

# The Dissociation of Strong Electrolytes

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The theory which, during the last decennia, has had the greatest importance for the development of chemistry is undoubtedly the theory of the free ions, which we owe to Arrhenius. It is first through this theory that we have obtained the right understanding of the nature of the acids, bases, and salts, and have learned to know the real difference between strong and weak acids, and between normal and complex salts.

The degree of dissociation  $\alpha$  for a *weak* electrolyte calculated from the electrical conductivity by means of the equation  $\alpha = \mu/\mu_\infty$  varies with the concentration just as it should according to the mass-action law of Guldberg and Waage. This fact has contributed much to the victory of the theory of ionization in the years following its appearance. However, when one calculates, in the same way, the degree of dissociation for a *strong* electrolyte, there appear a series of anomalies, which have caused considerable difficulties to the theory: the degree of dissociation calculated from the conductivity does, in general, not agree with that computed from osmotic data by means of the equation  $\alpha = i - 1$ , where  $i$  is the so called van't Hoff's coefficient,\* and neither of the values agree with the law of mass action. It is the intention with the following considerations to try to show how these and other difficulties for the 'Arrhenius' theory have arisen because the quantities  $\mu/\mu_\infty$  and  $i - 1$  for the strong electrolytes have erroneously been considered as measures of a degree of dissociation. The fact that  $\mu/\mu_\infty$  and  $i - 1$  for strong electrolytes decrease more and more below unity with increasing concentration, must not necessarily be explained as a consequence of decreasing

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\* The van't Hoff's coefficient  $i$  denotes the ratio between the observed osmotic pressure (freezing-point depression, boiling-point elevation) and that calculated without the assumption of dissociation.

dissociation, but may be interpreted in another way. An examination of the available material has led me to the opinion that the strong electrolytes ought to be considered as practically completely dissociated. The new view may therefore appropriately be designated as *the hypothesis of the complete dissociation of the strong electrolytes*.

*The reasons for the hypothesis.* A series of examinations of the salts of chromium had in 1906 led me to the result that the strong electrolytes, both in dilute and concentrated solution, possess the colour of the ion, if only complex compounds are not formed in the solution<sup>1</sup>, and Hantzsch had simultaneously arrived at the same conclusion through other examinations. This fact, that the colour of a strong electrolyte is independent of its concentration, led me in 1909 to propose the hypothesis, that the strong electrolytes in solution are completely dissociated into ions (when complex compounds are not formed)<sup>2</sup>. This hypothesis involves that the influence of the concentration on the molar conductivity and on the van't Hoff's coefficient  $i$  must be explained in another way than hitherto. It was already then pointed out that it should probably be possible to explain these effects as a consequence of the electrical forces between the ions. In favour of this explanation spoke the fact, otherwise difficult to understand, that the effect is mainly determined by the electrical properties of the system (number of ions, magnitude of the electric charge of the system, and dielectric constant of the solvent). It was further emphasized that the anomalies of the strong electrolytes would disappear when  $\mu/\mu_\infty$  and  $i - 1$  were no longer considered as measures of a degree of dissociation. But it is of course evident that the justification for assuming the hypothesis of the complete dissociation of the strong electrolytes depends upon whether it is possible, in a plausible way, to explain the values of  $\mu/\mu_\infty$  and  $i - 1$  as a consequence of the electric charges of the ions.

Some time ago, I resumed working with the hypothesis, and I succeeded in calculating approximately how much the electric forces between the ions must reduce the osmotic pressure. In this way I found that the effect was approximately as great as it should be. Having reached so far, I discovered, however, that Milner<sup>3</sup> in the years 1912-13 had carried through a similar calculation. I have based the following statements on his results because his calculations have been carried out with a considerably greater degree of accuracy than my own.

