equation (5), k_1 is a constant depending on the particular liquid under consideration, while the exponent n has the same value for all liquids. The value of this exponent is here equal to one-third.

The fact that the exponent is in this equation an aliquot fraction introduces a simplification into the formula, both for its practical application and for theoretical considerations. On examinction with typical normal liquids, the formula is found to hold exactly from ordinary temperatures up to temperatures well above the boiling-point of the liquid. As the critical temperature is approached, however, the volume of the liquid becomes extremely sensitive to the large pressures exerted upon it, and the equation ceases to be exact in its application, the calculated densities being always smaller than those found by experiment. Nevertheless, by a slight alteration in the value of the exponent n, namely to $n = 0{\cdot}320$, the formula may be made to apply over all temperatures from zero Centigrade to the critical point. By this change in the exponent, however, the accuracy of the equation at the lower temperatures, where the power of one-third applies exactly, is necessarily somewhat impaired, and the simple nature of the formula is destroyed.

As typical examples of the agreement of equation (11) with the results of experiment the figures for fluobenzene and ethyl propionate (with the exponent equal to one-third) and for ethyl acetate (with the exponent equal to 0·320) are given in Tables VI to VIII below.

Table VI. Fluobenzene. $\sqrt[3]{d} - \sqrt[3]{d_c} = 0{\cdot}0466\,(559{\cdot}55 - T)^{\frac{1}{3}}$

t	d (calc.)	d (expt.)	t	d (calc.)	d (expt.)
0	1·0448	1·0465	120	0·8955	0·8955
20	1·0223	1·0225	140	0·8660	0·8665
40	0·9990	0·9986	160	0·8344	0·8363
60	0·9749	0·9744	200	0·7626	0·7671
80	0.9497	0·9496	240	0·6702	0·6789
100	0·9233	0·9233	286·55	0·3541	0·3541

Table VII. Ethyl propionate. $\sqrt[3]{d} - \sqrt[3]{d_c} = 0{\cdot}0467\,(545{\cdot}9 - T)^{\frac{1}{3}}$

t	d (calc.)	d (expt.)	t	d (calc.)	d (expt.)
0	0·9105	0·9104	120	0·7689	0·7692
20	0·8893	0·8901	140	0·7406	0·7413
40	0·8673	0·8672	160	0·7101	0·7115
60	0·8445	0.8440	200	0·6396	0·6443
80	0·8206	0·8201	240	0·5458	0·5501
100	0·7952	0·7951	272·9	0·2965	0·2965

Table VIII. Ethyl acetate. $\sqrt[3]{d} - \sqrt[3]{d_c} = 0{\cdot}0509\,(523{\cdot}1 - T)^{\cdot 320}$

t	d (calc.)	d (expt.)	t	d (calc.)	d (expt.)
0	0·9213	0·9244	220	0·5644	0·5648
50	0·8607	0·8636	230	0·5277	0·5281
100	0·7995	0·7972	240	0·4778	0·4778
150	0·7226	0·7210	247	0·4189	0·4195
200	0·6211	0·6210	250·1	0·3077	0·3077

The agreement in the first two of the above tables is seen to be satisfactory from ordinary temperatures up to temperatures well above the boiling-point; in the third table the calculated and observed values are concordant right up to the critical temperature, but this result is obtained only at the cost of greater divergences at the lower temperatures. We may therefore consider that normal liquids, under ordinary conditions, obey the law expressed in equation (11) above, with the exponent n equal to one-third.

The values of the specific constant k_1 for the various liquids investigated by YOUNG are given in the general table below (Table IX). It will be seen that the constant is of the same order of magnitude for all the liquids tabulated; in members of the same homologous series, especially, the variation is very small. For the associated liquids (water, acetic acid, and the alcohols) no satisfactory agreement with equation (11) can be obtained, as is only to be expected. These liquids are reserved for future consideration.

Table IX.

	k_1	k_2	μ' (Mills)	$\mu' k_1$	$\mu' k_2$
Ether	·0454	·0389	103·76	4·71	4·03
Di-isopropyl	·0422	·0361	97·53	4·12	3·52
Di-isobutyl	·0420	·0355	87·58	3·68	3·11
Isopentane	·0429	·0368	105·46	4·52	3·88
Pentane	·0429	·0368	109·94	4·72	4·05
Hexane	·0425	·0362	102·80	4·37	3·72
Heptane	·0422	·0358	98·64	4·16	3·53
Octane	·0421	·0352	93·16	3·92	3·28
Hexamethylene . . .	·0424	·0353	103·63	4·39	3·66
Benzene	·0441	·0367	109·26	4·82	4·01
Fluobenzene	·0466	·0389	85·65	3·99	3·33
Chlorobenzene . . .	·0458	·0371	81·66	3·74	3·03
Bromobenzene . . .	·0494	·0395	55·47	2·74	2·19
Iodobenzene	·0513	·0406	43·37	2·22	1·76
Carbon tetrachloride.	·0538	·0447	44·01	2·37	1·97
Stannic chloride . .	·0596	·0485	26·51	1·58	1·29
Methyl formate . . .	·0497	·0419	119·86	5·96	5·02
Ethyl formate . . .	·0480	·0402	107·14	5·14	4·31
Methyl acetate . . .	·0485	·0411	109·59	5·31	4·50
Propyl formate . . .	·0466	·0390	98·79	4·60	3·85
Ethyl acetate	·0474	·0401	98·88	4·69	3·97
Methyl propionate .	·0472	·0398	99·02	4·67	3·94
Propyl acetate . . .	·0465	·0390	93·12	4·33	3·63
Ethyl propionate . .	·0467	·0390	91·59	4·28	3·57
Methyl butyrate . .	·0462	·0387	91·31	4·22	3·53
Methyl isobutyrate .	·0464	·0390	88·45	4·10	3·45

We now come to the question of the variation of the density of the saturated vapour with the temperature. In this case a formula of the same type:

$$\sqrt[3]{d_c}-\sqrt[3]{D}=k_2(T_c-T)^n \tag{12}$$

is once more found to be applicable; k_2 is a specific constant for each particular substance, while the exponent n has the same value for all substances. Here the value for n is found to be one-half.

The equation holds exactly for all normal substances from the temperature of zero Centigrade to temperatures well over the boiling-point of the liquid. Near the critical temperature the agreement becomes less satisfactory, as in the case of the similar equation for liquids. Typical examples of the agreement of the formula with the results of experiment are given below in Tables X and XI, which show the calculated and observed densities of the saturated vapour for octane and ethyl acetate respectively.

Table X. Octane. $\sqrt[3]{d_c} - \sqrt[3]{D} = 0{\cdot}0352\,(569{\cdot}2 - T)^{\frac{1}{2}}$.

t	D (calc.)	D (expt.)	t	D (calc.)	D (expt.)
40	·000141	(·0002)	160	·008565	·008591
60	·000414	(·0004)	180	·01313	·01316
80	·000939	(·0009)	200	·01970	·01965
100	·001835	(·0017)	220	·02923	·02874
120	·003255	·003247	260	·06567	·06223
140	·005405	·005405	296·2	·2327	·2327

Table XI. Ethyl Acetate. $\sqrt[3]{d_c} - \sqrt[3]{D} = 0{\cdot}0401\,(523{\cdot}1 - T)^{\frac{1}{2}}$.

t	D (calc.)	D (expt.)	t	D (calc.)	D (expt.)
0	·000069	(·0001)	120	·01033	·01030
20	·000299	(·0003)	140	·01646	·01650
40	·000829	(·0008)	160	·02555	·02577
60	·001828	(·0018)	180	·03909	·03883
80	·003523	·003495	200	·05991	·05797
100	·006216	·006158	250·1	·3077	·3077

The values of the constant k_2 for the normal substances investigated by Young are shown in the second column of the general table (Table IX) above. It will be seen that, as in the case of the constant k_1 for liquids in equation (11), the values are of the same order of magnitude for all substances, and in a homologous series the figures are almost constant.

5. The Heat of Vaporization (continued).

The above equations having been established, we now return to the relations obtained by the conjunction of the various formulae expressing the heat of vaporization. Introducing the results of equations (11) and 12) into equation (10), we have:

$$(13) \qquad \begin{aligned} Q = k\,(T_c - T)^{\cdot 386} &= 0{\cdot}0_4 31833\, P(V - v) \\ &\quad + k_1 \mu' (T_c - T)^{\frac{1}{3}} + k_2 \mu' (T_c - T)^{\frac{1}{2}}. \end{aligned}$$

The figures obtained by MILLS for the constant μ' for the liquids investigated by YOUNG are given in Table IX above, where the values of $k_1\mu'$ and $k_2\mu'$ are also calculated. On comparison with Table V, it will be seen that the values of k, $k_1\mu'$, and $k_2\mu'$ for each substance are in a constant proportion to each other. The approximate ratios are:

$$k : k_1\mu' : k_2\mu' :: 1{\cdot}00 : 0{\cdot}40 : 0{\cdot}33.$$

We are now in a position to examine the significance of the value of the exponent, $n = 0{\cdot}386$, in equation (5) for the heat of vaporization;

$$(5) \qquad Q = k\,(T_c - T)^{\cdot 386}$$

For it appears, from equation (13) above, that the expression $k\,(T_c - T)^{\cdot 386}$ is equivalent to the sum of three quantities. The first of these, representing the external heat of vaporization, is variable in magnitude, but at most temperatures is comparatively small. Of the other two quantities, the first varies as $(T_c - T)^{\frac{1}{3}}$, the second as $(T_c - T)^{\frac{1}{2}}$. It therefore becomes evident that the formula represented by equation (5) above is merely an interpolation formula, with an exponent $n = 0{\cdot}386$ intermediate between the values one-third and one-half. The variation with temperature of the three quantities on the right-hand side of equation (13) is fortuitously of such a nature as to render the value of this intermediate exponent n practically constant for all temperatures between zero Centigrade and the critical temperature.

We have no sure grounds, however, for supposing that the relation expressed in equation (5) will be applicable for the expression of the heat of vaporization at temperatures far below zero Centigrade. If either of the equations (11) or (12) fails at such low temperatures, equation (5) will also become inapplicable. The validity of the formulae developed above at very low temperatures, and at absolute zero of temperature, is considered in the following sections.

6. The Heat of Vaporization at Absolute Zero.

The value of the heat of vaporization at absolute zero, and its variation with temperature near this point, are important from theoretical considerations. At the absolute zero of temperature we have the heat of vaporization equal to the free energy, and also, by the theory of NERNST,[1] the condition:

$$\frac{dQ_0}{dT} = 0.$$

Now the equation (5) obtained above for the heat of vaporization is evidently in disagreement with this condition, since the heat of vaporization is continually increasing as the temperature falls. Also the absolute values of the heat of vaporization at absolute zero, as calculated by this equation, i. e.,

$$Q_0 = k T_c^{.386},$$

are consistently higher than those obtained by other methods, such as the formula of ARRHENIUS.[2]

It must be concluded, therefore, that equation (5) for the heat of vaporization is inapplicable at very low temperatures, in spite of the excellent agreement at temperatures between zero Centigrade and the critical point. The cause of its failure may be explained by the consideration of the validity of equations (11) and (12), on which it depends, at these low tempe-

---

[1] NERNST, Theoretische Chemie, 6 Aufl., p. 699, (1909).

[2] ARRHENIUS, loc. cit.

ratures. We have, as the alternative form of the interpolation formula (5), the equation (13) above:

$$(13) \qquad Q = 0{\cdot}0_4 31833\, P(V - v) + k_1 \mu' (T_c - T)^{\frac{1}{3}} + k_2 \mu' (T_c - T)^{\frac{1}{2}}.$$

The first part of this expression, representing the external heat of vaporization, becomes at low temperatures, where the gas laws may be assumed to hold exactly, equal to $\frac{R}{M} . T$. The validity of the second part of the expression at low temperatures depends upon equation (11), of the third part upon equation (12) above.

The former of these, representing the variation in the density of liquids with temperature, will be shown in the next section of the paper to hold — if not exactly, at least very nearly so — even at absolute zero of temperature. That is, the density of a liquid increases slowly, as demanded by equation (11), with falling temperature until the absolute zero is reached.

It is otherwise with the equation (12), for the densities of saturated vapours. This equation gives good agreement with the figures of experiment for temperatures down to zero Centigrade, but when carried far below this temperature it is found to be quite inapplicable. The density of the saturated vapours of the liquids considered is already extremely small at ordinary temperatures, and decreases asymptotically towards zero as the temperature falls. The expression $k_2(T_c - T)^{\frac{1}{2}}$, however, steadily increases as the temperature falls, and at very low temperatures equation (12) can be satisfied only by negative values for the density of the saturated vapour. The equation must therefore be quite inapplicable at very low temperatures, and must be regarded as an empirical formula, valid throughout the ordinary range of temperatures, but breaking down when the density of the saturated vapour becomes very small.

The failure of equation (5) at low temperatures is thus seen to be due to the failure of equation (11). We may avoid the difficulty thus raised, however, and obtain the true values of the heat of vaporization at absolute zero, by the following method.

At very low temperatures the density of the saturated vapour (and even the cube root of the density) becomes so nearly equal to zero that equation (13) above may be written as follows:

$$Q = \frac{R}{M} . T + k_1 \mu' (T_c - T)^{\frac{1}{3}} + \mu' \sqrt[3]{d_c}. \qquad (14)$$

Hence we obtain:

$$Q_0 = k_1 \mu' . T_c^{\frac{1}{3}} + \mu' \sqrt[3]{d_c} \qquad (15)$$

And also,

$$\frac{dQ}{dT} = \frac{R}{M} - \frac{k_1 \mu'}{3 (T_c - T)^{\frac{2}{3}}};$$

from which we have, at the absolute zero of temperature,

$$\frac{dQ_0}{dT} = \frac{R}{M} - \frac{k_1 \mu'}{3\, T_c^{\frac{2}{3}}}.$$

This should now satisfy the condition $\frac{dQ_0}{dT} = 0$; that is, the following relation should hold:

$$\frac{k_1 \mu' M}{3\, T_c^{\frac{2}{3}}} = R. \qquad (16)$$

The application of equations (15) and (16) to the experimental results of YOUNG is shown in the general table (Table XII) below. The first column in this table shows the values obtained for the molecular heat of vaporization (or free energy) at absolute zero, MQ_0. In most cases the agreement of these values with those calculated by the formula of ARRHENIUS[1] is excellent; in others, however, expecially in those cases where a long extrapolation is necessary, the differences may amount to several per cent. The expression $\frac{MQ_0}{T_c}$ investigated by ARRHENIUS[1] is

---

[1] ARRHENIUS, loc. cit.

found, in accordance with his results, to be practically constant; the values of this expression are also included in the general table.

The truth of the relation expressed in equation (16) is tested by calculating the values of $\frac{k_1 \mu' M}{T_c^{\frac{2}{3}}}$ for each particular substance, and comparing the figures obtained with the constant of the gas equation, $R = 1{\cdot}988$. This is also done in Table XII below. It will be seen that the results obtained for the normal substances examined vary between 1·80 for carbon tetrachloride and 2·20 for propyl acetate. The mean value obtained for twenty-six liquids is 2·01, the maximum variation from the gas constant R being ten per cent. (The run of the values obtained for R throughout the series corresponds extremely closely with those obtained for the values of the constants $\frac{Mk}{T_c^{\cdot 614}}$ in Table V and $\frac{MQ_0}{T_c}$ in Table XII; a comparison will show that the parallelism is too striking to be devoid of significance.)

Table XII.

	MQ_0	$\frac{MQ_0}{T_c}$	R	d_0	$\frac{d_0}{d_c}$	Mv_0
Ether	7628	16·3	1·93	0·978	3·73	75·7
Di-isopropyl	8044	16·1	1·88	0·878	3·64	98·1
Di-isobutyl	9625	17·5	2·09	0·891	3·77	128·1
Isopentane	7202	15·6	1·82	0·851	3·63	84·7
Pentane	7520	16·0	1·88	0·853	3·67	84·5
Hexane	8318	16·4	1·97	0·873	3·72	98·6
Heptane	9480	17·6	2·09	0·885	3.78	113·1
Octane	10246	18·0	2·17	0·896	3.85	127·4
Hexamethylene . .	8689	15·7	1·83	0·992	3·63	84·8
Benzene	8842	15·8	1·84	1·114	3·66	70·1
Fluobenzene	8988	16·1	1·88	1·301	3·67	73·9
Chlorobenzene . . .	10177	16·1	1·90	1·361	3·72	82·7
Bromobenzene . . .	10623	15·9	1·87	1·808	3·72	86·8
Iodobenzene	11438	15·9	1·88	2·170	3·73	93·9
Carbon tetrachloride	8569	15·4	1·80	2·027	3.64	75·9

	MQ_0	$\frac{MQ_0}{T_c}$	R	d_0	$\frac{d_0}{d_c}$	Mv_0
Stannic chloride . .	9715	16·4	1·95	2·770	3·73	94·1
Methyl formate . .	7880	16·2	1·93	1·332	3·82	45·1
Ethyl formate . . .	8492	16·7	1·99	1.223	3·79	60·5
Methyl acetate . . .	8718	17·2	2·06	1·240	3·81	59·7
Propyl formate . .	9181	17·1	2·04	1·175	3·80	74·9
Ethyl acetate . . .	9208	17·6	2·12	1·182	3·84	74·5
Methyl propionate .	9249	17·4	2·09	1·193	3.82	73·8
Propyl acetate . . .	9952	18·1	2·20	1·149	3·88	89·0
Ethyl propionate . .	9792	17·9	2·17	1·153	3·89	88·5
Methyl butyrate . .	9776	17·6	2·13	1·155	3.85	88·4
Methyl isobutyrate .	9463	17·5	2·10	1·152	3.83	88·6

7. **Specific Volume at Absolute Zero.**

The results of the preceding section depend upon the validity of the equation:

$$\sqrt[3]{d}-\sqrt[3]{d_c}=k_1\,(T_c-T)^{\frac{1}{3}} \qquad (11)$$

through all temperatures down to absolute zero. This assumption can be tested by a comparison of the values obtained by the above equation for the density at absolute zero with those obtained by previous methods of investigation. At absolute zero the equation becomes:

$$\sqrt[3]{d_0}=\sqrt[3]{d_c}+k_1\,T_c^{\frac{1}{3}}, \qquad (17)$$

whence the value of d_0 for the substances investigated by YOUNG is easily calculated.

GULDBERG[1] has calculated the «minimum volume» of liquids by two methods — by the estimation of the effect of an infinite pressure at ordinary temperatures, and by the extrapolation of an empirical density formula to absolute zero. The results obtained by the two methods are concordant, but are not in

---

[1] GULDBERG, Zeitschrift f. physikalische Chemie, 32, 116, (1900).

agreement with the condition demanded by the equation of VAN DER WAALS. According to this equation the result $d_0 = 3\, d_c$ should be obtained. The values obtained by GULDBERG for the ratio of d_0 to d_c are indeed approximately the same for all normal substances examined, but the ratio is consistently higher than 3. The average value is $d_0/d_c = 3{\cdot}75$.

The density of liquids at absolute zero has also been calculated by D. BERTHELOT[1] by the application of the rule of the rectilinear diameter, discovered by CAILLETET and MATHIAS.[2] By this rule the mean values of the densities of any substance in the states of liquid and saturated vapour, when plotted against the temperature, fall upon a straight line. Since at low temperatures the density of the saturated vapour becomes negligible, the density of a liquid at absolute zero becomes equal to twice the mean density given by the extremity of the diameter.

YOUNG[3] has shown, however, that for all substances with the exception of pentane, these is a slight curvature of the diameter. Hence the results of BERTHELOT, calculated on the assumption of a rectilinear diameter, are only approximately correct, owing to the extrapolation through a long range of temperature under a false assumption. The average ratio of the densities at absolute zero and at the critical point obtained by BERTHELOT is slightly less than 4. If the densities are calculated by the more accurate expression of the rule of CAILLETET and MATHIAS, given by YOUNG,[4] the values obtained are in most cases a little smaller, and the average ratio of d_0 to d_c is brought somewhat nearer to the value 3·75 obtained by the method of GULDBERG.

The densities at absolute zero, as calculated from equation (17) above, for the substances investigated by YOUNG, are shown in Table XII under the heading d_0. In this table in also given the ratio d_0/d_c. It will be seen that this ratio is approximately constant for all substances; the highest value obtained is 3·89 for ethyl propionate, the lowest 3·63 for isopentane and hexamethylene. The average ratio, 3·75, is identical with that obtained by GULDBERG. For particular substances the agree-

---

[1] D. BERTHELOT, Compt. rend.. 130, 173, (1900).

[2] CAILLETET and MATHIAS, Compt. rend., 102, 1202, (1886); 104, 1563, (1887).

[3] YOUNG, Phil. Mag., (5), 50, 291, (1900).

[4] YOUNG, Proc. Roy. Soc. Dublin, 12, 413, (1900).

ment is not always good, the divergence sometimes amounting to four per cent. This is, however, the error limit admitted by GULDBERG for his values at absolute zero, so that the differences are always within the errors introduced by extrapolation.

The run of the values for d_0/d_c obtained throughout the series is precisely the same as those obtained for the other constants given in Tables V and XII. It would appear that, while the properties of liquids may be expressed by formulae of the same type for all liquids, yet the specific nature of each liquid influences, in some slight degree, the numerical values of the constants contained in these formulae.

The last column of Table XII shows the molecular volume of the liquids examined at the absolute zero of temperature. The values obtained cannot be fully discussed here; two general rules obvious from their inspection may, however, be stated:

(i) The molecular volumes of isomeric substances are equal.

