# On Electric Forces Between Ions and Their Effects

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After the enunciation in 1887 by Svante Arrhenius of his famous theory of electrolytic dissociation much work was devoted to the further development of this theory. Nevertheless one aspect of the theory was not taken up for further discussion until fairly late, viz. the study of the interionic forces. For many years the effects of the electric forces between the ionic charges were neglected. The existence of such *interionic forces* was hardly questioned, but most emphasis was justly laid upon the feature which is so characteristic of the theory, namely that the behaviour of free ions is essentially like that of neutral molecules, while the small difference between free ions and neutral molecules caused by the interionic forces was neglected. During the last decennium work on the interionic forces has, however, gathered momentum and has resulted in an interesting development of the classical ionization theory, and in the following we shall consider the results of these investigations more closely.

## I

1. When applying Coulomb's and Faraday's laws to the forces acting between two ions, each having an electric charge $E$, and being a distance $r$ apart, in a solvent with a dielectric constant $D$, we find the following formula for the force,

$$K = \frac{E^2}{Dr^2} \tag{1}$$

For large values of $r$ this formula is no doubt justified, but when $r$ is of molecular dimensions, i. e. when only a few, a single or perhaps none of the molecules of the solvent occur between the ions, the justification is more questionable. Without going further into a theory about the dielectric constant $D$ and the application of the usual value of $D$ even to small values of $r$, I shall state a number

of experimental results which indicate that the above formula maintains — if not its correctness — at least its applicability even down to very small distances.

2. The first scientist to direct his attention to the effect of interionic electric forces was probably W. Ostwald. In 1892 he drew attention to the fact that the second-stage dissociation constant of a dibasic acid is always less than the first-stage constant, and explained this condition as a consequence of the fact that the electric attraction between the hydrogen ion and the single negative charge on the acid ion ($HR^-$) impedes the dissociation of the second hydrogen atom. In agreement with this view it was ascertained by Ostwald that the difference between the two dissociation constants is the larger the closer the two hydrogen atoms in the acid are to each other, e. g. greater in oxalic acid than in glutaric acid.

Ostwald's qualitative consideration may be given a quantitative form[1]. Let us consider a solution of a dibasic symmetrical acid $H_2R$. In the proximity of a negative ion $HR^-$ the hydrogen-ion concentration will be greater than in the proximity of $H_2R$. According to Boltzmann the concentration is proportional to

$$e^{\frac{\varphi}{kT}}$$

(where $k$ is Boltzmann's constant, $T$ the absolute temperature, and $\varphi$ the work required to remove the ions $HR^-$ and $H^+$ from each other). According to Coulomb's law (equation 1), this work (in a sufficiently dilute solution) is equal to

$$\varphi = \frac{E^2}{Dr}$$

(where $r$ is the distance between the charges on the ions). According to this the ratio of the concentrations of hydrogen ions close to $HR^-$ and $H_2R$ respectively will be equal to

$$e^{\frac{E^2}{kTDr}}$$

Hence we find the following formula for the ratio between the first and the second dissociation constants of the acid:

$$\frac{K_1}{K_2} = 4 \cdot e^{\frac{E^2}{kTDr}} \tag{2}$$

In this formula $r$ will denote the intramolecular distance between the hydrogen atom and the negative charge of the ion $HR^-$. The factor 4 is a statistical factor which is a result firstly of the fact that the acid $H_2R$ has two hydrogen ions which may be dissociated, and secondly of the fact that in the anion $R^{--}$ there are two points to which the hydrogen ions may link themselves. The exponential term represents the actual electrostatic effect caused by the interionic forces between the free charges. For water at 18° C $D = 81$ and equation 2 may be written

$$\log \frac{K_1}{K_2} = \log 4 + \frac{3.1}{r} \tag{3}$$

In this formula $r$ is to be measured in Ångström.

When calculating $r$ according to this formula for a series of normal dibasic acids of the oxalic acid series, the following values are obtained (table 1, column 4).