The lowering of the osmotic pressure which the electric charges of the ions produce, and which may appropriately be called the *Milner effect*, is in Fig. 1 represented by the continuous curve. The curve shows the lowering for an electrolyte consisting of two monovalent ions. For comparison is given, by means of crosses, the lowering which has been found experimentally for potassium chloride from freezing-point determinations. It is seen that the Milner effect has the right order of magnitude, especially at concentrations which are neither



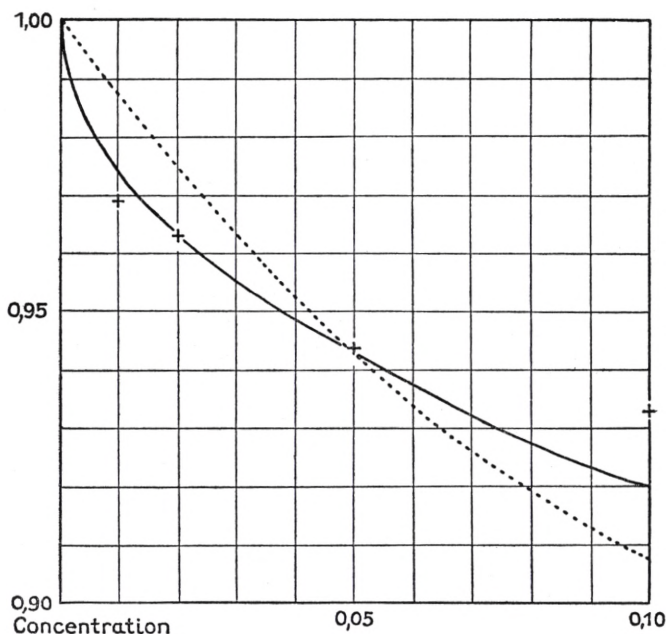


Fig. 1. The decrease of the osmotic pressure.

————— according to Milner  
 - - - - - according to the mass-action law  
 + + from freezing-point determinations.

so small that the experimental determinations are too uncertain, nor so great that Milner's calculations, the accuracy of which decreases with increasing concentration, are too unreliable. The dotted curve shows how the osmotic pressure would decrease if it should be explained from the assumption of undissociated molecules formed according to the law of Guldberg and Waage. This curve makes a much poorer fit than that of Milner although a suitably chosen dissociation constant has been used for its calculation, while the Milner curve has been calculated without any arbitrarily chosen constant.

The Milner effect is a direct consequence of the mutual attraction and repulsion of the ions according to Coulomb's laws, and if the variation of the osmotic pressure is to be interpreted from the assumption of incomplete dissociation, one must first explain why the Milner effect may be neglected.

If one will assume that the strong electrolytes are completely ionized, one ought also to be able to explain the variation of the conductivity with the concentration as a consequence of the electric charges of the ions. Hertz<sup>4</sup> has in 1912 examined how the conductivity of the ions is affected by the electric forces

which are active between them, and he has found that this effect, which appropriately may be called the *Hertz effect*, must produce a decrease of the conductivity of the ions with increasing concentration. He has also deduced a formula for this effect and shown that it may be used for explaining the observed variation of the conductivity, *e. g.* for sodium chloride. His formula contains, however, quantities which are only little known (thus, the free path of the ions in the solution), and the values which he must use for these quantities are not the most probable. For this reason, more work is needed before it may be considered to be certain that the Hertz effect is fully able to account for the change of the conductivity of strong electrolytes with concentration.

We have now seen that measurements of freezing-points and conductivities, owing to the Milner and the Hertz effect, respectively, are not suitable for the determination of the degree of dissociation of the strong electrolytes. A third method which has been used for this purpose, and which is based upon the catalytic effect of the ions, remains yet to be examined. It is especially the hydrogen ions which have a catalytic effect. It is therefore primarily the dissociation constants of the acids which one has tried to determine in this way. Most investigators who have examined strong acids by this method have found that the catalytic activity of the acid is proportional to its gross concentration, irrespective of the fact that the molar conductivity of the acid varies within wide limits. As an example I shall refer to some measurements by Goldschmidt and Thuesen<sup>5</sup> of the esterifying effect of hydrogen chloride on organic acids dissolved in methyl alcohol.