(ii) The difference between the molecular volumes of the successive members of a homologous series is constant. The addition of CH_2 to the molecule increases the molecular volume by 14·4.

8. General Conclusions.

The equation representing the variation in the density of liquids with temperature:

$$\sqrt[3]{d} - \sqrt[3]{d_c} = k_1 (T_c - T)^{\frac{1}{3}} \tag{11}$$

has been shown in the preceding pages to give results in agreement with the figures of experiment throughout the ordinary range of temperature, to give results in agreement with those obtained by other methods at the absolute zero of temperature, and to lead to the required condition in equation (14) for the heat of vaporization that $\frac{dQ_0}{dT} = 0$. The validity of the formula is therefore established; its theoretical significance is stated below.

Let $1/S$ be the distance apart of the molecules of the liquid, then for any liquid we have S proportional to $\sqrt[3]{d}$. Equation (11) thus becomes:

$$S - S_c = \text{const.}\,(T_c - T)^{\frac{1}{3}}.$$

And this on differentiation gives:

$$(18) \qquad \frac{dS}{dT} = \text{const.}\,\frac{1}{(T_c - T)^{\frac{2}{3}}}$$

Also, from the results of MILLS, the molecular attraction between the particles varies inversely as the square of their distance apart;[1] i. e. if α be the molecular attraction, α is proportional to S^2. Hence we obtain:

$$(19) \qquad \frac{d\alpha}{dT} = \text{const.}\,\frac{S}{(T_c - T)^{\frac{2}{3}}} = \text{const.}\,\frac{\sqrt[3]{d}}{(T_c - T)^{\frac{2}{3}}}.$$

Equations (18) and (19) above give the variation of the distance between the molecules and of the molecular attraction with temperature.[2]

Conclusions of a similar type may be drawn from equation (12) for the densities of saturated vapour and from equation (13) for the heat of vaporization, but, since these formulae have not the same general validity as equation (11) above, the subject is not developed further here.

By the examination of certain of the equations in the preceding pages, we may arrive at the significance of certain of the constants used in the formulae obtained. From the equation of MILLS for the heat of vaporization:

$$(2) \qquad Q = 0{\cdot}0_4 31833\,P(V - v) + \mu'(\sqrt[3]{d} - \sqrt[3]{D})$$

---

[1] The theory of molecular attraction, as advanced by MILLS, has been recently attacked by KLEEMAN, who has at different times proposed formulae in which the molecular attraction varies inversely as the fifth power (Phil. Mag. [VI] 19, 795, (1910)) or the seventh power (Phil. Mag. [VI], 20, 678, (1910)) of the distance between the molecules. MILLS, however, has shown conclusively in his replies (Phil. Mag. [VI] 21, 84, (1911), and 24, 483, (1912)) that the agreement with the experimental results of YOUNG, obtained by the use of his own equation, is far superior to that given by the formulae of KLEEMAN. The results obtained in this paper, and the form of the equations derived, must also be regarded as affording support to the position of MILLS.

[2] Temperature *per se* has no influence on the molecular attraction (MILLS, Phil. Mag. [VI), 21, 97, (1911)); the variation with temperature is due to the accompanying change in density.

we obtain, by bringing the equation to apply at absolute zero, as we are entitled to do from the results obtained from equation (14);

$$Q_0 = \mu' \sqrt[3]{d_0}. \tag{20}$$

The constant μ' is thus the quotient of the heat of vaporization at absolute zero by the cube root of the density at absolute zero.

Similarly, from equation (17) for the density of liquids:

$$\sqrt[3]{d_0} = \sqrt[3]{d_c} + k_1\, T_c^{\frac{1}{3}} \tag{17}$$

we obtain, since $d_0 = 3{\cdot}75\, d_c$, the result,

$$k_1 = \frac{0{\cdot}553 \sqrt[3]{d_c}}{T_c^{\frac{1}{3}}}. \tag{21}$$

By the help of this, equation (11) may be simplified to the form:

$$\sqrt[3]{d} - \sqrt[3]{d_c} = \frac{0{\cdot}553 \sqrt[3]{d_c}}{T_c^{\frac{1}{3}}} (T_c - T)^{\frac{1}{3}}$$

or

$$\sqrt[3]{\frac{d}{d_c}} - 1 = 0{\cdot}553 \left(1 - \frac{T}{T_c}\right)^{\frac{1}{3}} \tag{22}$$

This equation is applicable to all normal liquids, since the numerical variable has been removed; it is, however, in common with the similar equation (7) obtained for the heat of vaporization, only an approximation. For exact agreement with the results of experiment, the constant 0·553 in the above equation must be replaced by a specific constant for the liquid under consideration. The values for this constant, in the substances investigated by YOUNG, range from 0·527 to 0·572.

9. Summary.

In the above investigation it has been shown that the properties of liquids are closely connected with their critical constants, and may be expressed as functions of these constants. Two typical properties — the heat of vaporization and the specific volume — have been examined, and formulae for their expression have been developed, with the help of the accurate experimental data of YOUNG.

For the heat of vaporization the equation obtained is:

$$Q = k\,(T_c - T)^n, \tag{5}$$

where, for all normal substances, $n = 0{\cdot}386$. By conjunction with the rule of TROUTON this formula can be reduced to the form:

$$MQ = 20{\cdot}7\ T\,(1 - T/T_c)^n. \tag{7}$$

The value 20·7 is an average value, which is only slightly departed from by normal liquids.

For the specific volume of liquids the formula obtained is:

$$\sqrt[3]{d} - \sqrt[3]{d_c} = k_1\,(T_c - T)^{\frac{1}{3}}; \tag{11}$$

while for the specific volume of saturated vapours the following equation applies:

$$\sqrt[3]{d_c} - \sqrt[3]{D} = k_2\,(T_c - T)^{\frac{1}{2}}. \tag{12}$$

The former of these equations is found to be valid over all temperatures from zero absolute to temperatures well above the boiling-point of the liquid; the latter equation, however, becomes inapplicable at temperatures much lower than zero Centigrade. Equation (11) may be reduced to the form:

$$\sqrt[3]{\frac{d}{d_c}} - 1 = 0{\cdot}553\left(1 - \frac{T}{T_c}\right)^{\frac{1}{3}} \tag{22}$$

which is approximately true for all normal liquids.

The above equations have been connected by means of the equation of MILLS for the heat of vaporization:

$$Q = 0{\cdot}0_{4}31833\,P(V-v) + \mu'(\sqrt[3]{d}-\sqrt[3]{D}); \tag{2}$$

which, by conjunction with equation (11) and (12) above, becomes:

$$Q = 0{\cdot}0_{4}31833\,P(V-v) + k_1\mu'(T_c-T)^{\frac{1}{3}} + k_2\mu'(T_c-T)^{\frac{1}{2}}. \tag{13}$$

From this equation it is seen that equation (5) above for the heat of vaporization is an interpolation formula, with an exponent $n = 0{\cdot}386$ intermediate between the values one-third and one-half. At temperatures below zero Centigrade it must become inapplicable, owing to the failure of equation (12).

For such low temperatures, however, the heat of vaporization may be obtained by transforming equation (13) to the form:

$$Q = \frac{R}{M}.\,T + k_1\mu'(T_c-T)^{\frac{1}{3}} + \mu'\sqrt[3]{d_c}. \tag{14}$$

In this equation the condition demanded by the theory of NERNST, $\frac{dQ_0}{dT} = 0$, is fulfilled if the following relation holds:

$$\frac{k_1\mu' M}{3\,T_c^{\frac{2}{3}}} = R. \tag{16}$$

This is shown to be true in the case of normal liquids. The absolute values of the molecular heat of vaporization at absolute zero, MQ_0, are also calculated from equation (14), and found to be, in general, in good agreement with those obtained by ARRHENIUS. The expression $\frac{MQ_0}{T_c}$ is shown to be approximately constant.

The densities of liquids at the absolute zero of temperature have been calculated by means of equation (11); the values obtained are in good agreement with those found by GULDBERG by extrapolation. The ratio d_0/d_c is found to the approximately the same for all normal liquids, with an average value of $3{\cdot}75$, which is identical with the value obtained by GULDBERG. The equation of VAN DER WAALS requires the ratio d_0/d_c equal to 3. Finally, certain additive properties in the values of the molecular volume at absolute zero have been indicated.

The significance of the numerical constants employed in the various equations has been considered. In common with the results of previous investigators, however, it has been found that, while the properties of all liquids may be expressed by equations of one general form, the variable numerical factor in any such equation cannot be entirely removed, but depends to some small extent upon the particular liquid under consideration. Also, in different formulae, the run of the values of the «constants» is the same throughout a series of liquids examined. It is clear that the specific properties of particular liquids cannot be altogether suppressed in any general formula, but make themselves evident in the small variation of the numerical factor, as in equations (7) and (22) above, and as in the rule of TROUTON.

The significance of the equations obtained from the point of view of molecular attraction has been briefly indicated. Further theoretical discussion, however, as well as the questions of the applicability of the critical constants for the expression of the properties of associated liquids, is left for a future communication.

In conclusion, I have great pleasure in expressing to Professor SVANTE ARRHENIUS my thanks for his valuable criticism and advice during the course of these investigations.

Nobel Institutet, Experimentalfältet, November 1912.

◆

Tryckt den 14 mars 1913.

Uppsala 1913. Almqvist & Wiksells Boktryckeri-A.-B.

9

MEDDELANDEN
FRÅN
K. VETENSKAPSAKADEMIENS NOBELINSTITUT
BAND 2. N:O 36.

THE HEAT OF
VAPORIZATION OF ASSOCIATED LIQUIDS

BY

JAMES KENDALL

WITH ONE FIGURE IN THE TEXT

UPPSALA & STOCKHOLM
ALMQVIST & WIKSELLS BOKTRYCKERI-A.-B.

BERLIN
R. FRIEDLÄNDER & SOHN
II CARLSTRASSE

LONDON
WILLIAM WESSLEY & SON
28 ESSEX STREET. STRAND

PARIS
LIBRAIRIE C. KLINCKSIECK
II RUE DE LILLE

1913

MEDDELANDEN
FRÅN
K. VETENSKAPSAKADEMIENS NOBELINSTITUT
BAND 2. N:o 36.

The Heat of Vaporization of Associated Liquids.

By

JAMES KENDALL.

With one Figure in the Text.

Communicated April 23rd. 1913 by S. ARRHENIUS and Å. G. EKSTRAND.

1. Introductory.

In a previous communication[1] it has been shown that, for normal non-associating liquids, the following relations hold:

$$Q = k(T_c - T)^n \tag{1}$$

$$\sqrt[3]{d} - \sqrt[3]{d_c} = k_1(T_c - T)^{\frac{1}{3}} \tag{2}$$

$$\sqrt[3]{d_c} - \sqrt[3]{D} = k_2(T_c - T)^{\frac{1}{2}} \tag{3}$$

Q is the total heat of vaporization of one gramme of the liquid, expressed in calories; T_c is the critical temperature, T the temperature of observation; d is the density of the liquid and D the density of its saturated vapour at the temperature T, d_c is the common density of liquid and saturated vapour at the critical point; k, k_1, and k_2 are constants for each particular liquid.

---

[1] Meddel. från K. Vet.-Akad:s Nobelinstitut Band 2. N:o 29, (1912).

The value of the exponent n in equation (1) is found to be the same for all of the twenty-six normal liquids investigated by YOUNG,[1] and equal to 0·386. The three equations are connected by means of the formula derived by MILLS[2] for expressing the heat of vaporization:

$$(4) \qquad Q = 0{\cdot}0_4 31833\, P(V - v) + \mu'(\sqrt[3]{d} - \sqrt[3]{D}).$$

In this equation the numerical factor is the reciprocal of the mechanical equivalent of heat in the units employed; D is the vapour pressure measured in millimetres of mercury; v is the volume of one gramme of the liquid, V the volume of one gramme of the saturated vapour; μ' is a constant for each particular liquid.

It is of interest to examine the behaviour of associated liquids with regard to the above equations. Exact experimental data are available in the case of the associated liquids investigated by YOUNG[3] — water, methyl alcohol, ethyl alcohol, propyl alcohol, and acetic acid. These liquids are considered in the following pages.

2. The Heats of Vaporization.

In the previous paper it has been shown that the validity of equation (1) above is dependent upon the validity of equations (2) and (3). Equation (1) is, in fact, only an interpolation formula, the value of the exponent, $n = 0{\cdot}386$, being intermediate between the values, one-third and one-half, of the exponents in equations (2) and (3) respectively. The true formula for the heat of vaporization is obtained by combining equations (2) and (3) with equation (4) above, when the following result is obtained:

$$(5) \quad Q = 0{\cdot}0_4 31833\, P(V - v) + \mu' k_1(\sqrt[3]{d} - \sqrt[3]{d_c}) + \mu' k_2(\sqrt[3]{d_c} - \sqrt[3]{D}.$$

Equation (1) for the heat of vaporization cannot, therefore, be expected to apply in the case of any liquid unless, as a

---

[1] YOUNG, Proc. Roy. Soc. Dublin, 12, 374, (1910).

[2] MILLS, Journ. Amer. Chem. Soc., 31, 1099, (1909).

[3] YOUNG, loc. cit.; MILLS, loc. cit.

first condition, the densities of the liquid and of its saturated vapour follow the normal courses indicated by equations (2) and (3) above.

The densities of the associated liquids, however, do not vary in a normal way with temperature, owing to the change in the degree of association with temperature. The density of the liquid in the associated state is not the same as in the unassociated state, and, contrary to expectation, the associated molecules are less dense than the simple molecules. In all of the above liquids, the rate of increase in density as the temperature falls is smaller than the value demanded by equation (2) above, owing to this expansion which accompanies association. Water is especially exceptional, since through a small range of temperature just above the freezing-point (from 4° C. to 0° C.) the density of the liquid decreases with falling temperature.

It is evident, therefore, that equation (1) as it stands cannot be valid throughout the same large range of temperature for associated liquids as for normal non-associated liquids. In some cases, indeed, (see methyl alcohol in Table II below) the agreement at high temperatures is satisfactory. In others, however, agreement with the experimental values can be obtained only by changing the value of the exponent n. The results obtained are shown in Tables I to V below; in Table VI the figures for a normal non-associated liquid (ethyl acetate) are given for comparison. In these tables, the first column shows the temperature in degrees Centigrade, the second the experimental values for the heat of vaporization, obtained by the use of the thermodynamical equation of CLAUSIUS and CLAPEYRON:

$$Q = 0{\cdot}0_4 31833 \left(\frac{dP}{dT} \cdot T\right) (V - v), \qquad (6)$$

the third column shows the values calculated by means of equation (1) above.

Table I. Water. $Q = 83{\cdot}06\,(T_c - T)^{\frac{1}{3}}$. $T_c = 370°$ C.

t	Q (expt.)	Q (calc.)	t	Q (expt.)	Q (calc.)
0	595·8	596·4	160	494·2	493·8
20	584·8	585·3	180	479·7	477·6
40	573·5	573·9	200	465·3	460·1
60	561·8	562·2	220	449·4	441·4
80	549·8	549·8	240	429·5	420·8
100	537·5	536·9	260	402·5	398·0
120	523·0	523·2	270	390·3	385·5
140	508·5	508·8			

Table II. Methyl Alcohol. $Q = 36{\cdot}50\,(T_c - T)^{\cdot 386}$. $T_c = 240{\cdot}0°$ C.

t	Q (expt.)	Q (calc.)	t	Q (expt.)	Q (calc.)
0	289·2	302·8	160	198·3	198·1
20	284·5	292·7	180	177·2	177·3
40	277·8	282·2	200	151·8	151·6
60	269·4	271·0	220	112·5	116·0
80	259·0	258·9	230	84·5	88·8
100	246·0	246·0	236	61·7	62·3
120	232·0	231·7	238·5	44·2	42·7
140	216·1	215·9			

Table III. Ethyl Alcohol. $Q = 26{\cdot}61\,(T_c - T)^{\cdot 400}$. $T_c = 243{\cdot}1°$ C.

t	Q (expt.)	Q (calc.)	t	Q (expt.)	Q (calc.)
0	220·9	239·5	140	171·1	170·1
20	220·6	231·4	160	156·9	155·9
40	218·7	222·9	180	139·2	139·6
60	213·4	213·8	200	116·6	119·9
80	206·4	204·2	220	88·2	93·6
100	197·1	192·9	240	40·3	41·8
120	184·2	182·4	242·5	22·1	21·7

Table IV. Propyl Alcohol. $Q=12{\cdot}79(T_c-T)^{\frac{1}{2}}$. $T_c=263{\cdot}7°$ C.

t	Q (expt.)	Q (calc.)	t	Q (expt.)	Q (calc.)
0	194·4	207·5	180	116·3	117·0
80	173·0	173·4	200	102·2	102·1
100	164·0	163·7	220	85·3	84·6
120	153·0	153·4	240	63·4	62·3
140	142·4	142·3	260	33·5	24·6
160	129·0	130·3			

Table V. Acetic Acid. $Q=14{\cdot}80\,(T_c-T)^{\cdot386}$. $T_c=321{\cdot}65°$ C.

t	Q (expt.)	Q (calc.)	t	Q (expt.)	Q (calc.)
20	84·05	—	240	78·18	80·95
60	89·69	—	260	72·26	72·66
100	92·32	—	280	63·48	62·43
140	91·83	—	300	48·97	48·52
180	87·71	—	310	37·77	36·21
200	85·55	94·47	320	20·92	17·96
220	82·02	88·10			

Table VI. Ethyl Acetate. $Q=11{\cdot}67\,(T_c-T)^{\cdot386}$. $T_c=250{\cdot}1°$ C.

t	Q (expt.)	Q (calc.)	t	Q (expt.)	Q (calc.)
0	100·61	98·40	180	59·87	60·18
80	85·78	84·80	200	52·71	52·88
100	82·15	80·80	220	42·63	43·43
120	77·53	76·44	240	27·17	28·50
140	72·24	71·69	247	17·12	18·07
160	65·91	66·31	249	12·03	12·11

The agreement between the calculated and experimental values is seen to be, in general, satisfactory, except at the lower temperatures for the alcohols and for acetic acid. The fact that in two cases — water and propyl alcohol — the value of the exponent n is equal to a simple fraction — one-third and one-half respectively — must be regarded as merely fortuitous.

The curves representing the variation with temperature of the heats of vaporization of the above associated liquids, as obtained from the experimental data of YOUNG, are shown in the annexed figure (page 8). The curve for ethyl acetate is also given for comparison. For the sake of clearness in the diagram, the scale for Q in the case of water is reduced to one-half, and in the case of ethyl acetate it is increased by one-half. Since the heats of vaporization are always, in effect, negative, the values of Q are plotted downwards. Temperatures are plotted from the critical-point.

In the discussion of the results, water and acetic acid are treated first, as in these cases a simple explanation of the abnormality is more obvious; the alcohols are grouped together in a later section.

3. Water and Acetic Acid.

From the diagram it will be seen that the normal curve for the heat of vaporization plotted against the temperature (Curve VI) exhibits very slight curvature after the sharp initial increase near the critical point; beyond the region of $T_c - T = 100°$ C. the change in the slope of the curve is very slow. The heat of vaporization of a normal liquid, therefore, at temperatures not too near to the critical temperature, shows a continuous increase, the rate of which diminishes only very slowly as the temperature falls.

In this respect water, as is seen from Curve I, follows the normal type of curve. The curves for the remaining associated liquids, however, indicate that in these liquids the change of slope persists even at low temperatures, and the curves, instead of approximating more and more to straight lines, are all, though in different degrees, bent in an upward direction. (This may be best observed by looking «along» the curves from the direction of the origin.) The value for the heat of vaporization thus shows signs of approaching, sooner or later, a maximum as the temperature falls, and in two cases indeed this maximum value is reached within the experimental range of temperature. Acetic acid possesses a maximum heat of vaporization at 120° C., ethyl alcohol at 10° C. (approximately).

This upward curvature in the values of the heat of vaporization for the alcohols and for acetic acid accounts for the disagreement between the calculated and observed values at low temperatures, as found in Tables II to V above. Water is thus seen to be, in this respect, more normal in its behaviour than the other associated liquids here considered.

This at first sight appears somewhat strange, from the fact that water, in regard to its variation of density with temperature, is most abnormal. In equation (5) above for the heat of vaporization, the second part of the equation, which represents the change in the density of the liquid, actually decreases, instead of increasing regularly with falling temperature, at temperatures just above zero Centigrade. Nevertheless, the increase in the heat of vaporization at low temperatures shows no signs of falling off.