Table 1. Dimensions of molecules of normal dicarboxylic acids of the oxalic acid series

| | Length of chain $(2 + 1.5\,(n-1))$ | $1.3\,n$ | $r$ in $H_2O$ | $r$ in $CH_3OH$ | $r$ saponification |
|---|---|---|---|---|---|
| $C_2$ | 3.5 | 2.6 | 1.33 | — | 0.8 |
| $C_3$ | 5.0 | 3.9 | 1.35 | — | 1.8 |
| $C_4$ | 6.5 | 5.2 | 3.8 | 5.0 | 4.4 |
| $C_5$ | 8.0 | 6.5 | 5.3 | — | — |
| $C_8$ | 12.5 | 10.4 | 7.2 | — | — |
| $C_9$ | 14.0 | 11.7 | 8.6 | — | — |
| $C_{10}$ | 15.5 | 13.0 | 7.4 | 8.9 | — |

From the structure of the diamond crystal we know that the distance between carbon atoms linked by single bonds is about 1.5 Å. If we add 1 Å for each of the oxygen atoms we can obtain figures for the length of the molecular chain measured along the carbon chain for the different acids; these figures have been stated in column 2 (under the heading: length of chain). The actual length of the molecules must on account of their curved or zig-zag formation be smaller. Langmuir[2] has, on the basis of his experiments on oil films on water, calculated the length of the acid molecules to be 1.3 Å per carbon atom (3rd column).

Apart from the lowest members of the acid series ($C_2$ and $C_3$) the $r$-values calculated from the dissociation constants seem very acceptable. The figures for oxalic acid and malonic acid seem to indicate that we ought to base the calculation on a smaller value of the dielectric constant (e. g. half as great). However, these deviations should not — or at any rate not exclusively — be explained by the assumption that it is incorrect to use the usual dielectric constant of water as, besides the actual electrostatic effect, we must also expect an effect through the atomic chain (by displacement of electrons). The effect of the introduction of hydroxyl and halogen on the strength of organic acids prove that even if the effect through the atomic chain is small in γ-positions and more remote positions, it has a considerable value in α- and β-positions, and may therefore explain why the calculated values of $r$ for oxalic acid and malonic acid are too small.

3. An interesting confirmation of the applicability of formula 3 is obtained by means of *phenolphthalein*. For this dibasic acid Rosenstein has found $K_1/K_2 = 4$

As $r$ on the basis of the formula of phenolphthalein must be assumed to be about 8 Å, we find from equation 3 that

$$\frac{K_1}{K_2} = \text{about } 10.$$

I have therefore concluded[1] that the double-charged phenolphthalein ion is only present to an extent of 40 per cent in a colourless form corresponding to the undissociated acid. If we take only the concentration of this form into account, we have $K_1/K_2 = 10$. The remaining 60 per cent must thus be present in the rearranged, red, quinoidal form. Acree and Birge[3] have on the basis of colorimetrical investigations considered it a warrantable conclusion that about 44 per cent of the double-charged ion is present as a coloured, rearranged ion. This result suggests a confirmation of my theory.

In alcohol, the dielectric constant of which is lower than that of water, the difference between the first and the second dissociation constants of the same acid (same value of $r$) is, according to the theory, greater than in water. For methyl alcohol ($D = 35$) the following equation should thus hold,

$$\log \frac{K_1}{K_2} = \log 4 + \frac{7.2}{r} \tag{4}$$

From Ebert's[4] determinations of the dissociation constants for succinic acid and suberic acid it is possible to calculate $r$ according to formula 4. The values found (table 1, column 5) are almost the same as those applying to water, but they are slightly larger. This might be expected, as the effect through the carbon chain on account of the greater influence of the free charges in the alcoholic solution must play a relatively smaller part than in aqueous solution.