*The esterifying effect of hydrogen chloride in methyl alcohol*

$c$  is the molar concentration of hydrogen chloride, and  $k$  the velocity constant for the esterification

| $c$   | $k/c$ for              |              |             | $\mu/\mu_\infty$ for<br>hydrochloric acid |
|-------|------------------------|--------------|-------------|---|
|       | <i>i</i> -butyric acid | benzoic acid | acetic acid |   |
| 0.1   |                        | 0.308        |             | 0.601                                     |
| 0.05  | 31.0                   | 0.311        | 97.1        | 0.672                                     |
| 0.025 | 31.7                   |              | 100.2       | 0.734                                     |
| 0.01  |                        |              | 92.7        | 0.806                                     |

Snethlage<sup>6</sup> has with special strength emphasized the peculiarity in this result, and he has pointed out that it indicates that the strong electrolytes are either not dissociated at all, or they are completely dissociated. But while Snethlage, for reasons to which I cannot attach any importance, prefers the former alternative, I am of the opinion that one should prefer the assumption that the strong electrolytes are completely dissociated, because it seems impossible to me to abandon the Arrhenius conception of the free ions. If one will maintain that  $i = 1$



and  $\mu/\mu_\infty$  are measures of a degree of dissociation of the strong acid, one must, in order to explain the catalytic measurements, assume that not only the hydrogen ions, but also the undissociated acid molecules catalyze the esterification, an auxiliary hypothesis which does away with all the beauty in the application of the ionic theory to the phenomena of catalysis.

Our present knowledge of the degree of dissociation of the strong electrolytes may therefore be summarized in the following few words:

The osmotic and the catalytic measurements indicate complete dissociation, and the conductivity measurements do not speak against complete dissociation.

Everyone who will maintain that  $i = 1$  and  $\mu/\mu_\infty$  are measures of the degree of dissociation of a strong electrolyte must first explain why the Milner effect and the Hertz effect should fail to appear, and must then, as an explanation of the catalytic measurements, make the auxiliary hypothesis of the catalytic activity of the undissociated acid molecules, and, having cleared these rocks, he has yet left to find applicable explanations of all the many "anomalies of the strong electrolytes" by means of new auxiliary hypotheses suitable for the purpose.

*The working programme of the hypothesis.* If one will assume that the strong electrolytes are completely dissociated, one may no longer by  $\mu/\mu_\infty$  understand the degree of dissociation of a strong electrolyte. The quantity  $\mu/\mu_\infty$  will only be a coefficient expressing the ratio between the conductivity of the ions in the solution considered and their conductivity in infinitely dilute solution. One may appropriately call it the *conductivity coefficient* and designate it as  $f_\mu$ . The van't Hoff coefficient  $i$ , which expresses the osmotic effect of an electrolyte (*e. g.* its influence on the freezing-point) may no longer be put equal to  $1 + x$  where  $x$  is the degree of dissociation. One must introduce an *osmotic coefficient*,  $f_o = p/p_0$ , where  $p$  is the osmotic pressure of the solution, and  $p_0$  is the osmotic pressure which one should have if the ions behaved like uncharged molecules (for binary electrolytes,  $f_o = i/2$ ). Finally, it is necessary to introduce an *activity coefficient*  $f_a$  which expresses the ratio between the active mass of the ion and its concentration, because one must not assume that this ratio is equal to the degree of dissociation defined by the conductivity coefficient. (Instead of the activity coefficient  $f_a$ , it may, in certain cases, be useful to introduce  $-\log f_a$ , and this quantity may appropriately be called the exponential or potential deviation).

$$\begin{aligned} f_\mu &= \mu/\mu_\infty; f_o = p/p_0 (= i/2); \\ f_a &= \text{active mass/concentration.} \end{aligned}$$

The hypothesis places us before the task, by experimental examinations and by theoretical considerations, to determine the values of these coefficients and to discover the laws holding for them, thus, among other things, to find out if there are relations between the different coefficients. As far as I have hitherto been

able to judge from the material, all these coefficients depend mainly upon the concentration of ions in the solution, the valency of the ions, and the dielectric constant of the solvent, but they are only to a small degree dependent upon the other properties of the ions, *e. g.* their weight and volume. Owing to these results, it is easy to obtain a survey of the values of these coefficients in a solution of an electrolyte. A formula as the following

$$-\log f_a = 26 \frac{n^2}{K} \sqrt[3]{c_{\text{ion}}}$$

where  $n$  is the valency of the ions,  $K$  the dielectric constant of the solvent, and  $c_{\text{ion}}$  the concentration of ions in the solution, gives with approximation the value of the activity coefficient in a large number of cases.