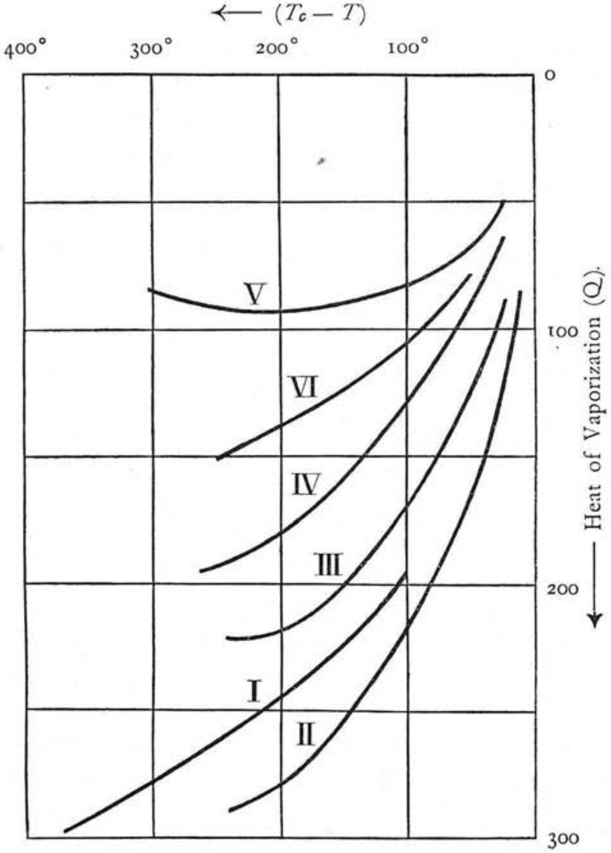
The explanation is that, in the case of associated liquids, there is another factor to be considered in the calculation of the heat of vaporization, namely the amount of heat required for the dissociation of the associated molecules into simple molecules. SUTHERLAND[1] has shown that the association of water is attended by the production of heat. This heat will be again absorbed during vaporization, since vaporization is accompanied by more or less complete dissociation of the complex molecules of the liquid. The value of the heat of vaporization is thus increased, especially at low temperatures, for the degree of association of the liquid increases as the temperature falls, while the degree of association of the saturated vapour diminishes, owing to its rapidly increasing dilution. The decrease in the heat of vaporization at low temperatures, due to the abnormal change of density of the liquid, is thus counterbalanced by this increase, due to dissociation during vaporization, and the curve for water is approximately of the normal type. Nevertheless, the slope of the curve is rather smaller than in the curve of normal type, as is seen by the fact that the value of the exponent, $n = 0{\cdot}333$, in the equation for the heat of vaporization, is lower than the value $n = 0{\cdot}386$ for normal liquids.

The curve for acetic acid (Curve V in the diagram) is evidently most abnormal; here again there is a simple explanation.

---

[1] SUTHERLAND, Phil. Mag., (5), 50, 460, (1900).

At low temperatures, even under the small vapour pressures there existing, the saturated vapour of acetic acid consists to a large extent of associated molecules, and the degree of association increases with falling temperature.[1] The density of the saturated vapour at low temperatures is therefore abnormally



I. Water (one-half normal scale).
II. Methyl alcohol.
III. Ethyl alcohol.
IV. Propyl Alcohol.
V. Acetic Acid.
VI. Ethyl Acetate ($^3/_2$ normal scale).

high, and this diminishes the third part of equation (5) above for the heat of vaporization, which represents the change in the density of the saturated vapour. At low temperatures the values for the heat of vaporization of the acid are consequently less

---

[1] YOUNG, loc. cit.

than normal, the diminuition being, indeed, so great that a maximum value is attained at 120° C., after which there is a regular decrease.

4. Methyl, Ethyl and Propyl Alcohols.

The three alcohols exhibit, just as acetic acid, though to a smaller degree, a noticeable falling-off in the increase of the heat of vaporization at low temperatures, as is seen by the comparatively rapid change in the slopes of the curves II, III and IV, when compared with the normal curve VI in the diagram. In one case, namely ethyl alcohol, a maximum value is attained in the experimental range of temperature, at 10° C. The explanation given for the abnormality of acetic acid is, however, not valid here, since the densities of the saturated vapours of the alcohols follow a perfectly normal course, and no indication of increasing association at low temperatures can be observed.[1] Also the variation of the densities of the liquids themselves with temperature, according to equation (2) above, is not, as in the case of water, considerably removed from the normal.

The abnormality in the values for the heat of vaporization of the alcohols at low temperatures has been accounted for by GUYE[1] as due to the heat required for the breaking-up of the complex molecules of the liquid during vaporization. On examination, however, this explanation is found to be insufficient, as will be seen below.

The conclusions of GUYE have been summarized by RAMSAY[3] in a paper «On the Complexity and the Dissociation of the Molecules of Liquids»; the following extract is from this paper:

«The heat required to vaporize a dissociating liquid is employed in two ways when the gas, as is always the case, has a simpler molecular formula than the liquid. A portion of the heat is employed in vaporization alone; while a portion is absorbed in effecting the decomposition of complex molecular groups. The heat of vaporization alone diminishes as tempera-

---

[1] YOUNG, loc. cit.

[2] GUYE, Archives des Sciences phys. et nat., Geneva, (3), 31, (1894).

[3] RAMSAY, Proc. Roy. Soc., A 56, 171, (1894).

ture rises, till at the critical point it is zero; but the heat required to dissociate molecular groups may increase, if that term is of importance, and may cause the total heat to increase.»

The assumption made here is that the heat required for the dissociation of molecular groups during vaporization may so increase with rising temperature that this increase will more than counterbalance the diminuition in the heat of vaporization due to the vaporization alone. But, as has already been pointed out in the case of water, the degree of dissociation of the liquid diminishes with rising temperature, while the degree of association of the saturated vapour increases. The change in the degree of dissociation during vaporization must therefore diminish rapidly as the temperature rises, and the heat absorbed by the dissociation of molecular groups will also diminish, unless the temperature coefficient of the dissociation process is large. The dissociation process may be represented by the thermochemical equation:

$$n\,(\mathrm{ROH}) \rightleftarrows (\mathrm{ROH})_n + x \text{ calories,} \tag{7}$$

where n is the number of simple molecules of the alcohol ROH in the complex molecular group, and x the number of calories absorbed in the dissociation of a gramme molecule. Now if x increases rapidly with rising temperature it is possible that the heat absorbed in dissociation during vaporization might also increase, in spite of the diminuition in the amount of liquid that dissociates. But for the heat absorbed so to vary that, over and above this, the diminuition in the heat of vaporization due to the vaporization alone may also be counterbalanced, the temperature coefficient of the dissociation process represented in the above equation must be very large indeed, i. e., x must increase extremely rapidly as the temperature rises.

The explanation of GUYE and RAMSAY will therefore be valid only if the tendency towards association increases rapidly with rising temperature. The reverse of this is, however, the case, since the degree of association of liquids invariable decreases with increase of temperature. An increase with the temperature in the amount of heat absorbed during dissociation would, in fact, be contrary to the general principle followed by physico-chemical processes, as enunciated by ARRHENIUS.[1] By this principle of ARRHENIUS, the heat liberated in a physico-chemical process (such as vaporization or dissociation) may be expressed by the formula:

$$U = A_0 - CT^2, \tag{8}$$

where A_0 and C are both negative constants. The amount of heat, U, liberated in the dissociation of a liquid, is therefore always negative at low temperatures and approaches zero with rise of temperature. In other words, heat is absorbed by dissociation, but the amount decreases as the temperature rises.

It is thus evident that the explanation of GUYE cannot account for the anomalous character of the curves of the heat of vaporization of the alcohols at low temperatures, but only accentuates the divergences observed. For a feasible explanation, it is necessary to examine more closely the nature of the energy changes that occur during the vaporization of a liquid. While, in the following pages, a definite explanation is not suggested, yet the precise direction in which such must be sought is indicated.

In the first place, during vaporization, work is done in overcoming the external pressure as the liquid expands into vapour. This accounts for the «external heat of vaporization»; the remaining portion, however, the so-called «internal heat of vaporization» is not so simple in its nature. It cannot be wholly accounted for (as has been done by some previous investigators) by the energy required to overcome the molecular attraction between the various molecules of the liquid, as they are forced apart from each other during the expansion into vapour. The expansion is also accompanied by a change in the intramolecular energy of the single molecules. For the specific heat of a liquid (or of a gas) at constant volume varies with the density, and from this it must follow that in an isothermal change in density, intramolecular energy is liberated. The specific heat of a substance at constant volume is considerably greater in the liquid state than in the gaseous state; this means that the energy change which takes place in an expanding liquid must involve

---

[1] ARRHENIUS, Meddel. från K. Vet.-Akad:s Nobelinstitut. Band 2. N:o 8, (1911).

a liberation of intramolecular energy.[1] Finally, in associated liquids, there is the energy required to effect the dissociation of complex into simple molecules.

It has already been shown that the abnormal heats of vaporization of the alcohols at low temperatures cannot be accounted for by this last-named feature in the process of vaporization. Also, since the vapour pressure curves of the alcohols, and the densities of the liquids and their saturated vapours, follow an approximately normal course with change of temperature,[2] the explanation of the abnormality is not to be found in the external heat of vaporization. Neither can the divergences be referred to moleculares attraction, for, although the exact nature of the law of molecular attraction is still a matter of dispute, it is clear that the law must be perfectly general in its application. The conclusion must therefore be drawn that it is in the change of intramolecular energy, due to the expansion during vaporization, that the alcohols exhibit abnormality.

The reason for such abnormality is not, indeed, evident, since the intramolecular energy is a function of a complex nature, very imperfectly understood. Furthermore, the experimental determination of the specific heats of liquids and of vapours at constant volume, throughout the necessary large range of temperature, has not yet been carried out within a sufficient degree of accuracy to enable us to obtain trustworthy data. In most of the cases investigated by TYRER,[3] extrapolation is necessary and the results derived are consequently somewhat uncertain. The exact determination of the specific heats of liquids and of vapours at constant volume, and the application of the results obtained to the question of the changes in intramolecular energy, may be expected to throw light upon the problems of vaporization and molecular attraction, and to advance the present unsatisfactory state of our knowledge of the laws governing association in liquids.[4]

---

[1] TYRER, Phil. Mag., (6), 23, 101, (1912).

[2] As has been previously pointed out, the curves differ slightly from the normal, but the divergences are quite insufficient to account for the large abnormalities observed in the heats of vaporization.

[3] TYRER, loc. cit.

[4] The validity of the conclusions drawn by TYRER on the question of intramolecular energy has been questioned by KLEEMAN (Phil. Mag. [VI], 23, 656, (1912)). KLEEMAN, however, makes use of the supposition that molecular attraction varies with the temperature, which is contrary to the simpler and

5. Summary.

The formula derived in a previous communication for expressing the heat of vaporisation of normal liquids:

$$Q = k\,(T_c - T)^n \tag{1}$$

where n is a constant equal to 0·386, has been tested in the case of the common associated liquids. It has been found that agreement between the experimental and calculated values can be obtained only by changing the value of the exponent n.

When the heats of vaporization of the associated liquids are plotted in a diagram against the temperature, it is seen that water approximates most nearly to the normal type, while acetic acid is most abnormal. The alcohols occupy an intermediate position.

The cause of the divergences has been examined in each case. In water there are two opposing factors — the abnormal variation of the density of the liquid with temperature, and the heat evolved in dissociation — which tend to counterbalance each other; the curve is therefore near to the normal type. In acetic acid the large divergences are accounted for by the association of the saturated vapour at low temperatures.

The case of the alcohols is not so simple, and the explanation put forward by GUYE and RAMSAY has been shown to be insufficient. An examination of the energy changes during vaporization suggests that the abnormality must be ascribed to the intramolecular energy. In an isothermal change in the density of a liquid, intramolecular energy is liberated, and the variation with the temperature of the quantity liberated during vaporization must differ, in the alcohols, from the normal type. Exact experimental data for the specific heats of liquids and of vapors at constant volume are needed for the further investigation of the problems involved.

---

more probable theory of MILLS (Phil. Mag. [VI] 21, 84, (1911), and 24, 483, (1912)). See also my previous paper (Meddel. från K. Vet.-Akad:s Nobelinstitut. Band 2. N:o 29, p 24, (1912)).

I have great pleasure in expressing my thanks to Professor ARRHENIUS for the interest be has taken in the development of the questions here considered.

Nobel Institutet, Experimentalfältet, March 1913.

Tryckt den 24 november 1913.

Uppsala 1913. Almqvist & Wiksells Boktryckeri-A.-B.

10

[Reprinted from the Journal of the American Chemical Society
Vol. XXXVI, No. 8. August, 1914.]

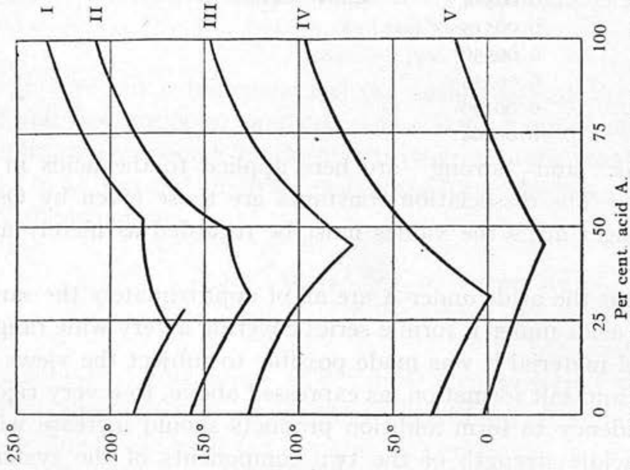
The Addition Compounds of Organic Acids in Pairs

By James Kendall

obtained in the previous investigation with dimethylpyrone. This was to be expected, since there the components were one acidic and one basic, while here both are primarily acidic.

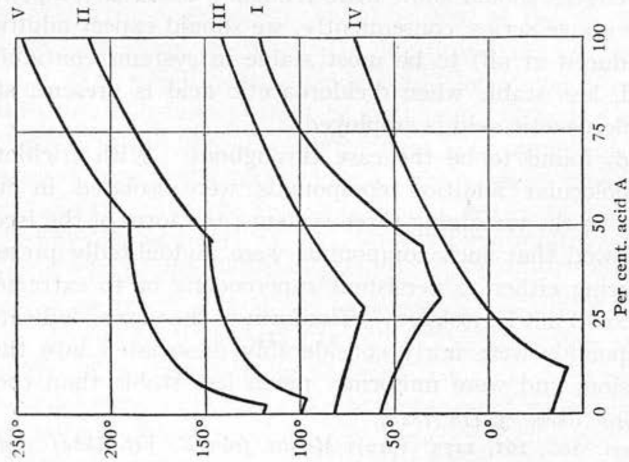
With systems containing dichloroacetic acid, addition products were obtained in two out of eight cases. In the remaining six, compounds were present in solution, but could not be isolated. (All solutions containing dichloroacetic acid were extremely difficult to investigate, owing to persistent supercooling.) The compounds obtained were much less stable than those with trichloroacetic acid.

From systems containing chloroacetic acid no addition compounds were obtained, and the curves indicate that the tendency towards com-



I. o-Toluic acid—Trichloroacetic acid. Subtract 130° from temperature scale.
II. m-Toluic acid—Trichloroacetic acid. Subtract 100° from temperature scale.
III. α-Toluic acid—Trichloroacetic acid. Subtract 70° from temperature scale
IV. α-Toluic acid—Dichloroacetic acid. Subtract 20° from temperature scale.
V. α-Toluic acid—Chloroacetic acid. Add 60° to temperature scale.

Fig. 1.



I. Benzoic acid—Trichloroacetic acid. Temperature scale correct.
II. Benzoic acid—Dichloroacetic acid. Subtract 90° from temperature scale.
III. Benzoic acid—Chloroacetic acid. Subtract 20° from temperature scale.
IV. Benzoic acid—Acetic acid. Add 50° to temperature scale.
V. Cinnamic acid—Dichloroacetic acid. Subtract 110° from temperature scale.

Fig. 2.

pound formation is extremely slight. This is in keeping with the relatively weak acidic nature of chloroacetic acid. The examination of several similar systems (in which both acids taken were either from Series A or Series B) confirmed the conclusion that, with acids of only slightly divergent strengths, no addition compounds are formed.

The experimental results are given in the tables below; these are arranged as in the previous paper. A few typical curves are shown in the accompanying diagrams.

Experimental.

1. Benzoic Acid—Trichloroacetic Acid.—The equimolecular compound, $C_6H_5.COOH$, $CCl_3.COOH$, was obtained, m. p. 36.4° (by extrapolation). The compound is not stable at its maximum, and crystallizes only from solutions containing excess of trichloroacetic acid. The freezing-point curve is shown in Fig. 2.

(*a*) Solid phase, $C_6H_5.COOH$.

% $C_6H_5.COOH$	100.0	80.1	68.3	63.6	60.1	55.5	52.0	47.1
T	121.0	105.6	89.7	79.9	72.8	64.0	54.4	43.1

(*b*) Solid phase, $C_6H_5.COOH$, $CCl_3.COOH$.

% $C_6H_5.COOH$	42.9	39.2	33.3	31.5
T	34.6	32.6	28.1	26.6

(*c*) Solid phase, $CCl_3.COOH$.

% $C_6H_5.COOH$	26.7	22.5	21.9	16.7	9.4	0
T	32.3	36.9	38.0	45.0	50.5	57.3

2. *o*-Toluic Acid—Trichloroacetic Acid.—The compound $C_7H_7.COOH$, $CCl_3.COOH$ was obtained, m. p. 52.9°; stable at its maximum. (See Fig. 1.)

(*a*) Solid phase, $C_7H_7.COOH$.

% $C_7H_7.COOH$	100.0	90.0	81.2	73.9	67.2	58.3	53.8
T	103.4	97.6	90.5	83.9	76.8	64.7	55.7

(*b*) Solid phase, $C_7H_7.COOH$, $CCl_3.COOH$.

% $C_7H_7.COOH$	49.8	45.5	40.8	37.6	33.1	28.8	23.5
T	52.9	52.6	51.8	50.4	48.1	45.1	39.4

(*c*) Solid phase, $CCl_3.COOH$.

% $C_7H_7.COOH$	27.9	21.5	15.0	8.7	0
T	30.7	38.9	45.5	51.3	57.3

3. *m*-Toluic Acid—Trichloroacetic Acid.—The compound $C_7H_7.COOH$, $CCl_3.COOH$ was obtained, unstable at its maximum; m. p. 37.4° (by extrapolation). (See Fig. 1.)

(*a*) Solid phase, $C_7H_7.COOH$.

% $C_7H_7.COOH$	100.0	89.3	78.1	65.7	60.2	55.7	51.4
T	107.6	100.2	89.8	75.3	66.6	56.9	45.4

(*b*) Solid phase, $C_7H_7.COOH$, $CCl_3.COOH$.

% $C_7H_7.COOH$	49.6	45.8	41.9	36.7
T	37.3	36.3	34.6	31.3

(*c*) Solid phase, $CCl_3.COOH$.

% $C_7H_7.COOH$	31.4	26.5	21.0	15.9	7.7	0
T	26.2	32.4	38.6	44.1	51.5	57.3

4. *p*-Toluic Acid—Trichloroacetic Acid.—An equimolecular compound was obtained, unstable at its maximum; m. p. 69.0° (by extrapolation).

(*a*) Solid phase, $C_7H_7.COOH$.

% $C_7H_7.COOH$	100.0	87.2	76.2	65.5	57.6	50.1	44.8	40.0	36.9
T	178.6	170.4	160.1	145.9	131.9	115.5	100.2	84.1	69.1

(*b*) Solid phase, $C_7H_7.COOH$, $CCl_3.COOH$.

% $C_7H_7.COOH$	34.5	30.5	25.7	22.3	18.1
T	63.5	60.3	55.7	51.8	45.0

(*c*) Solid phase, $CCl_3.COOH$.

% $C_7H_7.COOH$	12.9	6.9	0
T	46.6	52.2	57.3

5. α-Toluic Acid—Trichloroacetic Acid.—No compound was here isolated. The curve is shown in Fig. 1.

(*a*) Solid phase, $C_7H_7.COOH$.

% $C_7H_7.COOH$	100.0	90.5	81.4	70.8	63.1	55.4	47.9
T	76.7	70.8	63.3	51.7	40.1	25.9	9.2

(*b*) Solid phase, $CCl_3.COOH$.

% $C_7H_7.COOH$	41.2	34.9	28.4	20.8	11.7	0
T	10.2	21.2	31.3	41.2	49.3	57.3

6. Cinnamic Acid—Trichloroacetic Acid.—The compound $C_8H_7.COOH$, $CCl_3.COOH$ was obtained, unstable at its maximum; m. p. 63.0° (by extrapolation).

(*a*) Solid phase, $C_8H_7.COOH$.

% $C_8H_7.COOH$	100.0	87.0	76.1	65.8	56.6	50.3
T	136.8	122.2	108.5	94.8	79.9	68.5

(*b*) Solid phase, $C_8H_7.COOH$, $CCl_3.COOH$.

% $C_8H_7.COOH$	45.3	41.4	35.3	29.2	25.9
T	62.1	59.7	55.7	49.3	44.9

(*c*) Solid phase, $CCl_3.COOH$.

% $C_8H_7.COOH$	24.8	19.7	17.4	9.3	0
T	36.1	42.5	45.0	51.1	57.3

7. Acetic Acid—Trichloroacetic Acid.—No compound was here isolated.

(*a*) Solid phase, $CH_3.COOH$.

% $CH_3.COOH$	100.0	91.3	84.6	75.7	69.0
T	16.4	9.9	3.1	−10.1	−25.3

(*b*) Solid phase, $CCl_3.COOH$.

% $CCl_3.COOH$	51.0	46.1	38.5	30.2	22.5	12.8	0
T	−13.3	−0.1	15.4	28.4	37.6	47.3	57.3

8. Crotonic Acid—Trichloroacetic Acid.—Here also no compound was isolated.

(*a*) Solid phase, $C_3H_5.COOH$.

% $C_3H_5.COOH$	100.0	91.0	82.7	75.7	65.7	60.0	54.2	49.9
T	71.0	63.7	53.9	44.2	27.5	16.1	2.1	—9.9

(*b*) Solid phase, $CCl_3.COOH$.

% $C_3H_5.COOH$	45.1	40.7	34.4	26.6	19.1	10.2	0
T	—12.7	1.2	16.4	30.4	40.3	49.6	57.3

9. Benzoic Acid—Dichloroacetic Acid.—The compound $C_6H_5.COOH$, $CHCl_2.COOH$ was obtained; unstable at its maximum; m. p. 58.2° (by extrapolation). The freezing-point curve is shown in Fig. 2.