5. Analogous to the fact that a *negative charge* impedes the dissociation of a positive hydrogen ion, a *positive charge* will facilitate such a dissociation. Positive charges will thus make an acid stronger. It is of course also possible to apply equation 3 to this effect; it should be borne in mind, however, that the statistical factor is not always 4, but should be determined in each individual case. The following examples may be mentioned.

The first and second hydrolysis constants of the *hexaquochromic ion* have previously been determined to be about $1 \cdot 10^{-4}$ and $0.006 \cdot 10^{-4}$, respectively, at $17° C$[5]. These two constants are measures of the dissociation of hydrogen ion from $Cr(H_2O)_6^{+++}$ and $Cr(H_2O)_5OH^{++}$, respectively.

As the statistical factor in this case should probably be ascribed the value $^{12}/_1 \cdot ^2/_{10}$, we find, from the ratio of the hydrolysis constants, $r$ to be equal to 1.7 Å for the distance between the ionizing hydrogen atoms and the electrical centre of gravity of the complexes — a fairly reasonable value.

The hydrolysis constant of the *dichlorotetraquochromic ion* was determined to be $4 \cdot 10^{-6}$ at 25° C. This ion is consequently a much weaker acid (compare Brønsted's definition of an acid [6]) than the hexaquochromic ion, in spite of the fact that it contains two electronegative chlorine atoms, but in agreement with its single positive charge as against the three charges of the hexaquochromic ion.

6. The above electrostatic reasoning may also be applied to *ampholytes*.

I have previously [7] derived the formula:

$$\frac{K_S \cdot K_B}{K_{H_2O}} = \frac{n}{x\,(1-x)} \tag{5}$$

where $K_S$ and $K_B$ are the dissociation constants for the acid and basic groups of an ampholyte, $x$ is the fraction of the undissociated ampholyte which is present as a "zwitter-ion" or ampho-ion, and $n$ is a factor which indicates the ratio between the dissociation constants of the *acids*:

$$NH_2 \cdot R \cdot COOH \text{ and } NH_3^+ \cdot R \cdot COOH$$

or, which may be shown to be the same thing, of the *amines*

$$NH_2 \cdot R \cdot COOH \text{ and } NH_2 \cdot R \cdot COO^-.$$
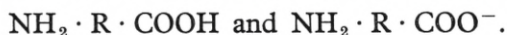
If we substitute the electrostatic expression for $n$ and take the logarithms, we obtain

$$\log \frac{K_S K_B}{K_{H_2O}} = \frac{3.1}{r} - \log x(1-x) \tag{6}$$

The difficulty experienced in testing the correctness of this formula is caused by the fact that $x$ is usually not known.

As regards amino-benzoic acids reasons have previously been given for the opinion that $x$ is between 0.1 and 0.9. According to Rørdam's [8] investigations, which, however, as regards this point, is somewhat uncertain, $x = 0.6$ for the *ortho*-acid and $x = 0.4$ for the *para*-acid. Euler has recently found that $x$ must be fairly small, but it is hardly less than $^1/_4$. If we substitute $x(1-x) = 0.2$, we find from the known dissociation constants
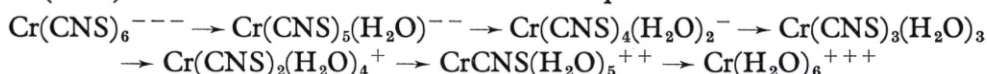
|  | o-acid | m-acid | p-acid |
|---|---|---|---|
| r (amino-benzoic acid) | 1.4 | 3.3 | 1.5 |
| r (phthalic acid) | 1.6 | 6.7 | — |

For comparison the $r$-values for phthalic acid and *iso*-phthalic acid calculated from formula 3 have been stated.