As to the value of the conductivity coefficient, an immense experimental material is, as is well known, available, and we are, especially through the investigations of Walden and Noyes, well acquainted with the laws for its magnitude. This coefficient has hitherto been used in a multitude of calculations where one really ought to have used the activity coefficient, *e. g.* in calculations of equilibrium constants of homogeneous and heterogeneous equilibria, and in calculations of electromotive forces. It has hitherto been assumed that the two coefficients are identical, but this is far from being the case, and at least a considerable part of the anomalies, for the explanation of which one has had to put forward the hypothesis of the effect of neutral salts on chemical equilibria, disappear when the correct value of the activity coefficient is applied instead of the conductivity coefficient.

*Methods for the calculation of the activity coefficient.* In the following, some examples of how the activity coefficient may be calculated will be given as an illustration of what one may expect to obtain by carrying out one's calculations on the basis of the new hypothesis. Although the activity coefficient, from a chemical point of view, is the most interesting of the coefficients mentioned, it has hitherto been overlooked. By the calculations we get an opportunity of seeing, how anomalies found by earlier calculations everywhere disappear when the values calculated for the activity coefficients are applied.

1. The activity coefficient may be determined from the osmotic coefficient by means of the following relation which may be deduced thermodynamically\*

\* For a mixture of  $x$  moles of the component 1 and  $1-x$  moles of the component 2, the following equation holds

$$x \frac{dA_1}{dx} + (1-x) \frac{dA_2}{dx} = 0$$

where  $A_1$  and  $A_2$  are the free energies which may be gained by adding one mole of the corresponding component to a large amount of the mixture. For ideal mixtures one has

$$A_1 = -RT \ln x \quad \text{and} \quad A_2 = -RT \ln(1-x). \quad (\text{continues})$$



$$f_o + c \frac{df_o}{dc} = 1 + c \frac{d \ln f_a}{dc}.$$

This thermodynamic relation is very interesting and it possesses many curious properties. We shall, however, not discuss the equation further at this occasion but only use it for the calculation of the activity coefficient of potassium chloride, for which salt the osmotic coefficient is known from freezing-point measurements. According to the statements of Noyes and Falk<sup>7</sup>, the available determinations may be summarized in the following interpolation formula ( $c$  is the molar concentration)

$$f_o = 1 - 0.146 \sqrt[3]{c}.$$

When this expression is introduced into the thermodynamic equation, one obtains

$$\ln f_a = -4 \cdot 0.146 \sqrt[3]{c}$$

or

$$\log f_a = -0.253 \sqrt[3]{c}.$$

In the following small table, the values of  $f_o$ ,  $f_a$ , and  $f_\mu$  for potassium chloride have been compared.

*Deviation coefficients for potassium chloride*

| Molar conc. | $f_o$ | $f_a$ | $f_\mu (= \mu/\mu_\infty)$ |
|-------------|-------|-------|----------------------------|
| 0.001       | 0.985 | 0.943 | 0.979                      |
| 0.01        | 0.969 | 0.882 | 0.941                      |
| 0.1         | 0.932 | 0.762 | 0.861                      |
| 1.0         | 0.854 | 0.558 | 0.755                      |

For non-ideal mixtures, the deviation from ideality is expressed by means of the osmotic coefficient and the activity coefficient in the following equations:

$$A_1 = -RT \ln(xf_a) \quad \text{and} \quad A_2 = -RTf_o \ln(1-x),$$

where the component 1 of the concentration  $x$  is considered as solute and the component 2 as solvent. When these expressions are substituted into the first equation, we obtain

$$f_o - (1-x) \ln(1-x) \frac{df_o}{dx} = 1 + x \frac{d \ln f_a}{dx}.$$

For dilute solutions (small values of  $x$ ),  $(1-x) \ln(1-x)$  is approximately equal to  $-x$ , and the equation may therefore be written as follows

$$f_o + x \frac{df_o}{dx} = 1 + x \frac{d \ln f_a}{dx}.$$

It follows from the form of this equation that one may, instead of  $x$ -concentrations, introduce other concentrations which are proportional to them, for dilute solutions, for instance, molar concentrations  $c$ .

Although the equation between  $f_a$  and  $f_o$  deduced here is only exact for dilute solutions, it may, as shown by a closer analysis, be used even at rather great concentrations without introducing any appreciable error.

The table shows that the activity coefficient, at all the concentrations, deviates more from unity than the conductivity coefficient. It is therefore not surprising that one has formerly found anomalies when the conductivity coefficient has been applied where one ought to have used the activity coefficient.