(*a*) Solid phase, $C_6H_5.COOH$.

% $C_6H_5.COOH$	100.0	81.5	70.7	61.1	50.8	48.4	45.7
T	121.0	104.0	91.6	79.1	64.6	61.2	56.7

(*b*) Solid phase, $C_6H_5.COOH, CHCl_2.COOH$.

% $C_6H_5.COOH$	44.3	40.2	37.4	34.9	29.4	25.3	16.9	11.6	8.3	5.4
T	57.8	57.2	56.4	55.6	52.8	50.1	42.6	33.6	25.5	15.3

(*c*) Solid phase, $CHCl_2.COOH$.

% $C_6H_5.COOH$	1.8	0
T	8.6	9.7

10. *o*-Toluic Acid—Dichloroacetic Acid.—No addition compound was here isolated.

(*a*) Solid phase, $C_7H_7.COOH$.

% $C_7H_7.COOH$	100.0	89.5	78.6	69.1	60.7	51.2	43.0	37.9	28.2	20.4	14.4
T	103.4	97.1	89.5	81.6	74.1	63.0	52.1	44.9	28.4	13.0	—1.9

(*b*) Solid phase, $CHCl_2.COOH$.

% $C_7H_7.COOH$	12.5	7.1	0
T	—1.0	3.9	9.7

11. *m*-Toluic Acid—Dichloroacetic Acid.—Here also no addition compound was isolated.

(*a*) Solid phase, $C_7H_7.COOH$.

% $C_7H_7.COOH$	100.0	87.4	74.6	66.1	56.4	46.4	35.9	28.2	23.0
T	107.6	98.5	87.5	79.4	68.2	53.8	35.8	19.9	6.1

(*b*) Solid phase, $CHCl_2.COOH$.

% $C_7H_7.COOH$	17.1	11.0	6.1	0
T	—6.1	—0.2	4.2	9.7

12. *p*-Toluic Acid—Dichloroacetic Acid.—No compound was isolated.

(*a*) Solid phase, $C_7H_7.COOH$.

% $C_7H_7.COOH$	100.0	85.1	71.6	59.5	50.0	40.9	33.1	26.1	20.4	15.5	10.8
T	178.6	168.1	154.9	139.6	125.2	109.0	91.3	75.2	59.7	42.3	23.1

(*b*) Solid phase, $CHCl_2.COOH$.

% $C_7H_7.COOH$	5.2	0
T	5.1	9.7

13. α-Toluic Acid—Dichloroacetic Acid.—No compound was isolated. (See Fig. 1.)

(*a*) Solid phase, $C_7H_7.COOH$.

% $C_7H_7.COOH$	100.0	93.3	81.4	71.8	63.9	59.2	50.0	42.9	36.9
T	76.7	72.4	63.4	53.6	43.9	37.6	22.3	9.0	−5.5

(*b*) Solid phase, $CHCl_2.COOH$.

% $C_7H_7.COOH$	25.9	15.3	7.5	0
T	−14.6	−3.3	3.5	9.7

14. Cinnamic Acid—Dichloroacetic Acid.—The equimolecular compound $C_8H_7.COOH$, $CHCl_2.COOH$ was obtained; unstable at its maximum; m. p. 80.1°. (See Fig. 2.)

(*a*) Solid phase, $C_8H_7.COOH$.

% $C_8H_7.COOH$	100.0	86.1	74.1	62.8	55.0	51.5
T	136.8	124.3	111.0	97.6	86.1	80.0

(*b*) Solid phase, $C_8H_7.COOH$, $CHCl_2.COOH$.

% $C_8H_7.COOH$	51.5	50.0	44.8	37.3	29.8	24.6	17.1	12.8	7.8	6.0	4.1
T	80.0	80.1	79.7	77.8	74.2	69.6	61.4	54.0	42.8	35.7	24.7

(*c*) Solid phase, $CHCl_2.COOH$

% $C_8H_7.COOH$	1.6	0
T	8.6	9.7

15. Acetic Acid—Dichloroacetic Acid.—No addition compound was isolated. The central portion of the curve could not be completed, since at the very low temperature required for solidification the mixture sets to a hard, glassy mass.

(*a*) Solid phase, $CH_3.COOH$.

% $CH_3.COOH$	100.0	91.4	79.2	70.5	63.6	55.0
T	16.4	10.3	−0.7	−10.8	−21.5	−37.0

(*b*) Solid phase, $CHCl_2.COOH$

% $CH_3.COOH$	43.4	29.7	17.9	8.6	0
T	−40.8	−18.2	−4.2	3.9	9.7

16. Crotonic Acid.—Dichloroacetic Acid.—No addition compound could be isolated.

(*a*) Solid phase, $C_3H_5.COOH$

% $C_3H_5.COOH$.	100.0	93.6	86.8	80.6	71.1	65.3	55.8	47.4	40.4
T	71.0	65.5	59.1	52.6	41.4	34.0	20.5	5.1	−9.7

(*b*) Solid phase, $CHCl_2.COOH$.

% $C_3H_5.COOH$.	31.0	17.1	8.9	0
T	−18.5	−4.2	2.7	9.7

17. Benzoic Acid—Chloroacetic Acid.—No compound was obtained in any system containing chloroacetic acid. The freezing-point curve is given in Fig. 2.

(*a*) Solid phase, C_6H_5.COOH.

% C_6H_5.COOH	100.0	81.0	69.8	58.5	52.9	44.2	38.6	32.0
T	121.0	107.2	96.8	86.1	80.4	69.9	62.4	52.6

(*b*) Solid phase, CH_2Cl.COOH.

% C_6H_5.COOH	25.1	21.1	14.4	5.9	0
T	48.7	50.7	54.5	58.6	61.4

18. *o*-Toluic Acid—Chloroacetic Acid.

(*a*) Solid phase, C_7H_7.COOH.

% C_7H_7.COOH	100.0	89.1	77.0	66.4	57.4	50.5	44.4	38.2	32.4
T	103.4	97.0	89.6	82.3	75.5	70.2	64.9	58.8	52.3

(*b*) Solid phase, CH_2Cl.COOH.

% C_7H_7.COOH	27.5	22.1	16.5	11.5	5.8	0
T	47.9	50.7	53.3	55.7	58.5	61.4

19. *m*-Toluic Acid—Chloroacetic Acid.

(*a*) Solid phase, C_7H_7.COOH

% C_7H_7.COOH	100.0	90.1	79.6	68.4	56.9	45.2	35.7
T	107.6	101.0	93.6	84.7	75.3	64.1	53.9

(*b*) Solid phase, CH_2Cl.COOH.

% C_7H_7.COOH	28.4	21.2	14.4	7.7	0
T	46.7	50.5	54.2	57.7	61.4

20. *p*-Toluic Acid—Chloroacetic Acid

(*a*) Solid phase, C_7H_7.COOH.

% C_7H_7.COOH	100.0	83.1	70.4	56.9	45.4	34.0	22.7	17.1	12.9
T	178.6	167.2	155.8	141.8	128.5	114.0	95.5	83.1	71.1

(*b*) Solid phase, CH_2Cl.COOH.

% C_7H_7.COOH	9.3	4.7	0
T	56.8	59.1	61.4

21. α-Toluic Acid—Chloroacetic Acid.—The freezing-point curve is shown in Fig. 1.

(*a*) Solid phase, C_7H_7.COOH.

% C_7H_7.COOH	100	89.5	80.9	72.5	64.8	56.6	49.9
T	76.7	70.1	63.8	56.9	49.9	42.3	35.2

(*b*) Solid phase, CH_2Cl.COOH.

% C_7H_7.COOH	41.6	32.9	23.9	14.9	6.7	0
T	33.6	40.0	46.7	52.7	57.9	61.4

22. Cinnamic Acid—Chloroacetic Acid.

(*a*) Solid phase, C_8H_7.COOH.

% C_8H_7.COOH	100	89.3	77.5	68.0	54.4	44.7	36.4	31.4
T	136.8	128.2	118.6	109.0	95.9	83.8	70.2	60.5

(*b*) Solid phase, CH_2Cl.COOH.

% C_8H_7.COOH	25.0	19.0	13.9	8.2	0
T	48.3	51.2	54.0	57.1	61.4

23. Acetic Acid—Chloroacetic Acid.

(*a*) Solid phase, $CH_3.COOH$.

% $CH_3.COOH$	100	91.8	79.6	71.0
T	16.4	10.7	1.7	—4.5

(*b*) Solid phase, $CH_2Cl.COOH$.

% $CH_3.COOH$	71.0	62.0	50.3	40.3	29.4	15.5	0
T	5.0	12.8	22.2	29.7	38.0	49.4	61.4

24. Crotonic Acid—Chloroacetic Acid.

(*a*) Solid phase, $C_3H_5.COOH$.

% $C_3H_5.COOH$	100	91.2	83.4	75.4	65.9	56.5
T	71.0	64.4	57.7	50.7	41.1	30.9

(*b*) Solid phase, $CH_2Cl.COOH$.

% $C_3H_5.COOH$	46.8	38.6	30.0	19.9	10.4	0
T	29.9	36.5	42.6	50.0	55.8	61.4

25. Benzoic Acid—α-Toluic Acid.—In this and the two following systems the acids are both from Series A; no compound formation was indicated.

(*a*) Solid phase, $C_6H_5.COOH$.

% $C_6H_5.COOH$	100	91.0	82.1	70.0	57.9	48.7	38.3
T	121.0	115.2	108.5	97.8	85.3	74.0	57.4

(*b*) Solid phase, $C_7H_7.COOH$.

% $C_6H_5.COOH$	28.9	18.9	10.1	0
T	56.9	63.7	69.5	76.7

26. Benzoic Acid—Cinnamic Acid.

(*a*) Solid phase, $C_6H_5.COOH$.

% $C_6H_5.COOH$	100	86.8	76.9	69.9	61.7
T	121.0	111.0	102.0	95.4	87.2

(*b*) Solid phase, $C_8H_7.COOH$.

% $C_6H_5.COOH$	52.5	42.3	33.1	19.9	9.6	0
T	87.3	100.5	109.5	121.5	130.1	136.8

27. Benzoic Acid—Acetic Acid.—The freezing-point curve is shown in Fig. 2.

(*a*) Solid phase, $C_6H_5.COOH$.

% $C_6H_5.COOH$	100	87.6	72.6	61.0	50.6	43.4	35.3	28.3	20.8	14.5
T	121.0	111.5	100.3	90.1	79.1	71.5	60.9	50.9	38.2	19.2

(*b*) Solid phase, $CH_3.COOH$.

% $C_6H_5.COOH$	9.7	5.2	0
T	10.4	13.0	16.4

28. Chloroacetic Acid—Dichloroacetic Acid.—In this and the following systems the acids are both from Series B; no addition compounds were isolated.

(*a*) Solid phase, $CH_2Cl.COOH$.

% $CH_2Cl.COOH$	100	90.1	82.5	75.8	66.4	54.0	40.4	32.7
T	61.4	56.8	52.5	47.5	40.5	29.6	10.8	—5.5

(*b*) Solid phase, $CHCl_2.COOH$.

% $CH_2Cl.COOH$	24.7	12.2	0
T	—5.8	2.8	9.7

29. Chloroacetic Acid—Trichloroacetic Acid.

(*a*) Solid phase, $CH_2Cl.COOH$.

% $CH_2Cl.COOH$	100	84.8	74.5	65.5	58.2	51.4
T	61.4	53.5	46.5	38.9	31.0	22.4

(*b*) Solid phase, $CCl_3.COOH$.

% $CH_2Cl.COOH$	41.7	31.9	24.1	15.5	0
T	24.3	33.2	39.9	46.1	57.3

30. Dichloroacetic Acid—Trichloroacetic Acid.

(*a*) Solid phase, $CHCl_2.COOH$.

% $CHCl_2.COOH$	100	93.7	82.2	68.7
T	9.7	7.0	1.0	—7.9

(*b*) Solid phase, $CCl_3.COOH$.

% $CHCl_2.COOH$	56.9	46.5	31.8	21.2	12.2	0
T	—0.6	14.5	32.9	42.5	49.6	57.3

Consideration of Results.

The general conclusions of the investigation have already been stated in the introduction. In the following pages, by closer examination of the freezing-point curves obtained, some quantitative results are deduced and discussed.

From the diagrams given, it will be seen that the freezing-point curves are different in type, even where no addition compound is isolated, according to which acid of Series B is present in the system. In systems containing chloroacetic acid, the curves obtained are approximately linear, the change in slope as the eutectic point is approached being very slight. In systems where dichloroacetic acid is present, the curves deviate more from the straight line, and the "dip" before the eutectic is more pronounced. Finally, in systems containing trichloroacetic acid, the curves fall away rapidly in the neighborhood of the eutectic point.

It remains to show how this difference in character is connected with the relative extent of compound formation in the mixture. The freezing point of a pure substance, A, will, under normal conditions,[1] be equally

---

[1] That is, provided the substance added is not *associated* or *dissociated* in the solution.—It is not intended to imply, in the following discussion, that association or dissociation of the substances present in the systems considered can be entirely disregarded. Organic acids, as a class, are certainly associated to some extent in the liquid state, also the conception that the addition reaction taking place in the solution is *ionic* (Kendall, THIS JOURNAL, 36, 1242 (1914)) assumes dissociation. Nevertheless, the regularity of the results obtained indicates clearly that the figures given in Table I are legitimately comparable, and that the above disturbing influences are only of secondary importance.

depressed on addition of equimolecular amounts of different foreign substances, provided no chemical reaction has occurred. If, however, the addition of a second substance, B, to A is accompanied by the formation of an addition compound, AB, then the freezing point of A will be abnormally lowered, since part of the original solvent will have been replaced by a foreign substance, the compound AB. The more stable the addition product is, the greater will be the abnormal depression of the freezing point. Hence, the form of the curves obtained, when different substances are added to A, indicates the relative extent of compound formation in each case.

In the systems examined above, chloroacetic acid shows no tendency to compound formation throughout, and the freezing point curves approximate to straight lines.[1] Where dichloroacetic acid is present, on the other hand, addition products are formed and can in some cases be isolated, although they are evidently, from the flatness of their curves near the maximum point, largely dissociated into their components in the liquid state. On first addition of dichloroacetic acid to an acid in Series A, the extent of compound formation will be very small.[2] Further addition of dichloroacetic acid will increase the amount of the compound present,[3] and that this corresponds with an abnormal depression of the freezing point is indicated by the "falling away" of the curves as the eutectic is approached. Systems in which trichloroacetic acid is a component are similar in type, but the addition products formed are more stable. In accordance with this, the freezing point depression in the central part of the curve becomes still more abnormal, as is evidenced by the systems shown in Diagram I.

We are, therefore, able to discover by comparison to what extent compound formation has occurred in any particular system, from the form of the freezing-point curve alone, even if it is not possible actually to isolate the compound. This is illustrated by the figures given in Table I, where the freezing-point depressions of the acids in Series A, due to addition of equimolecular amounts of the various acids in Series B, are col-

---

[1] Where the point of fusion of the second acid of the system is very high (*e. g.*, *p*-toluic acid) a sharp final bend in the curve is necessary to enable it to reach the eutectic point at all. The main portion of the curve, however, still remains linear. Compare Fig. 2, Curve IV.

[2] The reversible reaction $A + B \rightleftharpoons AB$ gives the equation for equilibrium:

$$c_{AB}/c_A c_B = k$$

(c = molecular concentration, k = constant.) If the compound AB is largely dissociated on fusion, the constant k of the reaction will be small. Hence, when c_B is small, c_{AB} is also very small. The extent of compound formation will obviously be greatest in the central portion of the curve.

[3] Not only for the reason given in the previous note, but also since the addition products formed are more stable, the lower the temperature.

lected. The values given are obtained directly by interpolation from the freezing-point curves.[1] (T_{50} = freezing point of 50% mixture: Δ = depression.)

TABLE I.

	Trichloroacetic.		Dichloroacetic.		Chloroacetic.	
Acid A.	T_{50}.	Δ.	T_{50}.	Δ.	T_{50}.	Δ.
Benzoic	50.6	70.4	63.7	57.3	77.2	43.8
o-Toluic	47.2	56.2	61.6	41.8	69.8	33.6
m-Toluic	40.4	67.2	59.4	48.2	68.8	38.8
p-Toluic	115.2	63.4	125.2	53.4	134.1	44.5
α-Toluic	14.4	62.3	22.3	54.4	35.3	41.4
Cinnamic	68.0	68.8	77.5	59.3	90.9	45.9
Crotonic	—9.6	80.6	9.8	61.2	23.2	47.8

The above results show that, throughout the entire series, the freezing-point depression caused by trichloroacetic acid is greater than that caused by dichloroacetic acid, which is in turn greater than that caused by chloroacetic acid.

This dependence of compound formation upon difference in acidic strength is evidently in complete accordance with the views on oxonium salt formation developed in the introduction. The regularity of the values obtained indicates that the results are not greatly influenced by any disturbing factors (association or dissociation in the solution).[2] Further evidence on the point is to be obtained from systems containing acids of similar strengths (25–27, above). From these we have:

TABLE II.

Original acid.	Acid added.	T_{50}.	Δ.
Benzoic	α-Toluic	75.5	45.5
Benzoic	Cinnamic	75.6	45.4
Benzoic	Acetic	78.5	42.5
Benzoic	Chloroacetic	77.2	43.8)
Cinnamic	Benzoic	90.4	46.4
Cinnamic	Chloroacetic	90.9	45.9)

Here T_{50} and Δ have the same significance as in Table I; the figures for chloroacetic acid are included for comparison. The constancy of Δ for benzoic acid with different acids exhibiting no tendency to compound formation shows that conditions in the above systems are, if not normal, at least comparable.[3] The freezing-point depression caused by chloro-

---

[1] In a few cases a short extrapolation is necessary. The figures for acetic acid are not given, since here a longer extrapolation is required and accurate values cannot be obtained. The curves indicate, however, that the results are qualitatively similar to those given above.

[2] See note on page 1731.

[3] For small additions of B to A (up to 20%), the freezing-point curves are practically identical, whatever acid in Series B is added. In this region the extent of compound formation is small in all cases (see Note 2, page 1732).

acetic acid is approximately normal; it is evident that its acidic strength is insufficient to suppress the acidic properties of the weaker acid of the system so far as to induce combination.

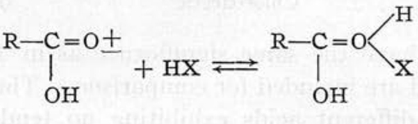
Addition reactions of the nature dealt with in this paper have been little investigated; a few compounds of the type acid—acid have been previously described[1] but not systematically examined. The similarity of the components accounts for the small number of compounds isolated in the present research, but further experiments indicate that formation of addition products is of very general occurrence in organic reactions, *e. g.*, as an intermediate stage in condensations.[2] That this is not generally recognized is due to the neglect of the freezing-point method in the study of organic reactions.

It seems to be still the rule in experimental work to torture substances into combination by the drastic method (inherited from the alchemists) of applying *heat*. This certainly gives us the final products of a reaction (or series of reactions), but affords no clue to its mechanism. If, on the other hand, we mix the components at as low a temperature as possible and then, by *freezing* the mixture, isolate addition products, we have obtained definite knowledge of an intermediate stage of the reaction. This will be exemplified in a forthcoming paper on sulfonation.

Summary.

The freezing-point curves of a series of weak organic acids with the chloro-substituted acetic acids have been investigated. The tendency towards formation of addition compounds is found to be dependent upon the difference in acidic strengths of the two components. Acids widely divergent in strength give addition compounds which may readily be isolated.

The reaction is regarded as an oxonium salt formation, and may be expressed as follows:



$$\mathrm{R{-}\underset{\begin{smallmatrix}\mid\\ OH\end{smallmatrix}}{C}{=}O}\pm + \mathrm{HX} \rightleftharpoons \mathrm{R{-}\underset{\begin{smallmatrix}\mid\\ OH\end{smallmatrix}}{C}{=}O}\begin{smallmatrix}\diagup \mathrm{H}\\ \diagdown \mathrm{X}\end{smallmatrix}$$

The quantitative results obtained are in complete agreement with this view.

NICHOLS LABORATORIES OF INORGANIC CHEMISTRY,
COLUMBIA UNIVERSITY, NEW YORK CITY.

---

[1] Hoogewerff and van Dorp, *Rec. trav. chim. Pays-Bas*, **21**, 353 (1902); Pfeiffer, *Ber.*, **47**, 1593 (1914).

[2] Compare Guye, *J. chim. physique*, **8**, 119 (1910). The view has also been advanced by Michael that an addition process represents an intermediate stage in substitution reactions (THIS JOURNAL, **32**, 1001 (1910)).

[Reprinted from the Journal of the American Chemical Society
Vol. XXXVI. No. 6. June, 1914.]

The Addition Compounds of Dimethylpyrone with Organic Acids

By James Kendall

[Reprinted from theJournal of the American Chemical Society,
Vol. XXXVI. No. 6. June, 1914.]

[CONTRIBUTIONS OF THE DEPARTMENT OF CHEMISTRY OF COLUMBIA UNIVERSITY,
No. 234.]

THE ADDITION COMPOUNDS OF DIMETHYLPYRONE WITH ORGANIC ACIDS.[1]

BY JAMES KENDALL.

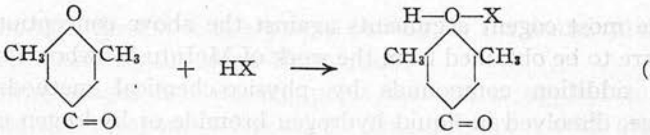
Received April 20, 1914.