Considering the uncertainty of this material the values found for the $o$- and $m$-acids must be said to be acceptable, while the small value of $r$ found for the $p$-acid suggests that a renewed determination of the dissociation constants and $x$ of this amino-acid is required. An explanation of the higher values of $r$ for $m$-phthalic acid than for $m$-amino-benzoic acid may be found in the fact that the ionized carboxyl groups in a phthalic acid have like charges and thus repel each other, while the ionized amino and carboxyl groups have opposite charges and attract each other. In the former case the molecule will be stretched, and in the latter it will be more or less doubled up.

The above treatment of amino-acids gives an example of the way in which it is possible to calculate electrostatic effects in asymmetrical molecules the ionizing hydrogen atoms of which are *linked in different ways*.

7. The electrostatic reasoning may also be applied to the *consecutive dissociation of other ions* than hydrogen ions. As an example we may use the complexity constants of the chromic thiocyanates[9]. This is a question of dissociation of the six thiocyanate groups in the complex $Cr(CNS)_6^{---}$ and addition of $H_2O$ instead of $(CNS)^-$ so that the end-result will be a hexaquochromic ion:

$$Cr(CNS)_6^{---} \rightarrow Cr(CNS)_5(H_2O)^{--} \rightarrow Cr(CNS)_4(H_2O)_2^- \rightarrow Cr(CNS)_3(H_2O)_3$$
$$\rightarrow Cr(CNS)_2(H_2O)_4^+ \rightarrow CrCNS(H_2O)_5^{++} \rightarrow Cr(H_2O)_6^{+++}$$

Column 2 in the following table gives the values of the six dissociation constants previously published by me.

Table 2. *The dissociation constants for the hexathiocyanato-chromiate complex at 50° C.*

| | Bjerrum | Corrected to $C_{Ion}=0$ | Statistical factor | Corrected for stat. factor | Diff. $(=\frac{3.3}{r})$ |
|---|---|---|---|---|---|
| $\log K_1$ | 0.39 | 1.6 | $^6/_1$ | 0.8 | |
| $\log K_2$ | 0.09 | 0.7 | $^5/_2$ | 0.3 | 0.5 |
| $\log K_3$ | —0.29 | —0.3 | $^4/_3$ | —0.4 | 0.7 |
| $\log K_4$ | —0.66 | —1.0 | $^3/_4$ | —0.9 | 0.5 |
| $\log K_5$ | —1.24 | —1.7 | $^2/_5$ | —1.3 | 0.4 |
| $\log K_6$ | —2.52 | —3.1 | $^1/_6$ | —2.3 | 1.0 |
| | | | | mean value: | 0.6 |
| | | | | | $r = 5.5$ Å |

The calculation of these values is based on concentrations, not on activities. When these values are converted — as best we can for the time being — into activitie, whisch means that the values are extrapolated to an ionic concentration equal to zero, the figures of column 3 are obtained. For statistical reasons the ratio of the constants must be as the fractions of column 4. If we correct for the

statistical effect, we obtain the values given in column 5. When we explain the decrease of these values with increasing index figure exclusively as a consequence of the increasing positive charge of the complex caused by the dissociation of the thiocyanate ion, the effect of the individual charge will be measured by the differences stated in the 6th. column. From the mean value of these differences, $r$ is calculated to be 5.5 Å. This value appears somewhat large, but the order of magnitude is acceptable. The fact that it is too large does not at any rate suggest that the value of $D$ used should be lower than the usual $D$ of water, not even in case of thiocyanate ions which, so to speak, touch the complex.

8. The interionic forces does not only influence chemical equilibria, but also the *velocity of chemical reactions*.

In 1898 it was stated by Emil Fischer in a paper that he had observed that the saponifying or decomposing effect of hydroxyl ions is usually greater towards a neutral substance than towards an analogous acid substance. Thus the saponification of dimethylacetoacetic ester proceeds much more rapidly than that of the acid acetoacetic ester. He adds that van't Hoff has drawn his attention to the fact that this may be explained by assuming the *acid forms* to occur in the basic solution as negative ions, e. g.:

$$CH_3CO^- : CHCOOC_2H_5$$

The negative charges of these ions repel the hydroxyl ions and thus impede the decomposing effect of the latter.