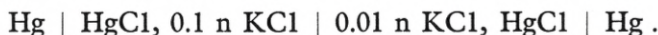
The osmotic coefficient is nearly the same for all monovalent electrolytes. The value is, however, according to the compilation of Noyes and Falk, on an average a little greater than for potassium chloride. For a binary, monovalent strong electrolyte in aqueous solution one may use the formula

$$f_o = 1 - 0.17 \sqrt[3]{c},$$

from which we deduce

$$\log f_a = -0.3 \sqrt[3]{c}.$$

2. The activity coefficient may be determined from measurements of electromotive force, and it is this coefficient, and not the conductivity coefficient, which must be used in the calculation of the electromotive force of concentration cells and other galvanic elements. As an illustration, we shall use an earlier measurement<sup>8</sup> of the cell



After elimination of the diffusion potential, the electrode potential was found to be  $\varepsilon = 0.0548$  volts. By means of the Nernst formula

$$\varepsilon = 0.0591 \log \frac{c_2}{c_1},$$

we calculate,

|  |                         |
|--|-------------------------|
| from the gross concentrations,                   | $\varepsilon = 0.0591,$ |
| applying the conductivity coefficient $f_{\mu},$ | $\varepsilon = 0.0569,$ |
| applying the activity coefficient $f_a,$         | $\varepsilon = 0.0553.$ |

The deviation of the last value from that found by experiment is so small that it is without any importance.\*

3. A very important method for the determination of the activity coefficient is the examination of chemical equilibria. One may thus find the activity coefficient for the ions of picric acid in methyl alcohol by determining how the degree of dissociation of picric acid in that solvent changes with the concentration. The degree of dissociation of picric acid may be calculated from some conductivity

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\* It is the activity coefficient of the chloride ion that enters into the calculation of the electromotive force. From the determinations of the freezing-points of solutions of potassium chloride, one finds the average of the activity coefficients for the potassium and the chloride ion. The above calculation is therefore only exact if we may assume that the two coefficients are equal; but we may expect that this assumption holds with good approximation.



measurements which have been published by Goldschmidt and Thuesen<sup>5</sup>. This example will also illustrate how, according to the new hypothesis, the degree of dissociation of a weak electrolyte may be calculated from its conductivity. The fact is that the formula usually applied, according to which the degree of dissociation is equal to  $\mu/\mu_\infty$ , ought no more to be used, because we cannot expect to get correct results from it except for the weakest electrolytes. It ought to be noticed that Goldschmidt and Thuesen, calculating in the old way, have obtained values for the degree of dissociation of picric acid which do not agree with the mas-action law but show anomalies of the kind which has been characterized as neutral salt effect.

Picric acid dissolved in methyl alcohol is a weak electrolyte, and its molar conductivity deviates from the conductivity at infinite dilution, partly because it is only incompletely dissociated, and partly because the ions, just as in strong electrolytes, affect one another. If  $\alpha$  denotes the degree of dissociation, and if the conductivity coefficient, which expresses the influence of the mutual interaction of the ions, is designated as  $f_\mu$ , the following formula must hold

$$\mu/\mu_\infty = \alpha f_\mu.$$

By means of this equation we may calculate  $\alpha$  when  $\mu/\mu_\infty$  is taken from the conductivity measurements, and for  $f_\mu$  is used the value found for hydrochloric acid in methyl alcohol at the same ionic concentration. The values used for  $\mu/\mu_\infty$  and  $f_\mu$ , and those calculated for  $\alpha$ , are given in the following table.

| Molar conc. | $\mu/\mu_\infty$ | $f_\mu$ | $\alpha$ | $K_c$                | $f_a$ | $f_a$ (calcd.) |
|-------------|------------------|---------|----------|----------------------|-------|----------------|
| 0.2         | 0.0372           | 0.81    | 0.046    | $4.44 \cdot 10^{-4}$ | 0.673 | 0.679          |
| 0.1         | 0.0512           | 0.84    | 0.061    | 3.96 -               | 0.712 | 0.714          |
| 0.05        | 0.0700           | 0.86    | 0.0815   | 3.615 -              | 0.746 | 0.745          |
| 0.025       | 0.0960           | 0.875   | 0.1095   | 3.4 -                | 0.769 | 0.773          |
| 0.0125      | 0.1309           | 0.89    | 0.147    | 3.17 -               | 0.797 | 0.802          |
| 0.00625     | 0.1760           | 0.90    | 0.195    | 2.95 -               | 0.825 | 0.822          |
| 0.003125    | 0.2358           | 0.91    | 0.259    | 2.83 -               | 0.843 | 0.843          |
| 0.001562    | 0.3117           | 0.92    | 0.339    | 2.72 -               | 0.860 | 0.861          |
| 0           |                  |         |          | 2.01 -               |       |                |