The addition products of dimethylpyrone with acids are of special interest in view of their connection with the oxonium theory of Collie and Tickle.[2] The hypothesis that oxygen may function as a quadrivalent atom was first brought into prominence by a study of these compounds, the action being regarded as proceeding according to the equation:

---

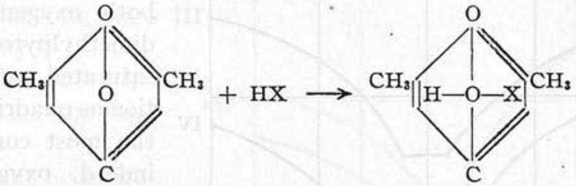
[1] Presented at the Cincinnati meeting of the American Chemical Society, April 9, 1914.

[2] *J. Chem. Soc.*, **75**, 710 (1899).


(I)

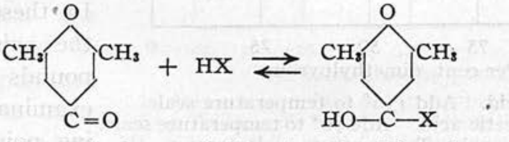
It is assumed in this equation (no reason being given) that addition takes place by means of the oxygen in the ring. Subsequent investigators have regarded the "carbonyl" oxygen in the side-chain as active, the addition products formed being considered as analogous with those given by aldehydes and ketones with acids. Since, however, ethers also react with acids to form addition compounds, it is evident that either assumption may be correct.

Collie's later views regarding the structural formulae of dimethylpyrone and its salts[1] lead to the following equation:


(II)

Here dimethylpyrone itself is considered as containing a quadrivalent oxygen atom, and, in the addition compound, both oxygen atoms are regarded as quadrivalent. These assumptions are supported by the work of Homfray on molecular refraction,[2] and also by the spectroscopic measurements of Baly.[3] On the other hand, Willstätter and Pummerer[4] have advanced reasons against the assumption of quadrivalent oxygen in dimethylpyrone itself.

It does not seem to be regarded as definitely established, indeed, that oxygen functions as a quadrivalent atom at all in the above reaction. Werner[5] has explained the constitution of the addition products with the help of his theory of subsidiary bonds. Gomberg and Cone[6] have denied the formation of an oxonium salt entirely, and consider the action as taking place according to the scheme:


(III)

A great deal of evidence in favor of this view is adduced.

---

[1] *J. Chem. Soc.*, 85, 973 (1904).

[2] *Ibid.*, 87, 1443 (1905).

[3] *Ibid.*, 96, 144 (1909).

[4] *Ber.*, 37, 3740 (1904); 38, 1461 (1905).

[5] *Ann.*, 322, 296 (1902).

[6] *Ibid.*, 376, 217 (1910).

Hence the freezing point curve exhibits, in this case, a maximum, the position of the maximum on the axis of molecular concentration indicating the composition of the compound. A series of compounds is indicated by a series of maxima on the curve.

Now the action $x\mathrm{A} + y\mathrm{B} \longrightarrow \mathrm{A}_x\mathrm{B}_y$ is a reversible reaction, and the addition compound is always more or less dissociated into its two components. The maximum of the curve, therefore, is not sharp, but more or less "rounded-off." The flatness of the curve in the neighborhood of the maximum serves, indeed, as a measure of the degree of the dissociation.[1] This is important in the consideration of the relative dissociation of the various compounds described below.

In certain cases a compound is not stable at its maximum. Its composition must then be determined either from the curve, by extrapolation, or experimentally by analysis of the solid phase separating from the solution.

Experimental.

The ordinary Beckmann freezing point apparatus was employed. The outer bath (paraffin, water, ice—salt, or ether—carbon dioxide snow, according to the temperature required) was maintained at a temperature slightly below the freezing point of the mixture contained in the inner tube, and the latter slowly cooled, with constant stirring. In favorable cases the solid phase separated out after very slight supercooling, and the temperature rose rapidly to the true freezing point.[2] More frequently, however, considerable supercooling took place before crystallization began; it was then necessary to melt up again, preserving a small portion of the solid phase in the upper part of the tube, and repeat the experiment, seeding the liquid at intervals with crystals by means of the stirrer. In cases where crystallization was so sluggish that no rise of temperature on freezing could be obtained, the first sign of crystallization *in* the liquid under the above conditions was taken as indicating the freezing point. The temperature thus obtained could be confirmed by raising the temperature of the outer bath very slowly, and observing the disappearance of the solid phase.

The thermometers employed in the investigation were:

(*a*) a mercury thermometer, —10° to 110°, graduated in 1/10°.

(*b*) a mercury thermometer, 90° to 200°, graduated in 1/5°.

(*c*) an alcohol thermometer, 50° to —50°, which could be read to 1/5°.

The thermometers were standardized at the freezing point and boiling point of water by the usual methods, and at other temperatures by com-

---

[1] Kremann, *Monats.*, 25, 1222 (1904).

[2] This method is obviously inapplicable on steep portions of the curve, where the freezing point of the mixture changes rapidly with change of composition. Here also it was necessary to employ the more tedious method of observing appearance or disappearance of solid phase.

parison with a standard thermometer. A temperature-correction curve for exposed stem was also obtained, and the necessary correction applied to every reading taken.[1] The constancy of the thermometers during the course of the investigation was examined by careful repetition of the above tests at intervals. The temperatures given in the tables below may be taken as having the following degree of accuracy:

(*a*) between 200° and 100°: 0.2–0.5°.
(*b*) between 100° and 0°: 0.1–0.2°.
(*c*) between 0° and —50°: 0.2–0.5°.

The difficulty of measurement varied very considerably with the system under examination. In some systems, especially at low temperatures, a glassy mass was obtained in which it was extremely difficult to observe appearance or disappearance of crystals.

The composition of the mixtures examined is expressed throughout, in the tables below, in molecular percentages of the components. A known weight of one component was taken, and successive quantities of the second introduced into the apparatus through the side tube in the form of compressed tablets. Liquids were added by means of the Lunge pipet. Deliquescent substances were introduced from a weighing bottle after careful drying in a desiccator, and contact with the outer air was made as short as possible.

Dimethylpyrone melts at 132.1°, but begins to sublime below 80°, and above 100° the amount of sublimation in a short time is appreciable.[2] Hence the freezing points of mixtures containing, in general, more than 70% dimethylpyrone could not be determined by the ordinary Beckmann method. The following method was adopted, and, by it, results of approximate but sufficient accuracy were obtained. A weighed amount of dimethylpyrone (about 0.1 g.) and a smaller amount (unweighed) of acid were introduced into a narrow glass tube, the tube sealed, and attached to the thermometer. Thermometer and tube were now immersed together in sulfuric acid, contained in the inner freezing point tube, and the outer bath (paraffin) heated until the contents of the tube melted. It was usually necessary to repeat fusion several times before a homogeneous mixture was obtained. The freezing point could be determined, within 0.5° to 1.0°, by observing disappearance of crystals with a slowly rising temperature. Finally, the composition of the mixture was determined by cooling the tube, dissolving the contents in water, and titrating the acid against a standardized solution of barium hydroxide.[3]

---

[1] This correction varied from 0.1° at 50° to 1.6° at 180°.

[2] This does not apply to mixtures containing only a small percentage of dimethylpyrone. Such mixtures could be investigated up to 150° without appreciable sublimation.

[3] Where the acid was insoluble in water, or could not be titrated accurately against barium hydroxide, larger amounts were taken, and the acid used directly weighed.

The above procedure was necessary, in a few systems, throughout a more extended range of concentration, owing to the volatility of the acid employed (*e. g.*, formic acid, acetic acid) at high temperatures.

The purity of the substances used was tested by their point of fusion. For dimethylpyrone, Poma[1] has obtained the m. p. 132°, the value obtained with the Kahlbaum specimens employed[2] was 132.1°. Most of the acids were also pure Kahlbaum samples, and gave satisfactory points of fusion without preliminary purification. Only in a few cases was it necessary to obtain a purer product by crystallization from a suitable solvent (*e. g.*, trichlorobutyric acid from ligroin) or by freezing partially an impure liquid (*e. g.*, formic acid) and rejecting the liquid portion.

The following substances were investigated:

Aliphatic acids.

1. Formic
2. Acetic
3. Chloroacetic
4. Dichloroacetic
5. Trichloroacetic
6. Trichlorobutyric
7. Trichlorolactic
8. *β*-Iodopropionic
9. Crotonic
10. Chlorocrotonic

Aromatic acids.

11. Benzoic
12. *o*-Toluic
13. *m*-Toluic
14. *p*-Toluic
15. *α*-Toluic
16. Salicylic
17. *o*-Nitrobenzoic
18. Cinnamic
19. Hydrocinnamic
20. Mandelic

Phenols, etc.

21. Phenol
22. *o*-Cresol
23. *m*-Cresol
24. *p*-Cresol
25. *o*-Nitrophenol
26. *m*-Nitrophenol
27. *p*-Nitrophenol
28. (2,4)-Dinitrophenol
29. Picric acid
30. Trinitrotoluene
31. *α*-Naphthol
32. *β*-Naphthol

Dibasic acids and phenols are not considered in the present paper. The results obtained are given in tabular and graphical form below. The freezing point temperature is indicated by T.

1. Formic Acid.—A Kahlbaum sample froze at 7.3°. By means of repeated partial solidification, with rejection of the liquid remainder, the pure acid was obtained, melting at 8.5°.[3] With dimethylpyrone two compounds were obtained: $2C_7H_8O_2.3H.COOH$ and $C_7H_8O_2.2H.COOH$, melting at 19.6° and 19.0°, respectively; both were confirmed by analyses of the solid phases separating from the solutions. From the freezing point curve (page 1224, Fig. 1) it is evident that both compounds are considerably dissociated in the liquid state, the maxima on the curve being very flat. The following results are collected from several series of experiments:

(*a*) Solid phase, $C_7H_8O_2$.

% $C_7H_8O_2$...	100	85.6	76.0	65.9	60.1	54.6	50.8	47.8	45.9	44.1	43.5	43.3
T..........	132.1	122.5	112.5	98.0	84.5	70.9	58.1	45.0	35.1	24.9	20.4	19.0

[1] *Gazz. chim. ital.*, 41, II, 518 (1911).

[2] For one sample the author desires to express his thanks to Professor Gomberg.

[3] Compare Ewins, *J. Chem. Soc.*, 105, 350 (1914).

(*b*) Solid phase, $2C_7H_8O_2.3H.COOH$.

% $C_7H_8O_2$...	42.6	41.9	41.7	40.7	40.5	40.0	39.6	39.0	38.5	37.3	36.5	..
T..........	18.9	19.1	19.3	19.6	19.5	19.6	19.5	19.6	19.4	19.2	18.8	..

(*c*) Solid phase, $C_7H_8O_2.2H.COOH$.

% $C_7H_8O_2$...	36.1	34.9	34.6	33.3	33.0	31.5	30.9	29.5	28.2	26.0	25.0	..
T..........	18.7	18.9	18.9	19.0	19.0	18.9	18.7	18.3	17.6	16.3	15.5	..
% $C_7H_8O_2$...	23.9	21.5	18.9	15.3	13.6	..	..	..	..	..	..	..
T..........	14.3	11.1	7.0	—0.3	—4.3	..	..	..	..	..	..	..

(*d*) Solid phase, H.COOH.

% $C_7H_8O_2$...	12.0	8.3	5.7	0	..	..	..	..	..	..	..	..
T..........	—5.5	0.0	3.1	8.5	..	..	..	..	..	..	..	..

2. *Acetic Acid.*—From Kahlbaum's glacial acetic acid a pure product, freezing at 16.4°, was obtained by the method of partial solidification described above. With dimethylpyrone the compound $C_7H_8O_2.CH_3.COOH$ was obtained; m. p., 30° (by extrapolation). The compound is not stable at its maximum. This explains the failure of Collie and Tickle to isolate dimethylpyrone acetate, since the salt can be crystallized only from solutions containing excess of acetic acid. The composition was determined by analysis of the solid phase. The freezing point diagram is given on page 1225, Fig. 2.

(*a*) Solid phase, $C_7H_8O_2$.

% $C_7H_8O_2$..........	100	87.1	75.0	64.8	57.2	50.9	46.6	43.2	39.6	37.5
T..................	132.1	125.5	115.0	102.5	88.6	73.3	61.1	50.3	37.3	28.3

(*b*) Solid phase, $C_7H_8O_2.CH_3.COOH$.

% $C_7H_8O_2$..........	34.9	33.4	28.5	23.9	20.4	..	..	..	..	..
T..................	23.8	22.4	15.6	7.5	—0.4	..	..	..	..	..

(*c*) Solid phase, $CH_3.COOH$.

% $C_7H_8O_2$..........	17.7	15.3	9.0	0	..	..	..	..	..	..
T..................	—2.0	2.1	9.6	16.4	..	..	..	..	..	..

3. *Chloroacetic Acid.*—This acid has been shown to exist in three[1] (perhaps four)[2] crystalline modifications, melting at 61.3°, 56.2°, 50.2° (and 43.75°), respectively. The first three of these points were experimentally confirmed with the acid employed; all other values tabulated below are on the freezing point curve of the stable modification. An equimolecular compound was obtained, melting point 39.9°, just stable at its maximum, and comparatively little dissociated.

(*a*) Solid phase, $C_7H_8O_2$.

% $C_7H_8O_2$..........	100	90.5	79.9	67.2	62.8	58.4	55.2	51.8	50.8
T..................	132.1	126.0	116.5	97.2	87.9	75.0	63.4	46.8	41.0

(*b*) Solid phase, $C_7H_8O_2.CH_2Cl.COOH$.

% $C_7H_8O_2$..........	48.8	47.4	45.0	41.4	38.7	33.8	30.0	..	..
T..................	39.7	39.1	37.7	34.1	29.7	19.1	5.1	..	..

---

[1] Muller, *Z. physik. Chem.*, **86**, 196 (1914).

[2] Pickering, *J. Chem. Soc.*, **67**, 664 (1895).

(*c*) Solid phase, $CH_2Cl.COOH$.

% $C_7H_8O_2$	27.4	23.0	17.5	9.5	0	0	0	..	..
T	14.4	27.5	41.6	53.9	61.3	56.2	50.2	..	..

4. *Dichloroacetic Acid.*—The point of fusion of this acid is still given in all books of reference as —4°, although the value +10.8° was found by Pickering.[1] The Kahlbaum sample employed gave considerable difficulty owing to persistent supercooling, but finally two freezing points were obtained:

(*a*) +9.7° (by rapid cooling with ether—carbon dioxide). Attempts at further purification of the acid did not raise this point of fusion at all.

(*b*) —4.1° (by supercooling to —10° and long stirring). Hence it appears that the acid exists in two crystalline modifications. With dimethylpyrone the compound $C_7H_8O_2.CHCl_2.COOH$ was obtained, m. p., 22.9°, just stable at its maximum. It is possible that a second compound exists but was not isolated (the curve could not be completed between 31.4–20.0% $C_7H_8O_2$, owing to the mixture supercooling to a stiff glass without crystallization).

(*a*) Solid phase, $C_7H_8O_2$.

% $C_7H_8O_2$	100	85.9	75.5	69.0	63.6	59.8	56.4	54.1	51.5
T	132.1	124.0	111.0	99.1	85.3	72.5	56.6	43.2	26.0

(*b*) Solid phase, $C_7H_8O_2.CHCl_2.COOH$.

% $C_7H_8O_2$	50.1	47.2	43.3	40.2	35.1	31.4	..	..	..
T	22.9	21.7	17.1	11.1	—4.1	—21.2	..	..	..

(*c*) Solid phase, $CHCl_2.COOH$.

% $C_7H_8O_2$	20.0	14.1	8.1	0	0	..	..	..	..
T	—23.8	—9.0	0.8	9.7	—4.1	..	..	..	..

5. *Trichloroacetic Acid.*—The freezing point diagram is given on page 1224 (Fig. 1). Two compounds are obtained, $C_7H_8O_2.CCl_3.COOH$ (m. p. 44.8°) and $C_7H_8O_2.2CCl_3.COOH$ (m. p. 66.8°), both evidently quite stable and very little dissociated. Mixtures containing more than 60% $C_7H_8O_2$ decompose very rapidly at their melting points, with evolution of carbon dioxide, hence this part of the curve must be regarded as only approximate.

(*a*) Solid phase, $C_7H_8O_2$.

% $C_7H_8O_2$	100	85.0	71.4	66.1	61.1	57.6	55.5	..	..	..	..
T	132.1	124.5	110.0	99.2	83.8	67.1	52.9	..	..	..	..

(*b*) Solid phase, $C_7H_8O_2.CCl_3.COOH$.

% $C_7H_8O_2$	52.7	49.9	47.6	45.4	..	..	..	..	..	..	..
T	43.0	44.8	44.0	41.4	..	..	..	..	..	..	..

(*c*) Solid phase, $C_7H_8O_2.2CCl_3.COOH$.

% $C_7H_8O_2$	45.4	43.2	41.0	36.9	35.5	33.8	32.0	29.5	27.1	23.6	19.7
T	36.4	46.9	54.6	63.8	65.6	66.7	66.1	63.0	58.1	49.3	33.6

(*d*) Solid phase, $CCl_3.COOH$.

% $C_7H_8O_2$	19.0	16.5	12.9	7.5	0	..	..	..	..	..	..
T	12.5	28.1	41.0	51.5	57.2	..	..	..	..	..	..

---

[1] *Loc. cit.*

6. *Trichlorobutyric Acid.*—The curve obtained is very similar to that given by trichloroacetic acid above. Two compounds, $C_7H_8O_2.CH_3.$-$CHCl.CCl_2.COOH$ and $C_7H_8O_2.2CH_3.CHCl.CCl_2.COOH$ were obtained, melting at 56.2° and 33.8°, respectively. Mixtures containing excess of $C_7H_8O_2$ decompose slowly at their temperature of fusion, with evolution of carbon dioxide. The pure acid was obtained from a Kahlbaum sample by recrystallizations from ligroin.

(*a*) Solid phase, $C_7H_8O_2$.

% $C_7H_8O_2$	100	89.8	81.6	73.2	67.1	64.8	61.5	58.2
T	132.1	127.0	121.0	110.2	98.0	91.8	82.1	66.5

(*b*) Solid phase, $C_7H_8O_2.C_3H_4Cl_3.COOH$.

% $C_7H_8O_2$	54.4	50.4	46.1	41.2	38.8	36.8	36.6	..
T	53.4	56.1	53.8	47.8	42.5	35.2	35.1	..

(*c*) Solid phase, $C_7H_8O_2.2C_3H_4.Cl_3.COOH$.

% $C_7H_8O_2$	34.3	32.7	30.5	27.6	23.4	..	..	..
T	33.5	33.7	33.0	30.2	25.0	..	..	..

(*d*) Solid phase, $C_3H_4Cl_3.COOH$.

% $C_7H_8O_2$	28.1	24.9	20.4	17.3	13.1	7.5	0	..
T	—7.2	9.7	27.1	37.1	45.9	53.0	57.9	..

7. *Trichlorolactic Acid.*—An equimolecular compound $C_7H_8O_2.CCl_3.$-$CHOH.COOH$ (m. p. 54.5°) was obtained.

(*a*) Solid phase, $C_7H_8O_2$.

% $C_7H_8O_2$	100	90.0	77.7	69.2	65.0	62.2	...	...
T	132.1	126.5	113.0	92.9	77.1	65.1	...	...

(*b*) Solid phase, $C_7H_8O_2.CCl_3.CHOH.COOH$.

% $C_7H_8O_2$	58.5	55.3	50.5	44.9	41.8	39.3	36.8	33.9
T	49.5	52.7	54.4	52.6	49.8	46.9	43.6	38.5

(*c*) Solid phase, $CCl_3.CHOH.COOH$.

% $C_7H_8O_2$	33.9	30.0	26.8	22.0	17.0	10.1	0	...
T	21.2	43.2	59.3	83.0	95.4	106.6	113.8	...

8. *β-Iodopropionic Acid.*—Here no compound was isolated, but, from the form of the curves, it is evident that combination in the mixture has occurred. (The freezing point of each component is abnormally lowered by addition of the other; contrast with *o*-nitrophenol, page 1237.) It is possible that the melting point of the compound is so low that its curve never enters the stable region (compare *o*-toluic acid, page 1232; it is more likely, however, that supercooling persisted, preventing the isolation of the compound as the solid phase.

(*a*) Solid phase, $C_7H_8O_2$.

% $C_7H_8O_2$	100	85.0	75.7	65.0	57.2	50.3	44.4	..
T	132.1	123.5	108.0	87.4	67.2	44.0	18.4	..

(*b*) Solid phase, $CH_2I.CH_2.COOH$.

% $C_7H_8O_2$	41.2	37.8	31.6	27.3	23.8	20.5	11.7	0
T	8.9	18.8	35.4	45.1	52.2	58.4	70.9	81.2

9. Crotonic Acid.—An equimolecular compound, $C_7H_8O_2.CH_3.CH:CH.COOH$ is obtained; m. p. 52.2° (by extrapolation). The compound is unstable at its maximum, and crystallizes only from solutions containing excess of acid.

(*a*) Solid phase, $C_7H_8O_2$.

% $C_7H_8O_2$	100	87.6	76.1	62.8	54.6	49.9	45.4
T	132.1	125.5	116.5	100.7	86.0	75.2	62.3

(*b*) Solid phase, $C_7H_8O_2.C_3H_5.COOH$.

% $C_7H_8O_2$	41.0	36.8	32.8	28.7	..	..	..
T	50.0	47.5	44.1	39.2	..	..	..