In 1909 Julius Meyer again expounded this view. As it had already been shown, it is always more difficult to saponify the second alkyl than the first alkyl in the esters of dibasic acids. Meyer explained this by assuming that the semi-ester anion repels the hydroxyl ion electrically.

When formulating the electrostatic theory quantitatively the following equation is obtained

$$\log \frac{k_1}{k_2} = \log 2 + \frac{3.1}{r} \tag{7}$$

(where $k_1$ and $k_2$ are the velocity constants of the saponification of 1. and 2. alkyl).

The following equation holds, as previously mentioned, for the dissociation constants

$$\log \frac{K_1}{K_2} = \log 4 + \frac{3.1}{r} \tag{8}$$

The actual electrostatic effect is the same on the saponification constant and on the dissociation constant according to equations 7 and 8. The difference between these formulae are caused by the fact that the statistical factor in case of the saponification constants is 2, while in case of the dissociation constants it is 4.

Skrabal, who has lately carried on comprehensive studies of the saponification processes, has, on a purely empirical basis, concluded from his experiments that there is a certain parallelism between the ratio of the equilibrium constants of dibasic acids and the velocity constants of the saponification of the corresponding esters. He has also pointed out that with increasing distance between the acid groups in the molecule the ratio of the saponification constants approaches 2. (compare especially[10]). These observations agree closely with formulae 7 and 8.

Unfortunately Skrabal has performed most of his experiments in solutions the ionic concentration of which was above 0.1 normal, and as the ionic concentration has a great influence, especially on the 2. saponification constant (Holmberg's cation catalysis) it is not possible with certainty to estimate the value of the velocity constants at zero ionic concentration on the basis of Skrabal's measurements. Skrabal's experiments have moreover in a number of cases been performed in a mixture of 50 per cent alcohol and 50 per cent water. These conditions render a quantitative application of Skrabal's comprehensive and interesting experimental material very difficult.

When using, preferably, the determinations at low salt concentrations, the following values of the ratio of 1. to 2. saponification constants in water are obtained from measurements performed by Goldschmidt and Scholz, Jul. Meyer and Skrabal:

Oxalic acid: 19000 (high salt concentration).
Malonic acid: about 100. Succinic acid: about 10.

Using these values and formula 7 we find the $r$-values of the last column in table 1. These values are in good agreement with values determined by other methods.

9. Altogether it may be said that the material which has been referred to on the preceding pages show that we are entitled to consider the calculation of the forces between two ions based on Coulomb's law and the usual dielectric constants of the solvent to be a useful approximation even for ions very close to each other.

## II.

10. Some of the especially interesting effects of the interionic forces are their influence on the *osmotic pressure* of the ions, on their active mass or *activity*, and on their *conductivity*. Already van Laar, Malmström, Sutherland, Bjerrum and Kjellin have realized the importance of the interionic forces in this connection. But Milner (1913) was the first to grasp the essential characteristic of this phenomenon, namely the grouping of the ions in solution in such a manner that ions of opposite charges are on an average closer to each other than ions of like charges.
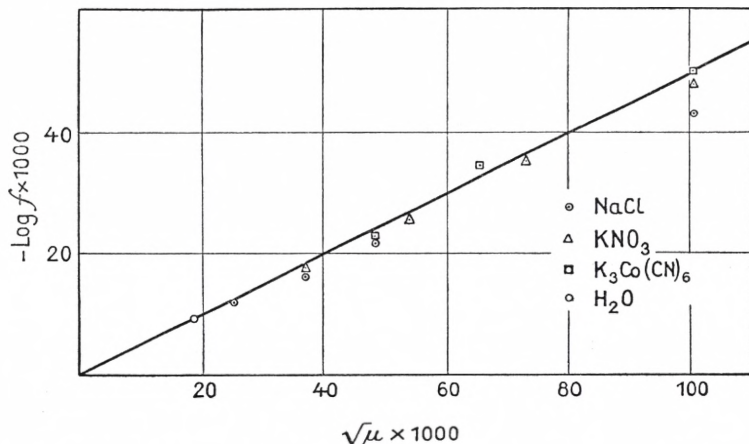
*Fig. 1. Connection between activity coefficient f and ionic strength of the uni-univalent salt*
$$[(NO_2)(CNS)(NH_3)_4Co][(C_2O_4)(NO_2)_2(NH_3)_2Co]$$
*in the presence of other salts. The line drawn represents the theoretical values according to Debye and Hückel. After Brønsted and La Mer.*