$K_c$  given in the fifth column is the value of the expression

$$K_c = \frac{c\alpha \cdot c\alpha}{c(1-\alpha)} = c \frac{\alpha^2}{1-\alpha}.$$

If the activity coefficient of the ions were equal to unity, this expression would have a constant value. The table shows, however, that the value varies consi-

derably with the concentration of picric acid, and from this variation we may calculate the activity coefficient of the ions in the following way. From the mass-action law we obtain, when the activity coefficients are introduced,

$$K = \frac{c \alpha f_a \cdot c \alpha f_a}{c(1 - \alpha)} = c \frac{\alpha^2}{1 - \alpha} f_a^2 = K_c f_a^2,$$

where  $K$  is a constant. Hence, one has

$$f_a = \sqrt{\frac{K}{K_c}}.$$

The value of  $K$  is equal to  $K_c$  at infinite dilution and may be calculated by extrapolation of the values of  $K_c$ . We find  $K = 2.01 \cdot 10^{-4}$ , and obtain for  $f_a$  the values given in the next to the last column of the table. These values for the activity coefficient in methyl alcohol agree excellently with those for aqueous solutions as it is seen from the following considerations.

The values found for the activity coefficient of the ions of picric acid in methyl alcohol may be summarized in the following interpolation formula

$$\log f_a = -0.8 \cdot \sqrt[3]{c_{\text{ion}}}.$$

Values of  $f_a$  calculated from this formula are presented in the last column of the table. The good agreement between the values in the two last columns shows how well the variation of the activity coefficient is expressed by the formula. As previously stated, we may, on an average, for water set

$$\log f_a = -0.3 \cdot \sqrt[3]{c_{\text{ion}}}.$$

Hence,  $-\log f_a$  is for methyl alcohol  $8/3$  times as great as for water, and this result agrees excellently with the fact that the dielectric constant of water is  $8/3$  times as great as that of methyl alcohol.

4. As a last example of the application of the hypothesis of the complete dissociation of the strong electrolytes, we shall discuss the interpretation of the important measurements, carried out by Goldschmidt and Thuesen, of the velocity of esterification of the organic acids in methyl alcohol with picric acid as a catalyst. When an acid, say acetic acid, is dissolved in methyl alcohol, the esterification, *i. e.* the formation of methyl acetate, will proceed extremely slowly, and it does not quicken until a moderately strong, or a strong acid, *e. g.* picric acid or hydrochloric acid, is added. One must, from the standpoint of the ionic theory, assume that it is the hydrogen ions, which are common to all acids, that accelerate the esterification. This view has, in fact, been embraced since the first days of the ionic theory. It has, however, been impossible to account for the newest and most accurate measurements of the velocity of esterification in this way. It has been



found that the velocity constant for the esterification is not exactly proportional to that hydrogen-ion concentration which is found when the degree of dissociation of the catalyzing acid is calculated by means of the formula  $\alpha = \mu/\mu_{\infty}$ . It has thus been stated by Goldschmidt and Thuesen that the esterification of organic acids is 8.24 times as fast in 0.05 n hydrochloric acid as in 0.1 n picric acid, while the ratio between the hydrogen-ion concentrations, when calculated from the conductivity measurements, is 6.56. In order to explain this discrepancy they must resort to the unsatisfactory auxiliary hypothesis that also the undissociated acid molecules catalyze the esterification.