(*c*) Solid phase, $C_3H_5.COOH$.

% $C_7H_8O_2$	21.3	15.8	9.0	0	..	..	..
T	49.4	56.7	63.6	71.0	..	..	..

10. α-Chlorocrotonic Acid.—The compound $C_7H_8O_2.CH_3.CH:CCl.COOH$ was obtained; m. p. 45.8°.

(*a*) Solid phase, $C_7H_8O_2$.

% $C_7H_8O_2$	100	89.5	78.6	68.2	62.8	59.0	54.1	51.2	..	..
T	132.1	125.5	115.0	100.1	89.6	78.5	60.8	46.5	..	..

(*b*) Solid phase, $C_7H_8O_2.C_3H_4Cl.COOH$.

% $C_7H_8O_2$	49.5	46.7	43.3	40.7	38.0	37.6	..	..	..	..
T	45.7	45.1	43.9	41.7	38.5	38.0	..	..	..	..

(*c*) Solid phase, $C_3H_4Cl.COOH$.

% $C_7H_8O_2$	38.0	35.6	35.3	34.5	31.8	28.3	25.9	19.0	10.4	0
T	39.0	46.3	47.4	49.9	57.3	65.4	71.1	82.8	92.9	99.0

11. Benzoic Acid.—The compound $C_7H_8O_2.C_6H_5.COOH$ was obtained, melting at 50.5°, and only just stable at its maximum.

(*a*) Solid phase, $C_7H_8O_2$.

% $C_7H_8O_2$	100	89.5	81.1	74.2	68.5	63.5	58.9	55.9	53.0	50.5	50.0
T	132.1	127.0	120.0	111.5	102.4	93.1	82.6	74.2	63.8	53.5	50.5

(*b*) Solid phase, $C_7H_8O_2.C_6H_5.COOH$.

% $C_7H_8O_2$	50.0	49.4	47.4	45.9	43.8	...	...	...	...	..	..
T	50.5	50.5	50.2	49.6	48.5	...	...	...	...	..	..

(*c*) Solid phase, $C_6H_5.COOH$.

% $C_7H_8O_2$	41.3	37.9	34.7	30.9	25.3	18.1	9.5	0	..	..	..
T	54.8	66.8	76.7	85.6	95.2	105.2	113.6	120.8	..	..	..

12. o-Toluic Acid.—The compound $C_7H_8O_2.C_7H_7.COOH$ was obtained, m. p. 48.0° (by extrapolation). The compound is unstable at its maximum; its total range of stability, from the freezing point diagram, extends only through 2% of the concentration range.

(*a*) Solid phase, $C_7H_8O_2$.

% $C_7H_8O_2$	100	90.1	80.5	70.2	64.9	60.5	55.7	51.1	48.3	45.1	44.9
T	132.1	126.0	117.5	104.0	94.9	86.1	74.6	62.0	53.4	43.6	43.0

(*b*) Solid phase, $C_7H_8O_2.C_7H_7.COOH$.

% $C_7H_8O_2$.......	45.2	44.3	43.8	...	..	..	..	..	..	...	..
T..............	47.2	46.6	46.2	...	..	..	..	..	..	...	..

(*c*) Solid phase, $C_7H_7.COOH$.

% $C_7H_8O_2$.......	44.9	43.8	42.2	40.1	35.4	29.6	20.7	10.5	0	...	..
T..............	43.0	46.2	50.4	55.7	66.0	77.2	89.3	97.8	103.4	...	..

13. m-Toluic Acid.—The compound $C_7H_8O_2.C_7H_7.COOH$ was obtained, melting at 64.1°. In common with the other compounds derived from the similar acids in 11, 12 and 14, this compound is considerably dissociated in the liquid state, as is shown by the flatness of the maximum.

(*a*) Solid phase, $C_7H_8O_2$.

% $C_7H_8O_2$.......	100	90.0	79.0	68.6	64.4	58.6	54.0
T..............	132.1	126.5	116.0	102.0	94.4	81.0	69.1

(*b*) Solid phase, $C_7H_8O_2.C_7H_7.COOH$.

% $C_7H_8O_2$.......	51.9	49.1	45.3	42.5	40.1	...	..
T..............	63.8	64.0	62.9	61.7	60.5	...	..

(*c*) Solid phase, $C_7H_7.COOH$.

% $C_7H_8O_2$.......	37.5	33.2	26.3	18.6	9.9	0	..
T..............	59.8	70.0	84.8	95.6	103.0	107.6	..

14. p-Toluic Acid.—The compound $C_7H_8O_2.C_7H_7.COOH$ (m. p. 88.0°, by extrapolation) was obtained. This compound is unstable at its maximum, and crystallizes only from solutions containing excess of dimethylpyrone. In this respect it is unique among the unstable compounds here obtained, since all others are crystallized from solutions with excess of acid. The difference is due merely to the very high point of fusion of the *p*-toluic acid. The freezing point curve of the system is given on page 1225, Fig. 2.

(*a*) Solid phase, $C_7H_8O_2$.

% $C_7H_8O_2$.......	100	87.3	79.2	72.6	67.4	63.0	60.1
T..............	132.1	126.5	120.0	112.0	103.1	93.4	86.3

(*b*) Solid phase, $C_7H_8O_2.C_7H_7.COOH$.

% $C_7H_8O_2$.....	59.5	57.2	55.0	53.2	...	...	...
T.............	85.0	86.2	87.1	87.7	...	...	...

(*c*) Solid phase, $C_7H_7.COOH$.

% $C_7H_8O_2$.....	50.6	47.3	41.4	32.1	21.4	10.3	0
T.............	93.2	106.9	124.4	143.2	158.6	170.0	178.5

15. Phenylacetic Acid (α-toluic acid).—The compound $C_7H_8O_2.C_7H_7.COOH$ was obtained; m. p. 24.6° (by extrapolation). The compound is unstable at its maximum.

(*a*) Solid phase, $C_7H_8O_2$.

% $C_7H_8O_2$........	100	88.0	76.3	70.1	64.4	60.0	54.1	48.9	47.0	43.4	40.2
T..............	132.1	125.0	113.0	105.5	94.9	85.1	69.0	51.6	44.2	25.4	5.5

(*b*) Solid phase, $C_7H_8O_2.C_7H_7.COOH$.

% $C_7H_8O_2$	41.1	40.2	38.5	38.0	...	..	..	..	..	..
T	21.7	21.0	19.2	18.7	..	..	..	..	..	..

(*c*) Solid phase, $C_7H_7.COOH$.

% $C_7H_8O_2$	36.0	34.3	30.1	23.6	16.4	8.0	0	..	..	..
T	19.2	25.9	37.8	51.6	62.4	70.8	76.7	..	..	..

16. Salicylic Acid.—The compound $C_7H_8O_2.C_6H_4.OH.COOH$ was obtained, m. p. 71.9°.

(*a*) Solid phase, $C_7H_8O_2$.

% $C_7H_8O_2$	100	90.1	79.3	67.8	63.4	60.4	57.3
T	132.1	128.0	119.5	100.5	89.2	80.1	68.9

(*b*) Solid phase, $C_7H_8O_2.C_6H_4.OH.COOH$.

% $C_7H_8O_2$	56.0	53.5	51.1	49.9	47.5	44.0	...
T	69.1	70.7	71.6	71.9	71.1	68.9	...

(*c*) Solid phase, $C_6H_4.OH.COOH$.

% $C_7H_8O_2$	43.2	39.3	32.7	27.7	17.4	10.1	0
T	70.3	92.1	115.8	127.6	144.2	152.2	158.9

17. o-Nitrobenzoic Acid.—The compound $C_7H_8O_2.C_6H_4.NO_2.COOH$, melting at 72.3°, was obtained.

(*a*) Solid phase, $C_7H_8O_2$.

% $C_7H_8O_2$	100	86.5	75.4	68.6	64.3	60.1
T	132.1	123.0	111.0	98.9	90.1	76.3

(*b*) Solid phase, $C_7H_8O_2.C_6H_4.NO_2.COOH$.

% $C_7H_8O_2$	57.0	52.1	49.9	46.9	43.9	40.8
T	68.9	71.6	72.3	71.6	69.6	66.1

(*c*) Solid phase, $C_6H_4.NO_2.COOH$.

% $C_7H_8O_2$	37.7	34.2	28.6	21.0	11.5	0
T	76.1	90.5	108.4	124.9	137.4	147.0

18. Cinnamic Acid.—The compound $C_7H_8O_2.C_6H_5.CH : CH.COOH$ (m. p. 73.2°) was obtained. The system is represented graphically on page 1224, Fig. 1. It is evident that the compound formed is considerably dissociated in the liquid state.

(*a*) Solid phase, $C_7H_8O_2$.

% $C_7H_8O_2$	100	90.2	81.0	71.9	64.3	60.6	56.9	54.3
T	132.1	126.5	119.5	107.8	95.7	88.4	79.9	72.7

(*b*) Solid phase, $C_7H_8O_2.C_8H_7.COOH$.

% $C_7H_8O_2$	52.0	50.0	48.2	44.6	...	...	...	...
T	73.1	73.2	73.1	72.4	...	...	...	...

(*c*) Solid phase, $C_8H_7.COOH$.

% $C_7H_8O_2$	43.5	40.3	36.3	30.5	24.8	15.9	9.1	0
T	75.0	87.0	97.4	109.0	116.4	126.3	131.8	136.8

19. Hydrocinnamic Acid.—Here no compound was isolated. The freezing point diagram of the system, however, indicates the presence of a compound in the solution (compare β-iodopropionic acid, page 1231).

(*a*) Solid phase, $C_7H_8O_2$.

% $C_7H_8O_2$	100	89.9	80.2	72.3	69.4	66.0	63.0	59.5	56.7	53.1	50.2
T	132.1	126.5	119.0	110.0	105.4	99.5	93.3	86.7	80.1	69.7	60.6
% $C_7H_8O_2$	47.0	43.3	39.9	36.6	...	..	..	..	..	..	..
T	49.7	35.3	22.0	4.8	...	..	..	..	..	..	..

(*b*) Solid phase, $C_8H_9.COOH$.

% $C_7H_8O_2$	33.7	26.7	21.1	15.3	8.6	5.0	0	..	..	..	..
T	5.9	21.1	29.4	35.8	41.0	43.2	45.2	..	..	..	..

20. *Mandelic Acid.*—Two compounds were obtained: $C_7H_8O_2.C_6H_5.CHOH.COOH$ (m. p. 69.3°) and $C_7H_8O_2.2C_6H_5.CHOH.COOH$ (m. p. 74.0°). The solutions of this system exhibit supercooling to a marked degree, consequently it was found possible to follow all the curves into their unstable regions, and to obtain several freezing points for the same mixture, according to the solid phase separating out. Results are shown in diagram form on page 1224, Fig. 1.

(*a*) Solid phase, $C_7H_8O_2$.

% $C_7H_8O_2$	100	88.5	81.0	76.0	72.4	67.5	62.4	58.4	55.9	..	..	..
T	132.1	123.5	116.0	109.7	104.7	94.8	82.0	68.1	66.4	..	..	..

(*b*) Solid phase, $C_7H_8O_2.C_6H_5.CHOH.COOH$.

% $C_7H_8O_2$	56.1	54.6	52.1	50.0	47.3	44.5	42.8	39.3	36.6	..	..	..
T	66.5	67.5	68.9	69.3	68.8	67.2	66.1	62.9	60.0	..	..	..

(*c*) Solid phase, $C_7H_8O_2.2C_6H_5.CHOH.COOH$.

% $C_7H_8O_2$	54.6	50.0	44.5	43.5	41.3	39.3	36.6	34.3	33.3	32.8	32.5	30.5
T	49.0	59.3	67.2	67.9	70.0	71.7	72.7	73.8	74.0	73.7	73.6	73.0

(*d*) Solid phase, $C_6H_5.CHOH.COOH$.

% $C_7H_8O_2$	36.6	32.5	30.5	28.4	25.3	18.8	10.6	0	..	..	..	..
T	61.7	73.6	78.2	82.8	88.6	98.5	108.0	117.0	..	..	..	..

21. *Phenol.*—No addition compounds of dimethylpyrone with phenols have been previously described. On examination, however, it was found that such compounds existed, and were little dissociated in the liquid state, the maxima obtained being usually quite sharp. With phenol itself the compound $C_7H_8O_2.2C_6H_5.OH$ was obtained, with m. p. 36.8°.

(*a*) Solid phase, $C_7H_8O_2$.

% $C_7H_8O_2$	100	89.1	77.5	68.4	60.8	53.7	50.9	48.4	45.4
T	132.1	126.0	116.0	103.5	88.9	69.1	59.3	46.6	32.1

(*b*) Solid phase, $C_7H_8O_2.2C_6H_5OH$.

% $C_7H_8O_2$	43.1	40.4	38.5	35.4	32.6	29.3	24.8	21.2	18.5
T	28.0	32.0	34.1	36.1	36.7	35.6	29.7	22.3	15.6

(*c*) Solid phase, C_6H_5OH.

% $C_7H_8O_2$	13.8	8.4	0	...	..	..	..	..	..
T	16.6	31.3	42.4	...	..	..	..	..	..

22. *o-Cresol.*—Here two addition compounds were obtained: $C_7H_8O_2.C_7H_7.OH$, melting at 54.4°, and $C_7H_8O_2.2C_7H_7.OH$, melting at 50.4°,

both compounds are stable at their maxima. (See diagram, page 1240, Fig. 3.)

(*a*) Solid phase, $C_7H_8O_2$.

% $C_7H_8O_2$	100	89.5	80.0	69.5	61.4	55.2	52.4	..	..
T	132.1	126.5	119.5	105.5	91.1	74.3	64.0	..	..

(*b*) Solid phase, $C_7H_8O_2.C_7H_7OH$.

% $C_7H_8O_2$	49.2	46.6	43.1	39.6	..	..	..	..	..
T	54.3	53.5	51.5	47.2	..	..	..	..	..

(*c*) Solid phase, $C_7H_8O_2.2C_7H_7OH$.

% $C_7H_8O_2$	39.6	36.6	33.4	29.5	24.0	20.6	17.2	15.2	13.9
T	47.2	49.4	50.4	49.2	43.2	37.0	27.5	21.8	16.6

(*d*) Solid phase, C_7H_7OH.

% $C_7H_8O_2$	13.9	11.0	5.5	0	..	..	..	..	..
T	16.6	21.0	26.9	30.3	..	..	..	..	..

23. *m-Cresol.*—The compound $C_7H_8O_2.2C_7H_7.OH$ was obtained; m. p. 25.4°.

(*a*) Solid phase, $C_7H_8O_2$.

% $C_7H_8O_2$	100	85.0	74.4	64.8	58.7	53.6	50.0	45.9	43.9	41.0
T	132.1	123.0	112.0	97.2	84.2	69.8	55.6	35.3	24.7	4.3

(*b*) Solid phase, $C_7H_8O_2.2C_7H_7OH$.

% $C_7H_8O_2$	41.6	38.2	34.7	32.0	28.4	23.0	19.0	14.3	..	..
T	21.3	23.9	25.0	25.3	23.7	17.4	9.5	−5.0	..	..

(*c*) Solid phase, C_7H_7OH.

% $C_7H_8O_2$	9.5	4.8	0	..	..	..	..	..	..	..
T	−1.2	6.1	10.9	..	..	..	..	..	..	..

24. *p-Cresol.*—Two compounds were obtained: $C_7H_8O_2.C_7H_7.OH$ (m. p. 29.5°, by extrapolation) and $C_7H_8O_2.2C_7H_7OH$ (m. p. 20.3°). The former compound is unstable at its maximum point. The form of the curve indicates strongly the presence of a third compound of the formula $C_7H_8O_2.4C_7H_7.OH$, but it was not found possible to isolate a compound of the composition, since the mixture of this composition supercools to a hard, glassy mass, and no freezing point can be obtained.

(*a*) Solid phase, $C_7H_8O_2$.

% $C_7H_8O_2$	100	88.5	77.2	67.6	61.4	54.9	51.0	48.2	44.9
T	132.1	125.5	115.0	102.0	90.2	73.6	59.6	46.6	31.8

(*b*) Solid phase, $C_7H_8O_2.C_7H_7OH$.

% $C_7H_8O_2$	41.5	38.7	37.0	..	..	..	..	..	..
T	25.7	22.4	19.6	..	..	..	..	..	..

(*c*) Solid phase, $C_7H_8O_2.2C_7H_7OH$.

% $C_7H_8O_2$	35.8	33.2	31.6	29.2	25.9	23.3	..	..	..
T	19.6	20.3	19.7	17.5	11.2	1.2	..	..	..

(*d*) Solid phase, C_7H_7OH.

% $C_7H_8O_2$	17.1	13.3	7.1	0	..	..	..	..	..
T	−0.5	14.6	26.6	34.1	..	..	..	..	..

25. *o-Nitrophenol.*—With this system the peculiar result was obtained that, not only could no compound be isolated, but the form of the curve shows conclusively that none exists in solution. The results are shown in graphic form, together with those of the other mononitrophenols, which exhibit quite different behavior, on page 1240, Fig. 3. It is evident that *o*-nitrophenol and dimethylpyrone have no tendency to form addition products; this is perhaps due to the influence of the nitro group in the *o*-position.

(*a*) Solid phase, $C_7H_8O_2$.

% $C_7H_8O_2$	100	90.4	79.7	68.0	61.5	56.1	51.3	46.8	42.2	37.3	32.3	27.5
T	132.1	126.5	119.0	110.4	104.9	98.6	92.9	85.9	77.9	68.3	57.1	45.8

(*b*) Solid phase, $C_6H_4.NO_2.OH$.

% $C_7H_8O_2$	22.7	18.7	13.2	7.6	0	..	..	..	..	..	..	..
T	32.7	35.1	38.2	41.0	44.7	..	..	..	..	..	..	..

26. *m-Nitrophenol.*—The compound $C_7H_8O_2.C_6H_4.NO_2.OH$, melting at 68.8°, was obtained.

(*a*) Solid phase, $C_7H_8O_2$.

% $C_7H_8O_2$	100	90.6	80.7	70.3	65.3	61.0	57.4	..	..
T	132.1	127.0	118.5	104.2	93.8	81.5	67.0	..	..

(*b*) Solid phase, $C_7H_8O_2.C_6H_4.NO_2.OH$.

% $C_7H_8O_2$	53.8	50.8	48.3	45.4	42.1	39.2	36.2	33.0	31.5
T	68.1	68.7	68.4	66.9	63.0	58.8	52.9	45.9	42.6

(*c*) Solid phase, $C_6H_4.NO_2.OH$.

% $C_7H_8O_2$	29.0	25.1	20.4	14.5	8.4	0	..	..	..
T	52.4	63.4	72.9	82.9	89.7	95.3	..	..	..

27. *p-Nitrophenol.*—Two compounds were obtained: $C_7H_8O_2.C_6H_4.NO_2.OH$, melting at 72.3°, and $C_7H_8O_2.2C_6H_4.NO_2.OH$, melting at 58.2°. Both compounds are stable at their maxima.

(*a*) Solid phase, $C_7H_8O_2$.

% $C_7H_8O_2$	100	88.1	77.0	68.8	64.6	60.8	57.8
T	132.1	125.5	114.5	101.3	91.4	80.2	68.3

(*b*) Solid phase, $C_7H_8O_2.C_6H_4.NO_2.OH$.

% $C_7H_8O_2$	57.2	53.5	50.6	47.2	43.8	40.4	37.4
T	68.3	71.3	72.2	70.9	67.2	62.1	56.4

(*c*) Solid phase, $C_7H_8O_2.2C_6H_4.NO_2.OH$.

% $C_7H_8O_2$	37.4	34.3	33.6	32.9	31.6	30.0	...
T	57.0	58.1	58.2	58.1	57.9	57.4	...

(*d*) Solid phase, $C_6H_4.NO_2.OH$.

% $C_7H_8O_2$	30.0	28.2	26.2	22.4	15.5	9.1	...
T	57.4	65.4	72.2	82.2	96.6	105.2	113.8

28. *2,4-Dinitrophenol.*—The compound $C_7H_8O_2.C_6H_3.(NO_2)_2.OH$ was obtained; m. p. 78.4°.

(*a*) Solid phase, $C_7H_8O_2$.

% $C_7H_8O_2$	100	89.4	80.1	69.9	63.9	58.2	...
T	132.1	126.0	118.0	105.6	95.2	83.2	...

(b) Solid phase, $C_7H_8O_2.C_6H_3.(NO_2)_2.OH$.

% $C_7H_8O_2$	55.2	51.8	48.1	45.0	41.8	...
T	77.5	78.3	78.1	77.5	75.8	...

(c) Solid phase, $C_6H_3.(NO_2)_2.OH$.

% $C_7H_8O_2$	37.7	34.8	31.9	25.1	17.1	9.3	0
T	75.0	81.1	86.3	95.1	102.9	109.0	114.0

29. *Picric Acid.*—The compound $C_7H_8O_2.C_6H_2(NO_2)_3.OH$ was obtained; point of fusion, 100.8°.

(a) Solid phase, $C_7H_8O_2$.

% $C_7H_8O_2$	100	88.0	78.7	74.4	70.6	67.5	...	...	...	..	..	..
T	132.1	124.0	111.2	101.1	90.0	83.5	...	...	...	..	..	..

(b) Solid phase, $C_7H_8O_2.C_6H_4.(NO_2)_3.OH$.