And it was not until 1923 that Debye and Hückel [11] succeeded in enunciating formulae for these effects which were applicable in practice and quite exact as regards sufficiently dilute solutions.

These scientists base their work on Coulomb-Faraday's law, assume the ions to be spherical with a diameter $a$ and with the charge located in the centre, and thus find the following formula for the *activity coefficient f* ($=$ activity/concentration) of an ion,

$$- \log f = 0.50 \, \frac{z^2 \sqrt{\mu}}{1 + 0.327 \sqrt{\mu} \, a} \tag{9}$$

In this formula the numerical values are those applying to water at 18° C, $z$ is the valency of the ion, and $\mu = \frac{1}{2} \Sigma \, cz^2$ is the *ionic strength*, introduced in the theory of electrolytes by Lewis and Randall. In case of low ionic strengths (small ionic concentrations) the denominator may be neglected and it will be found that $-\log f$ (which is positive) with increasing dilution will approach zero according to a simple square root law; $f$ is thus smaller than 1 and approaches 1 with decreasing concentration according to a square root law. A corresponding formula was proposed by Debye and Hückel for the osmotic pressure of the ions and a similar, although more complicated, formula for their conductivity (mobility).

11. Milner's and Debye and Hückel's investigations show that on account of the existence of the interionic forces it is not permissible to assume that the ratio of the osmotic effect (or the activity) of the ions to their concentration is constant. Nor is the mobility independent of the concentration. We must, on the contrary, expect all these quantities to decrease with increasing ionic concentration.
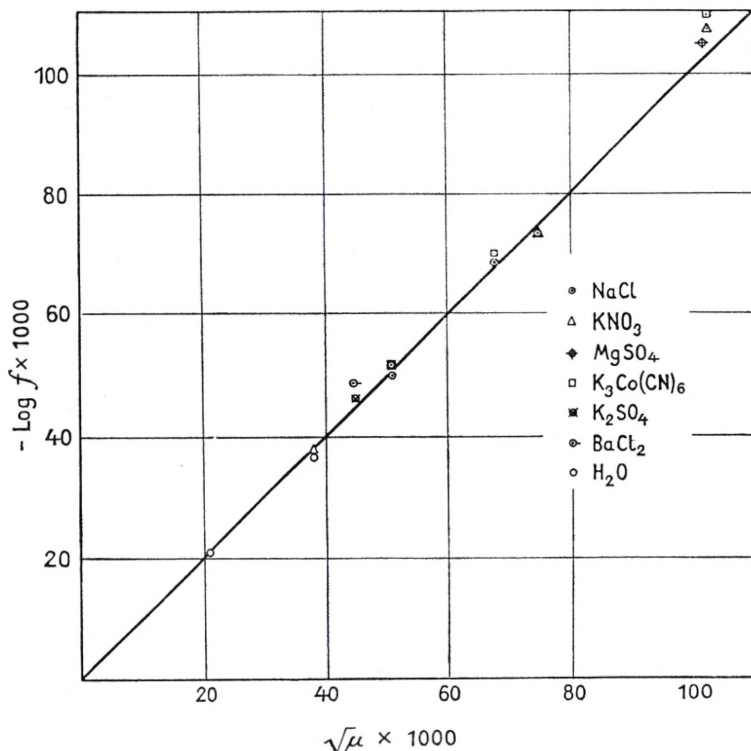
*Fig. 2. Connection between the activity coefficient f and ionic strength of the uni-bivalent salt* $[(C_2O_4)(NH_3)_4Co]_2S_2O_6$ *in the presence of other salts. The line drawn represents the theoretical values according to Debye and Hückel. After Brønsted and La Mer.*