The measurements of Goldschmidt and Thuesen present, however, no anomalies when the new hypothesis of the dissociation of the strong electrolytes is applied. This is shown in the following table.

|                        | 0.05 n HCl | 0.1 n picric acid |          | 0.1 n picric acid<br>+ 0.15 n picrate |          |
|------------------------|------------|-------------------|----------|---------------------------------------|----------|
|                        | $k$        | $k$               | $\alpha$ | $k$                                   | $\alpha$ |
| Phenyl-acetic acid     | 2.23       | 0.265             | 0.0595   | 0.047                                 | 0.0105   |
| Acetic acid            | 4.86       | 0.590             | 0.0607   | 0.100                                 | 0.0103   |
| <i>n</i> -Butyric acid | 2.23       | 0.277             | 0.0621   | 0.0535                                | 0.0120   |
| <i>i</i> -Butyric acid | 1.55       | 0.196             | 0.0632   | 0.0353                                | 0.0114   |
| <i>i</i> -Valeric acid | 0.583      | 0.0735            | 0.0630   | 0.00144                               | 0.0123   |
| Benzoic acid           | 0.0156     | 0.00175           | 0.0561   | 0.00026                               | 0.0084   |
|                        |            |                   | 0.0606   |                                       | 0.0108   |

In this table, we have first given the velocity constants ( $k$ ) for the esterification of different weak organic acids with, respectively, 0.05 n hydrochloric acid and 0.1 n picric acid as catalysts. If it is assumed that the hydrochloric acid is completely dissociated, and that the velocity of esterification is proportional to the hydrogen ion concentration, one may calculate the degree of dissociation ( $\alpha$ ) of 0.1 n picric acid in methyl alcohol. The average of the values found is 0.0606, in excellent agreement with the value 0.061 which has previously (page 66) been found for the degree of dissociation of 0.1 n picric acid in methyl alcohol by a correct method of calculation from conductivity measurements. The explanation of the somewhat deviating value of the degree of dissociation found for benzoic acid is possibly that this acid is esterified so slowly that it may not be permissible to neglect the esterification of the hydrochloric acid during the experiment.

Goldschmidt and Thuesen find an important support for the hypothesis of the catalytic activity of the undissociated acid molecules in some experiments on the esterifying effect of 0.1 n picric acid to which had been added 0.15 n aniline picrate. The velocity constants for the esterification with this mixture are given in

the table. From the velocity constants we calculate that the degree of dissociation of picric acid in the presence of 0.15 n picrate is 0.0108. Goldschmidt and Thuesen, thinking that the addition of the picrate must have depressed the dissociation of the picric acid much more, conclude that the observed catalytic effect must mainly be due to the undissociated picric acid. When we, however, conversely, from the value found for the degree of dissociation of picric acid, calculate the activity coefficient for the ions of picric acid in the picrate solution by means of the mass-action equation

$$f_a \cdot c_{H^+} \cdot f_a \cdot c_{\text{picrate ion}} / c_{\text{picric acid}} = K,$$

we obtain

$$f_a^2 \cdot 0.0108 \cdot 0.15 = 2.01 \cdot 10^{-4},$$

and, hence,

$$f_a = 0.353.$$

This value must be considered very plausible, for, when the activity coefficient in methyl alcohol at the ionic concentration 0.15 is calculated from the formula given before:

$$\log f_a = -0.8 \sqrt[3]{c_{\text{ion}}},$$

we obtain  $f_a = 0.376$ . The agreement is as good as one would dare to expect, considering that the formula has been derived on the basis of experiments at much lower ionic concentrations.

In the preceding calculations, it has been assumed that the catalytic effect of the hydrogen ion is proportional to its concentration, but otherwise independent of the concentration of ions in the solution. The agreement found demonstrates the justification of these assumptions. It would, in itself, not have been unreasonable if it had been found to be necessary to introduce into the calculation of the catalytic effect a coefficient expressing the influence of the concentration of ions upon the catalysis, a *catalytic coefficient*. This seems, however, not to be necessary.

It seems to me that the examples considered in the preceding, and many other similar examples, show conclusively, that it would be of the greatest importance for the development of our knowledge of the behaviour of the electrolytes if one, in future calculations, would cease using degrees of dissociation determined by conductivity where one, in reality, should apply activity coefficients. I feel sure, that the difficulties in calculating with activity coefficients, when one gets used to it, will not be greater than those in calculating with conductivity ratios, although it at first, as long as tables of activity coefficients as comprehensive as those of conductivities are not available, will give a little more trouble. The old method of calculating degrees of dissociation will surely, as long as it is still in use, act as a clog on the development.



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