% $C_7H_8O_2$	66.7	65.2	63.8	61.9	59.5	55.7	52.6	50.0	47.7	43.6	38.4	34.1
T	81.9	86.7	89.5	92.9	96.1	98.9	100.2	100.8	100.4	98.8	94.9	87.6

(c) Solid phase, $C_6H_2.(NO_2)_3.OH$.

% $C_7H_8O_2$	30.0	26.1	22.4	15.5	9.6	0	...	...	...	..	..	..
T	87.5	92.4	97.4	104.8	110.6	118.4	...	...	...	..	..	..

30. *Trinitrotoluene.*—The pseudo-acid trinitrotoluene was examined with dimethylpyrone, but no indication of compound formation could be observed. The curve resembles that of *o*-nitrophenol.

(a) Solid phase, $C_7H_8O_2$.

% $C_7H_8O_2$	100	86.3	75.3	65.0	57.2	51.1	46.1	41.0	35.4
T	132.1	124.5	115.5	105.3	97.5	90.3	84.0	77.6	70.2

(b) Solid phase, $C_7H_5.(NO_2)_3$.

% $C_7H_8O_2$	29.1	24.1	15.6	7.8	0	..	..	..	..
T	64.2	67.4	72.4	76.7	80.7	..	..	..	..

31. *α-Naphthol.*—Interesting results were obtained with the naphthols; the freezing point diagrams are given on page 1225, Fig. 2. α-Naphthol gives two compounds with dimethylpyrone: $C_7H_8O_2.C_{10}H_7.OH$ (m. p. 69.8°, by extrapolation), and $2C_7H_8O_2.3C_{10}H_7.OH$ (m. p. 79.1°). The former is unstable at its maximum.

(a) Solid phase, $C_7H_8O_2$.

% $C_7H_8O_2$	100	89.0	77.7	68.8	60.5	56.9	..	..
T	132.1	126.0	116.5	103.6	85.2	73.0	..	..

(b) Solid phase, $C_7H_8O_2.C_{10}H_7OH$.

% $C_7H_8O_2$	54.1	53.0	51.5	..	..	..	..	..
T	65.6	67.8	69.3	..	..	..	..	..

(c) Solid phase, $2C_7H_8O_2.3C_{10}H_7.OH$.

% $C_7H_8O_2$	50.0	48.8	47.3	45.3	42.7	40.6	38.8	37.3
T	70.5	73.2	75.6	77.4	78.3	79.0	78.8	78.4
% $C_7H_8O_2$	35.8	34.4	32.0	29.8	27.9	25.0	..	..
T	77.6	76.8	73.8	69.7	65.9	56.6	..	..

(d) Solid phase, $C_{10}H_7.OH$.

% $C_7H_8O_2$	23.4	20.7	17.7	12.0	6.2	0	..	..
T	56.0	65.7	73.8	84.2	90.7	96.1	..	..

32. β-Naphthol.—Two compounds were obtained: $2C_7H_8O_2.3C_{10}H_7.OH$ (m. p. 39.5°) and $C_7H_8O_2.2C_{10}H_7OH$ (m. p. 44.6°). The former compound is unstable at its maximum point, but, owing to the readiness with which solutions of this system exhibited persistent supercooling, it was found possible to carry the curve some distance into its unstable region. (See diagram, page 1225, Fig. 2.)

(*a*) Solid phase, $C_7H_8O_2$.

% $C_7H_8O_2$...	100	87.6	76.3	66.6	61.6	57.2	55.4	52.1	49.3	46.5
T..........	132.1	126.0	114.5	99.5	87.1	74.5	68.2	54.9	40.7	24.3

(*b*) Solid phase, $2C_7H_8O_2.3C_{10}H_7OH$.

% $C_7H_8O_2$...	46.5	44.7	43.8	42.2	40.6	37.3	35.0	..	..	..
T..........	36.6	38.0	38.4	39.0	39.4	38.8	37.4	..	..	..

(*c*) Solid phase, $C_7H_8O_2.2C_{10}H_7OH$.

% $C_7H_8O_2$...	43.8	40.2	38.1	35.9	33.6	33.0	...	..	..	..
T..........	34.4	40.3	42.5	43.9	44.5	44.6	...	..	..	..

(*d*) Solid phase, $C_{10}H_7OH$.

% $C_7H_8O_2$...	30.2	27.3	25.1	21.4	14.1	9.6	0	..	..	..
T..........	54.5	70.6	79.9	92.0	107.9	113.8	121.6	..	..	..

Consideration of Results.

Thirty-two organic substances of acidic nature have been examined with dimethylpyrone, and the existence of thirty-seven addition compounds has been indicated by the freezing point curve. These compounds may be divided into three classes:

(*a*) 24 of the general type $C_7H_8O_2.HX$.
(*b*) 3 of the general type $2C_7H_8O_2.3HX$.
(*c*) 10 of the general type $C_7H_8O_2.2HX$.

No instances of the formation of compounds containing excess of dimethylpyrone, or of mixed crystals, were observed.

The addition compounds exhibited, in general, beautiful crystalline structure, either in the form of needles radiating from a common center, star-clusters, or lustrous plates. Consequently, in practically all of the systems examined, it was extremely easy to identify changes in the solid phase.

The melting points of the compounds are usually much below those of their components. The few exceptions are to be found in those cases where the melting point of one component is also very low.

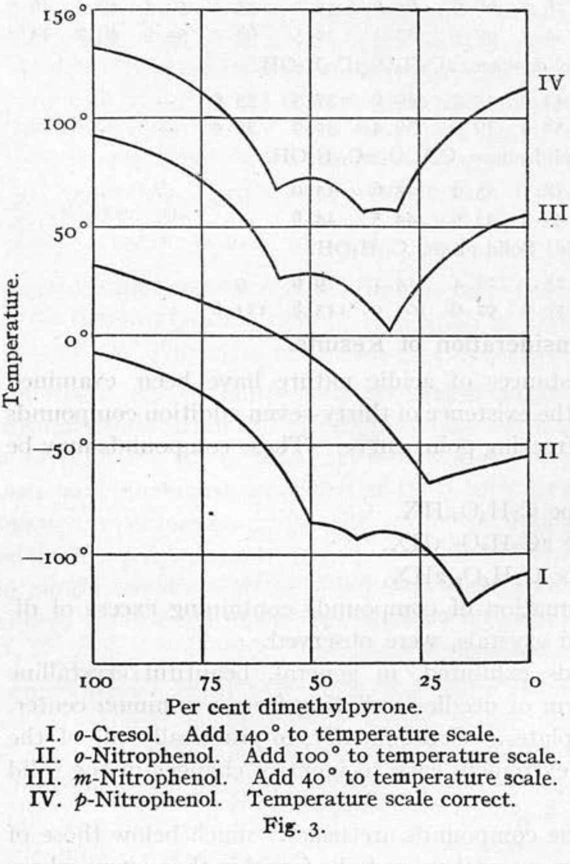
It is interesting to compare the difference in behavior of isomeric substances examined. As examples the following may be noted:

I. o-Toluic Acid.—The compound $C_7H_8O_2.C_7H_7.COOH$ crystallizes only from solutions containing excess of acid. *m-Toluic acid.* The compound formed is stable at its maximum. *p-Toluic acid.* The compound crystallizes only from solutions containing an excess of dimethylpyrone.

II. o-Nitrophenol.—No compound is formed. *m-Nitrophenol.* The compound $C_7H_8O_2.C_6H_4.NO_2OH$ is formed. *p-Nitrophenol.* Two compounds: $C_7H_8O_2.C_6H_4NO_2.OH$ and $C_7H_8O_2.2C_6H_4NO_2.OH$ are formed.

III. α-Naphthol.—The compounds $C_7H_8O_2.C_{10}H_7OH$ and $2C_7H_8O_2.3C_{10}H_7OH$ are formed. *β-Naphthol.* The compounds $2C_7H_8O_2.3C_{10}H_7OH$ and $C_7H_8O_2.2C_{10}H_7OH$ are obtained.

Particular attention is due to those compounds isolated, which are unstable at their maximum. These cannot be obtained at all by the simple method of mixing the components in the required proportions. The freezing point curve gives, however, all the necessary data for the preparation of such a compound. For example, dimethylpyrone acetate, which Collie and Tickle failed to isolate, may readily be obtained as follows (see diagram, page 1225, Fig. 2): A mixture of 35% dimethylpyrone and 65% acetic acid (molecular percentages) is taken. This melts at 24°, and, on cooling, the solid phase separating out is the equimolecular compound. The best yield may be obtained by cooling to 0°, filtering off the remaining liquid, and drying the crystals with filter paper. The compound thus obtained melts at 30°, at the same time decomposing into its components and depositing dimethylpyrone.



I. *o*-Cresol. Add 140° to temperature scale.
II. *o*-Nitrophenol. Add 100° to temperature scale.
III. *m*-Nitrophenol. Add 40° to temperature scale.
IV. *p*-Nitrophenol. Temperature scale correct.

Fig. 3.

The addition compounds obtained are always more or less dissociated into their components in the liquid state. For the acids examined, the rule holds, in general, that the extent of dissociation is greater, the weaker the acid is. The degree of dissociation may be approximately determined by the sharpness of the maximum, *i. e.*, the decrease in the temperature of fusion of the compound on addition of either component. If dissociation is slight the decrease is rapid, with more highly dissociated compounds the decrease is small and may even (in extreme cases) be converted into an increase.[1]

The following table shows the decrease in the temperature of fusion of the equimolecular compounds of dimethylpyrone and acid, due to the addition of 5% of acid, for all cases where data are available from the results given above. The dissociation constants of the acids[2] are included for comparison.

Acid.	T(50% $C_7H_8O_2$)—T(45% $C_6H_8O_2$).	100 K.
Chloroacetic	2.2°	0.155
Dichloroacetic	3.2	5.14
Trichloroacetic	4.3	121.0
Trichlorobutyric	3.5	10.0
Trichlorolactic	1.8	0.465
α-Chlorocrotonic	1.3	0.072
Benzoic	1.2	0.0060
m-Toluic	1.2	0.00514
Salicylic	2.1	0.102
o-Nitrobenzoic	1.8	0.616
Cinnamic	0.6	0.00355
Mandelic	1.6	0.0417

The connection between the degree of dissociation of the compound and the strength of the acid is made quite evident from the above figures; the two extreme cases (trichloroacetic and cinnamic acids) are illustrated in the diagram on page 1224, Fig. 1. The relation is important, but can, however, only be approximate, since for the acidic strengths we should compare values, not in aqueous solution, but in dimethylpyrone.[3] The dissociation of the compounds is also compared at their various points of fusion, whereas the temperature factor is important in regard to the degree of dissociation of addition compounds.[4]

The tendency to form addition products is greatest at low temperatures; this is well illustrated in the case of hydrates. The effect of temperature is best seen, in the results of the present investigation, in the compounds formed from phenol and its derivatives. These are little dissociated into their components in spite of the weak acidic nature of the substances employed, owing, in general, to their low temperatures of fusion. Temperature seems, indeed, to be more important here than acidic strength, thus (to compare the stable 50% compounds) the compound of *o*-cresol is less

---

[1] Kremann, *Monats.*, **25**, 1222 (1904).

[2] Ostwald, *Z. physik. Chem.*, **3**, 418 (1889).

[3] The researches of Walden indicate that the general order of acidic strengths in two solvents will be the same, although exceptions are to be found. That dimethylpyrone is a good ionizing medium has been shown by Poma, *Gazz. chim. ital.*, **41**, II, 518 (1911).

[4] The heat of fusion of the compound, which will vary in different cases, is also to be considered.

dissociated than that of dinitrophenol, or even than that of picric acid, both of which have considerably higher melting points.

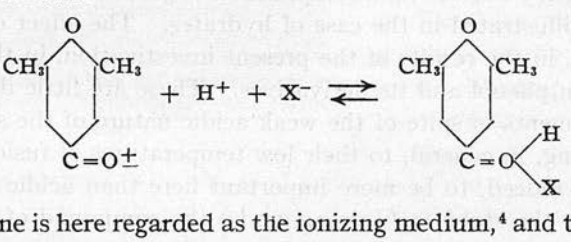
Constitution of Dimethylpyrone and its Addition Compounds.—It remains to discuss the bearing of the results obtained on the several hypotheses as to the constitution of dimethylpyrone and its addition products, considered in the introduction.

The difficulty of representing the structural formulae of compounds, more complex than equimolecular, except under the scheme (I), has already been mentioned. The thirteen compounds of the general types $2C_7H_8O_2.3HX$ and $C_7H_8O_2.2HX$, obtained in the research, cannot be accounted for by (II) or (III), but may readily be expressed structurally according to (I).

The mixture acid-dimethylpyrone was, in every system studied, colored. The color varied from pale yellow (with weak acids) to dark red (with strong acids). In this connection the view of Vorländer and Mumme,[1] that the change of color is due to a change in the degree of saturation of one or more elements composing the substances, is of importance.

A further point to be noticed is that the reaction between dimethylpyrone and acids is instantaneous. In no case could it be observed that the freezing point of a mixture changed at all with time; equimolecular mixtures gave the same point of fusion immediately after preparation as after several days. Similarly Baeyer and Villiger,[2] who first stated that time was necessary for the formation of dimethylpyrone hydrochloride, subsequently[3] withdrew this statement. Now, an organic reaction of the type (II), involving the breaking up of the simple acid molecule as well as of the carbonyl oxygen linkage, would probably be a time reaction. On the other hand, ionic reactions are *essentially* instantaneous.

We may consider the formation of the addition product $C_7H_8O_2.HX$ as proceeding as follows:



(IV)

Dimethylpyrone is here regarded as the ionizing medium,[4] and the carbonyl oxygen as primarily active. Formation of the more complex compounds involves the activity of the second oxygen atom.

---

[1] *Ber.*, **36**, 1470 (1903).

[2] *Ibid.*, **34**, 2679 (1901).

[3] *Ibid.*, **35**, 3612 (1902).

[4] The fact that dimethylpyrone is a good ionizing medium is also an indication of its unsaturated character. See Stieglitz, "Qualitative Chemical Analysis," Part I, **1912**, p. 64, and Kendall, THIS JOURNAL, **36**, 1069 (1914).

This view is supported by the fact that the equilibrium point of the above reversible reaction (*i. e.*, the extent of dissociation of the addition compound formed into its components) is a function of the acidic strength, as has been demonstrated above. The stronger the acid is, the more completely does the reaction from left to right proceed. In agreement with this, also, is the extent of color change on mixing the components; for example, cinnamic acid with dimethylpyrone gives the faintest tinge of yellow, while trichloroacetic acid gives a dark red solution.

The results of this investigation point, therefore, in favor of the assumption that the addition compounds of dimethylpyrone with acids are true oxonium salts, in which oxygen functions as a quadrivalent atom. The equilibrium of the reaction is best represented as in (IV) above.

In conclusion, the advantages of the method followed above, for the general study of addition reactions, may be pointed out. Its first advantage is its rapidity; after the technique has been mastered, a system presenting no special difficulties can easily be completed in two days. Secondly, it indicates *all* compounds formed between the components chosen, including such compounds as are not stable at their maxima and cannot be obtained by the ordinary methods. In few cases is a special analysis of the solid phase necessary, the composition of the compounds obtained is read directly from the freezing point curve.[1] It is possible that sometimes a compound cannot be isolated owing to supercooling; however, its existence may be recognized by the form of the curves. Finally the curves indicate also the degree of dissociation of the compounds into their simple components.

The method is being extended to other similar systems. It is hoped, also, that further evidence as to the nature of these reactions will be obtained from conductivity measurements.

Summary.

The freezing point curves of monobasic organic acids and phenols with dimethylpyrone have been examined. The existence of a large number of addition compounds has been demonstrated.

A consideration of the results obtained leads to the view that the reaction is ionic, and that the compounds formed are true oxonium salts.

NICHOLS LABORATORIES OF INORGANIC CHEMISTRY,
COLUMBIA UNIVERSITY,
NEW YORK CITY.

---

[1] Cases of "solid solutions" may be recognized by the fact that any maximum on the freezing point curve will not be (except by chance) at a point of simple molecular composition.

[Reprinted from the Journal of the American Chemical Society
Vol. XXXVI, No. 8. August, 1914.]

The Heat of Vaporization of Normal Liquids

By James Kendall

[Reprinted from the Journal of the American Chemical Society
Vol. XXXVI, No. 8 August, 1914.]

[CONTRIBUTIONS OF THE DEPARTMENT OF CHEMISTRY OF COLUMBIA UNIVERSITY,
No. 239.]

THE HEAT OF VAPORIZATION OF NORMAL LIQUIDS.

BY JAMES KENDALL.

Received May 25, 1914.

The theoretical study of the heat of vaporization of liquids—a branch of physical chemistry long neglected—has recently attracted a great deal of investigation. The subject is of interest from its connection with the equation of van der Waals and the problem of molecular attraction. A number of formulas for representing variation of heat of vaporization with temperature have lately been put forward; some of these claim a theoretical basis, some are admittedly empirical. During the past year, in particular, the rate of appearance of new formulas has increased to the proportions of an epidemic.

It has seemed of importance, therefore, to the author, in view of previous work upon the subject, to make a critical examination of the various equations that have been proposed. Their relative theoretical merits —a field already fruitful in polemics—are not touched upon at all in this paper. The sole point of investigation is agreement with the experimental data. In the present imperfect state of our knowledge of this subject, where even first principles are hotly disputed, it appears reasonable to apply to all equations the one practical test, free from any possible bias—the test of accuracy.

It is true that we possess no direct determinations of heats of vaporization for any normal liquid, throughout an extended temperature range, sufficiently trustworthy to be of value for the above purpose. However, the thermodynamical equation of Clausius and Clapeyron (see Equation 1 below) affords a method of obtaining the heat of vaporization indirectly by the measurement of other quantities. These quantities are all accurately determined for a large number of liquids and through a wide range of temperature in the extensive researches of Young and his collaborators.

The results of Young have recently been revised and published in collected form.[1] The necessary data are now available for thirty pure liquids, of which twenty-six are normal or non-associated.

It is impossible, from space considerations, to examine all of those in the present paper; consequently, a few typical cases have been selected. The agreement of the various formulas with the experimental results for octane, methyl, butyrate, carbon tetrachloride and fluorobenzene is tested in the tables given below.

The above liquids were chosen, without previous knowledge as to the nature of the results they would supply, for the following reasons. It is important, in testing any function which varies with temperature, to be able to consider as large a temperature range as possible. Hence octane was selected from the ten hydrocarbons investigated by Young, since it possesses the highest critical temperature. (The lowest temperature for which data are available is 0° in all cases.) Methyl butyrate was chosen as the typical example of the ten esters studied, for the same reason. The remaining liquids—carbon tetrachloride and fluorobenzene— are among those regarded by investigators as "characteristically" normal liquids;[2] both have, also, high critical temperatures. That the data selected are really representative may be confirmed by a study of the collected tables.[3]

---

[1] Young, *Proc. Roy. Soc. Dublin*, **12**, 374 (1910).

[2] Applebey and Chapman, *J. Chem. Soc.*, **105**, 742 (1914).

[3] Mills, THIS JOURNAL, **31**, 1099 (1909).

The equations examined are developed briefly below: The following notation is employed.

T—absolute temperature
t—temperature centigrade
V—volume of one gram of saturated vapor.
d—density of liquid
D—density of saturated vapor
P_c—critical pressure
M—molecular weight
R—constant of gas equation, $PV = RT$, equal, under the units employed, to $62340/M$
T_c—critical temperature
v—volume of one gram of liquid
d_c—critical density
P—vapor pressure in mm. of mercury
L—total heat of vaporization[1] of one gram of liquid, expressed in calories

With this notation, the thermodynamical equation is expressed as follows:

$$L = 0.0_{4}31833\ (dP/dT)T.\ (V - v) \qquad (1)$$

(The numerical factor is the reciprocal of the value of the mechanical equivalent of heat under the units stated.) The heat of vaporization at any temperature is thus obtained in terms of T, V, v and dP/dT, and the degree of accuracy of the calculated value will depend upon the limits of experimental error in the determination of these quantities, and upon the relative effect of such errors in the calculation of the equation. These points have been carefully examined by Mills.[2] The conclusion drawn is that, except at zero centigrade and in the neighborhood of the critical temperature, the calculated values for the heat of vaporization are substantially true. At 0° C. the values derived are usually too high; near T_c the difficulty in the exact determination of dP/dT renders the results somewhat uncertain. The above equation may, therefore, be safely employed as a basis for comparison throughout the greater part of the experimental range, small divergences at 0° C. and near T_c being disregarded.

A simple formula developed by Mills:[3]

$$L = 0.0_{4}31833\ P\ (V - v) + \mu'(\sqrt[3]{d} - \sqrt[3]{D}) \qquad (2)$$

(μ' is a constant varying with the liquid under consideration) has been thoroughly tested by him, and found to be in excellent agreement throughout with the thermodynamical equation for all normal liquids. For its theoretical significance reference must be made to the original papers.

A third formula, proposed by Dieterici:[4]

$$L = 0.0_{4}31833\ P\ (V - v) - 4.577\ c\ (T/M) \log (d/D) \qquad (3)$$

(c is a constant varying with the liquid) has also been examined by Mills.[2] It is found to be consistently inaccurate at low temperatures, although

---

[1] Internal + external, at constant temperature T.

[2] Mills, *Loc. cit.*

[3] Mills, *J. Phys. Chem.*, **6**, 209 (1902); **8**, 383 and 593 (1904); **9**, 402 (1905); **10**, 1 (1906); **11**, 132 and 594 (1907); **13**, 512 (1909); **15**, 417 (1911); **18**, 101 (1914).

[4] Dieterici, *Ann. Physik*, **25**, 569 (1908).

the agreement at higher temperatures is remarkably good. A similar equation was previously suggested by Crompton.[1]

Kleeman[2] has deduced mathematically, from assumptions regarding molecular attraction, the equation:

$$L = 0.0_431833\,P\,(V - v) - K\,(d^2 - D^2) \qquad (4)$$

(K is a constant varying with the liquid.) The same equation has also been put forward by Batschinski.[3]

The present author[4] has shown that the following simple relation holds:

$$L = k(T_c - T)^n \qquad (5)$$

(k is a constant varying with the liquid, n is for all normal liquids equal to 0.386.) Later investigation showed that the above is an interpolation formula, and is dependent upon the two equations:

$$\sqrt[3]{d} - \sqrt[3]{d_c} = k_1(T_c - T)^{1/3}$$
$$\sqrt[3]{d_c} - \sqrt[3]{D} = k_2(T_c - T)^{1/2}$$

which were demonstrated to hold satisfactorily for normal liquids. By combining these equations with that of Mills (Equation 2 above), we obtain:

$$K = 0.0_431833\,P\,(V - v) + k_1\mu'(T_c - T)^{1/3} + k_2\mu'(T_c - T)^{1/2} \qquad (5a)$$

This is the more correct expanded form of Equation 5 above. The first part of the equation represents the external heat of vaporization, which is variable in magnitude, but at most temperatures is comparatively small; the exponent $n = 0.386$ in Equation 5 is, consequently, intermediate between the two simple values (one-third and one-half) in Equation 5*a*. For associated liquids the equation still holds if the value of n is modified.[5]

Tyrer[6] has recently proposed a somewhat similar formula:

$$L = 0.0_431833\,P\,(V - v) + C(T_c - T)^{1/3}/(d^{1/3} + D^{1/3}) \qquad (6)$$

C is a constant varying with the liquid under examination.

Applebey and Chapman[7] have deduced the relation:

$$L = RT\log_e(V - b)/(v - b) + RT^2[1/(v - b) + 1/(V - b)]\,db/dT \qquad (7)$$

---

[1] Crompton, *Proc. Chem. Soc.*, **17**, 61 (1901).

[2] Kleeman, *Phil. Mag.*, [6] **20**, 665 (1910). A somewhat different formula was advanced in a previous paper, *Phil. Mag.*, [6] **19**, 795 (1910).

[3] Batschinski, *Ann. Physik*, **14**, 288 (1904).

[4] Kendall, *Meddel. från K. Vet-Akads. Nobelinstitut*, Band **2**, No. 29 (1912); "The Properties of Liquids as Functions of the Critical Constants." Since this paper is not generally available, the significance of the equation is briefly indicated above.

[5] Kendall, *Meddel. från K. Vet-Akads. Nobelinstitut*, Band **2**, No. 36 (1913); "The Heat of Vaporization of Associated Liquids."

[6] Tyrer, *J. Phys. Chem.*, **17**, 717 (1913).

[7] Applebey and Chapman, *J. Chem. Soc.*, **105**, 734 (1914). The equation, in the original paper, is referred to molecular volumes. These are here changed to V and v (volume of 1 g.). The constant b in 7 is consequently the usual van der Waals' constant divided by M (mol. wt.). The same holds for equation 10.

in which b (the constant of van der Waals' equation) is assumed to vary linearly with the temperature. Methods for the determination of b_c (the value of b at the critical temperature) and db/dT are developed; when these quantities are known, L can be evaluated.

Rodzewitz[1] has recently put forward the equation:

$$L = 0.0_431833\,KT^2\{(P_c - P)/P\}.\,(dP/dT) \qquad (8)$$

(K is a constant varying with the liquid.)

The validity of this equation depends on that of the relation:

$$(V - v) = KT(P_c - P)/P$$

On examination, however, it is found that, while the above relation is approximately true at low temperatures (as the figures given by Rodzewitz show), yet it fails entirely at temperatures approaching the critical point. This will be evident from the following tabulation where the results for octane and carbon tetrachloride are shown:

t.	80	100	120	140	160	180	200	220	240	260	280
100 $K(CCl_4)$..	1.16	1.15	1.15	1.16	1.19	1.21	1.26	1.35	1.54	1.99	6.44
100 K(octane)	..	..	2.79	2.81	2.83	2.85	2.90.	3.04	3.28	3.83	5.52

The equation can, therefore, be employed only at low temperatures. The same is true of the general equation of Arrhenius:[2]

$$L = A_0 - CT^2 \qquad (9)$$

where A_0 and C are constants dependent on the liquid. Similarly, the formula of Bakker:[3]

$$L = RT \log_e (V - b)/(v - b) \qquad (10)$$

although directly deduced from the equation of van der Waals, is not in agreement with the results of experiment. Finally, there may be mentioned the equation of McLewis:[4]

$$L = (T/\alpha)(d/\beta) \qquad (11)$$

(α = coefficient of expansion, β = compressibility) which gives approximate agreement with the experimental values for the few cases where data for normal liquids are available.

It will be seen that most of the above equations contain a constant dependent upon the liquid under consideration. It is usually possible to remove this, and so generalize the equation, by combination with the rule of Trouton or some similar law. Thus equation 5 becomes:

$$ML = 20.7\,T_c(1 - T/T_c)^n \qquad (5b)$$

a relation perfectly general for all normal liquids. Since, however, the rule of Trouton is only approximately correct, such equations will not

---

[1] Rodzewitz, *J. Russ. Phys. Chem. Soc., Phys.* **45**, 355 (1914).

[2] Arrhenius, *Meddel från K. Vet.-Akads. Nobelinstitut*, Band **2**, No. 8 (1911).

[3] Bakker, *Z. Physik. Chem.*, **18**, 519 (1895).

[4] McLewis, *Phil. Mag.*, [6] **22**, 268 (1911).

usually reproduce the experimental values sufficiently closely to be of practical utility.

In the following tables only those equations (2 to 7, inclusive) are compared with the thermodynamical Equation 1 which are applicable throughout the whole of the available experimental range. The constants employed are shown in Table I; values not tabulated previously, and calculated by the present author, are indicated by a star. The collected results are given in Tables II–V; divergences from the experimental values

TABLE I.—CONSTANTS OF EQUATIONS.

	Octane.	Methyl butyrate.	Carbon tetrachloride.	Fluorobenzene.
T_c....................	569.2	554.25	556.15	559.55
μ' (Mills).............	93.16	91.31	44.01	85.65
c (Dieterici)..........	1.858	1.824	1.667	1.711
K (Kleeman)..........	176.2	113.3*	19.74	81.44
k (Kendall)............	9.72	10.47	5.92	10.04
C (Tyrer)...............	134.4*	140.8*	133.0*	146.0*
b_c (Applebey)..........	190.63	131.74	107.54	105.85
db/dt (Applebey)........	0.11732	0.08459	0.06674	0.06472

TABLE II.—OCTANE. HEATS OF VAPORIZATION.

t.	Ther.	Mills.	Dieterici.	Kleeman.	Kendall.	Tyrer.	Applebey.
0	89.46	85.69	97.63	95.69	87.49	89.83	...
120	71.43	71.83	73.05	73.37	71.56	72.38	73.82
140	68.28	68.61	69.36	69.36	68.28	68.83	...
160	64.75	65.06	65.52	65.31	64.79	64.96	...
180	60.91	61.14	61.40	60.90	60.93	60.85	59.57
200	56.61	56.72	56.89	56.15	56.64	56.38	...
220	52.03	51.80	51.83	50.98	51.81	51.39	...
240	45.97	45.72	45.63	44.76	46.02	45.57	42.92
260	39.14	38.63	38.46	35.75	38.85	38.61	...
280	28.26	28.17	27.85	27.55	28.50	28.69	25.96
290	19.10	19.50	19.12	19.20	19.35	20.34	17.87

TABLE IIa.—OCTANE. DIVERGENCES.

t.	Mills.	Dieterici.	Kleeman.	Kendall.	Tyrer.	Applebey.
0	—3.77	+8.17	+6.23	—1.97	+0.37	...
120	+0.40	+1.62	+1.94	+0.13	+0.95	+2.39
140	+0.33	+1.08	+1.08	0.00	+0.55	...
160	+0.31	+0.77	+0.56	+0.04	+0.21	...
180	+0.23	+0.49	—0.01	+0.02	—0.06	—1.34
200	+0.11	+0.28	—0.46	+0.03	—0.23	...
220	—0.23	—0.20	—1.05	—0.22	—0.64	...
240	—0.25	—0.34	—1.21	—0.05	—0.40	—3.05
260	—0.51	—0.68	—1.39	—0.29	—0.53	...
280	—0.09	—0.41	—0.71	+0.24	+0.43	—2.30
290	+0.40	+0.02	+0.08	+0.25	+1.24	—1.23
Av. (120–280°)	0.27	0.65	0.93	0.11	0.44	2.13

are shown in Tables II*a*–V*a*. In the calculation of the "average divergence," the figures for 0° and for temperatures within 10° of the critical are disregarded.[1]

TABLE III.—METHYL BUTYRATE. HEATS OF VAPORIZATION.

t.	Ther.	Mills.	Dieterici.	Kleeman.	Kendall.	Tyrer.	Applebey.
0	95.79	90.91	101.88	101.17	92.35	95.08	...
100	77.80	7813.	79.58	80.41	77.95	79.02	...
120	74.31	74.72	75.58	76.10	74.48	75.17	80.79
140	70.84	71.04	71.61	71.62	70.77	71.13	...
160	66.53	66.87	67.08	66.87	66.69	66.77	65.88
180	62.00	62.26	62.45	61.79	62.26	62.01	...
200	57.41	57.19	57.31	56.43	57.18	56.86	55.20
220	51.31	51.07	51.08	50.23	51.28	50.83	...
240	44.14	43.69	43.61	42.70	44.00	43.74	...
260	34.44	34.06	33.85	33.26	34.10	34.25	32.00
280	11.16	11.98	11.64	12.42	11.59	12.62	11.77

TABLE III*a*.—METHYL BUTYRATE. DIVERGENCES.

t.	Mills.	Dieterici.	Kleeman.	Kendall.	Tyrer.	Applebey.
0	−4.88	+6.09	+5.38	−3.44	−0.71	...
100	+0.33	+1.78	+2.63	+0.15	+1.22	+2.99
120	+0.41	+1.27	+1.89	+0.17	+0.86	...
140	+0.20	+0.77	+0.78	−0.07	+0.29	...
160	+0.34	+0.55	+0.34	+0.16	+0.24	−0.65
180	+0.26	+0.45	−0.21	+0.26	+0.01	...
200	−0.22	−0.10	−0.98	−0.23	−0.55	−2.21
220	−0.24	−0.23	−1.08	−0.03	−0.52	...
240	−0.45	−0.53	−1.44	−0.14	−0.40	...
260	−0.38	−0.59	−1.18	−0.34	−0.19	−2.44
280	+0.82	+0.48	+1.26	+0.43	+1.46	+0.61
Av. (100–260°)	0.31	0.70	1.19	0.17	0.48	2.00

TABLE IV.—CARBON TETRACHLORIDE. HEATS OF VAPORIZATION.

t.	Ther.	Mills.	Dieterici.	Kleeman.	Kendall.	Tyrer.	Applebey.
0	51.87	52.40	54.13	56.14	52.36	53.62	...
80	46.00	46.44	46.11	47.41	46.03	46.60	...
100	44.15	44.58	44.20	45.16	44.23	44.58	44.33
120	42.08	42.54	42.18	42.75	42.30	42.44	...
140	39.92	40.36	40.11	40.35	40.22	40.21	...
160	37.95	38.08	37.99	37.92	37.95	37.86	38.38
180	35.40	35.46	35.47	35.22	35.43	35.25	...
200	32.61	32.52	32.67	32.18	32.62	32.39	...
220	29.45	29.14	29.35	28.77	29.33	29.13	29.72
240	25.56	25.10	25.35	24.76	25.33	25.24	...
260	20.07	19.70	19.89	19.49	19.90	20.05	...
280	10.43	10.45	10.48	10.48	9.22	10.29	10.71

---

[1] Applebey and Chapman have calculated all results (except for fluorobenzene) at intervals of 30°. In the tables their figures for intermediate temperatures are omitted to economize space, but for the final calculation of "average divergences" all results within the temperature range indicated above have been taken into account.

TABLE IVa.—CARBON TETRACHLORIDE. DIVERGENCES.

t.	Mills.	Dieterici.	Kleeman.	Kendall.	Tyrer.	Applebey.
0	+0.53	+2.26	+4.27	+0.49	+1.75	
80	+0.44	+0.11	+1.41	+0.03	+0.60	
100	+0.43	+0.05	+1.01	+0.08	+0.43	+0.18
120	+0.46	+0.10	+0.67	+0.22	+0.36	...
140	+0.44	+0.19	+0.43	+0.30	+0.29	...
160	+0.13	+0.04	—0.03	0.00	—0.09	+0.43
180	+0.06	+0.07	—0.18	+0.03	—0.15	
200	—0.09	+0.06	—0.43	+0.01	—0.22	
220	—0.31	—0.10	—0.68	—0.12	—0.32	+0.27
240	—0.46	—0.21	—0.80	—0.23	—0.32	...
260	—0.37	—0.18	—0.58	—0.17	—0.02	...
280	+0.02	+0.05	+0.05	—1.21	—0.14	+0.28
Av. (80–260°)	0.32	0.11	0.62	0.12	0.28	0.28

TABLE V.—FLUOROBENZENE. HEATS OF VAPORIZATION.

t.	Ther.	Mills.	Dieterici.	Kleeman.	Kendall.	Tyrer.	Applebey.
0	87.78	88.39	93.51	94.80	89.14	91.44	...
80	80.07	79.11	79.53	80.56	78.60	79.99	79.76
100	77.10	76.11	76.19	76.79	75.59	76.48	77.21
120	73.03	72.69	72.55	72.80	72.34	72.80	73.24
140	68.75	69.00	68.79	68.71	68.84	68.91	69.27
160	64.37	64.99	64.79	64.45	64.97	64.81	65.39
180	60.17	60.65	60.55	59.91	60.87	60.41	61.08
200	55.35	55.79	55.78	54.91	56.16	55.63	55.84
220	50.37	50.36	50.51	49.41	50.73	50.27	50.34
240	44.07	43.80	43.97	43.00	44.22	43.87	43.77
260	35.65	35.32	35.43	34.70	35.60	35.64	35.21
280	20.82	21.16	21.07	20.17	20.74	21.60	19.95

TABLE Va.—DIVERGENCES.

t.	Mills.	Dieterici.	Kleeman.	Kendall.	Tyrer.	Applebey.
0	+0.61	+5.73	+7.02	+1.36	+3.66	...
80	—0.96	—0.54	+0.49	—1.47	—0.08	—0.31
100	—0.99	—0.91	—0.31	—1.51	—0.62	+0.11
120	—0.34	—0.48	—0.23	—0.69	—0.23	+0.21
140	+0.25	+0.04	—0.04	+0.09	+0.16	+0.52
160	+0.62	+0.42	+0.08	+0.60	+0.44	+1.02
180	+0.48	+0.38	—0.26	+0.70	+0.24	+0.91
200	+0.44	+0.43	—0.44	+0.81	+0.28	+0.49
220	—0.01	+0.14	—0.96	+0.36	—0.10	—0.03
240	—0.27	—0.10	—1.07	+0.15	—0.20	—0.30
260	—0.33	—0.22	—0.95	—0.05	—0.01	—0.44
280	+0.34	+0.25	—0.65	—0.08	+0.78	—0.87
Av. (80–260°)	0.47	0.37	0.48	0.64	0.24	0.43

In the discussion of the above figures, Tables II–IV will be considered first, since the results obtained are essentially the same throughout.

Table V (fluorobenzene) gives results of a different nature, requiring further investigation; it is, therefore, dealt with subsequently.

From the results obtained with octane, methyl butyrate and carbon tetrachloride, it is evident that the equations of Kendall and of Mills afford values most consistent with the experimental figures. The divergences are always small, except at 0° and near the critical point, where the experimental values are liable to error. Even at these temperatures the divergences are usually smaller than those obtained with the remaining formulas. The equations of Kleeman and of Dieterici (and, to a smaller degree, that of Tyrer) are not so accurate, and lead to values at the lowest temperatures which are consistently too high. The equation of Applebey and Chapman gives values differing fairly considerably from the experimental. It must be mentioned, however, that the effect of small experimental errors upon the calculated values is much greater here than in any of the other equations.

The final table for fluorobenzene shows exactly the opposite results. The equations of Kendall and of Mills here give the poorest agreement with the experimental data. (Kleeman's values may be appreciably improved by a slight modification in the value of the constant employed by him.) Also, for practically all of the formulas, the calculated values at the lowest temperatures (80–120°) are uniformly too low.

This difference in behavior may be satisfactorily explained by a consideration of the experimental data. It is found on examination that the values for fluorobenzene at low temperatures are affected by errors of observation.

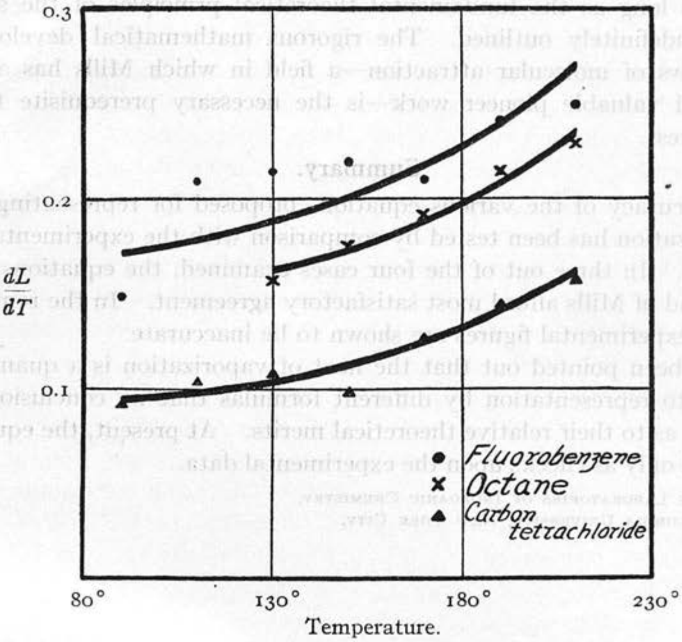
The method employed for illustrating this is as follows: The function dL/dT is plotted against temperature. Now, in all normal curves, the heat of vaporization, after a rapid increase with decreasing temperature near the critical point, increases more and more slowly as temperature is further lowered. When the rate of this increase (dL/dT) is plotted against T, therefore, we obtain a smooth curve, with rapid change of slope near the critical temperature, but approximating more nearly to a straight line at lower temperatures. The values for dL/dT will decrease continuously, but more and more slowly, as temperature falls.

The results for the lower temperatures are shown in the accompanying diagram. The values for dL/dT are found, at intervals of 20°, by interpolation from the preceding tables, *e. g.*, for octane at 130°, $dL/dT = 1/20\ (L_{120} - L_{140})$. It is evident that, while the results for octane and carbon tetrachloride lie fairly closely upon smooth curves of the required type, the values obtained in the case of fluorobenzene show considerable fluctuations.[1] The experimental data in this case are clearly inconsistent,

---

[1] The values for methyl butyrate are not plotted to avoid confusion in the diagram. The curve is almost identical with that for fluorobenzene. The agreement in this case is not quite so good as with octane or carbon tetrachloride.

and a repetition of the observations would probably lead to results in agreement with those obtained from other liquids, *i. e.*, exhibiting close concordance with Equations 2 and 5.



It is in this direction—the correction of the experimental data—that the equation of Mills has already repeatedly proved itself to be of service. Large divergences were existent between the original experimental values of Young and the calculated values of Mills for several liquids. It was invariably found, when the observations were repeated, that the *experimental values* were in error.[1]

The utility of the various equations proposed will probably be restricted, for the present, to this practical application. It is hard to conceive how much progress can be made on the theoretical side until the fundamental points at issue are settled. For the most obvious conclusion to be drawn from the present investigation is that the heat of vaporization is a quantity which is peculiarly adaptable to representation by empirical formulas. It is impossible that all of the equations considered can be of theoretical significance. Were this the case, an army of physicists might devote their lives to tabulating the different relations, between the quantities concerned, obtainable by the combination and recombination of these equations.[2] It will be evident, however, that the fact that a formula,

---

[1] Mills, *Phil. Mag.*, [6] **21**, 84 (1911); **24**, 483 (1912).

[2] From three equations alone, Mills obtained thirty-six new relations (THIS JOURNAL **31**, 1099 (1909)). The number possible soon increases to billions as more equations are introduced. (Compare Bridgman, *Phys. Rev.*, **3**, 273 (1914).)

in this field, fits the experimental results is no confirmation, taken alone, of the truth of the principles involved.

Further approximate or empirical relations will consequently be superfluous, so long as the fundamental theoretical principles of the subject remain indefinitely outlined. The rigorous mathematical development of the laws of molecular attraction—a field in which Mills has already performed valuable pioneer work—is the necessary prerequisite to any real progress.

Summary.

The accuracy of the various equations proposed for representing heats of vaporization has been tested by comparison with the experimental data of Young. In three out of the four cases examined, the equations of the author and of Mills afford most satisfactory agreement. In the remaining case the experimental figures are shown to be inaccurate.

It has been pointed out that the heat of vaporization is a quantity so adapted to representation by different formulas that no conclusions can be drawn as to their relative theoretical merits. At present, the equations are useful only as checks upon the experimental data.

NICHOLS LABORATORIES OF INORGANIC CHEMISTRY,
COLUMBIA UNIVERSITY, NEW YORK CITY.