It is well known that these quantities are observed to decrease with increasing ionic concentration in all electrolytes. This was originally — both with regard to strong and weak electrolytes — interpreted as an indication of incomplete dissociation. If, however, the decrease which is observed experimentally is compared with the decrease according to Debye and Hückel, it will appear that in the case of *strong electrolytes* the agreement is so good that there is no necessity of explaining anything by incomplete dissociation. I shall mention a number of examples of the agreement observed.

The most accurate method of measuring the activity of ions available at present is probably determination of salt solubilities. According to this method Brønsted and La Mer[12] have found values for —log $f$ which in dilute solutions, up to 0.01 molar, agree excellently with Debye and Hückel's formula. This may be seen from figs. 1–3.

This summer Rodebush and Hovorka[13] have performed a number of exceedingly accurate cryoscopic determinations in very dilute aqueous salt solutions (0.001–
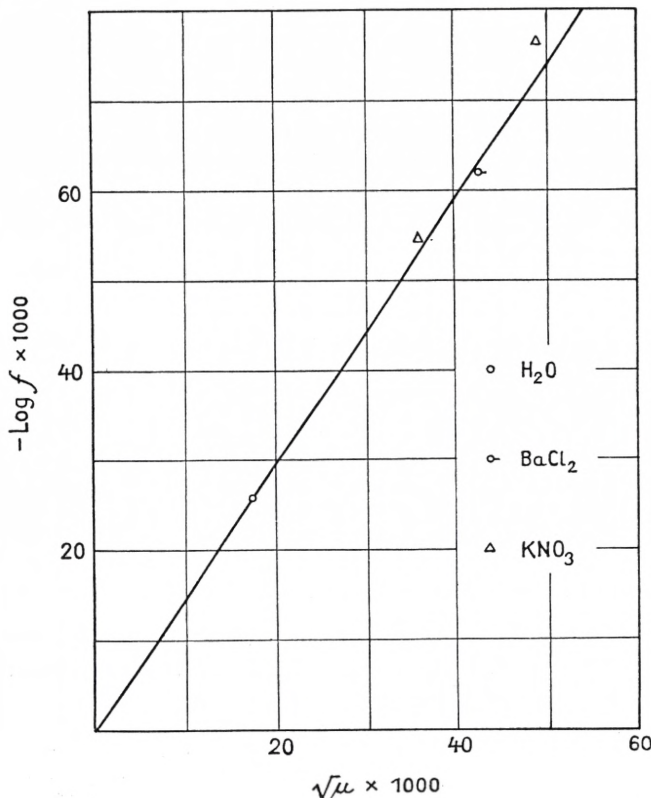
*Fig. 3. Connection between the activity coefficient f and ionic strength of the tri-univalent salt* $[(NH_3)_6Co][(C_2O_4)(NO_2)_2(NH_3)_2Co]_3$ *in the presence of other salts. The line drawn represents the theoretical values according to Debye and Hückel. After Brønsted and La Mer.*

0.01 molar). Figs. 4 and 5 show their results. The curves drawn represents the values according to Debye and Hückel. The slight curvature of these curves show that Rodebush and Hovorka have allowed for the diameter of the ions. Otherwise the curves would have been rectilinear (tangents to the curves at the point corresponding to concentration zero). The diameters (*a*) which they have allowed for are chosen so as to make the curves pass through the point corresponding to the highest concentration measured.

The ionic diameters used are:

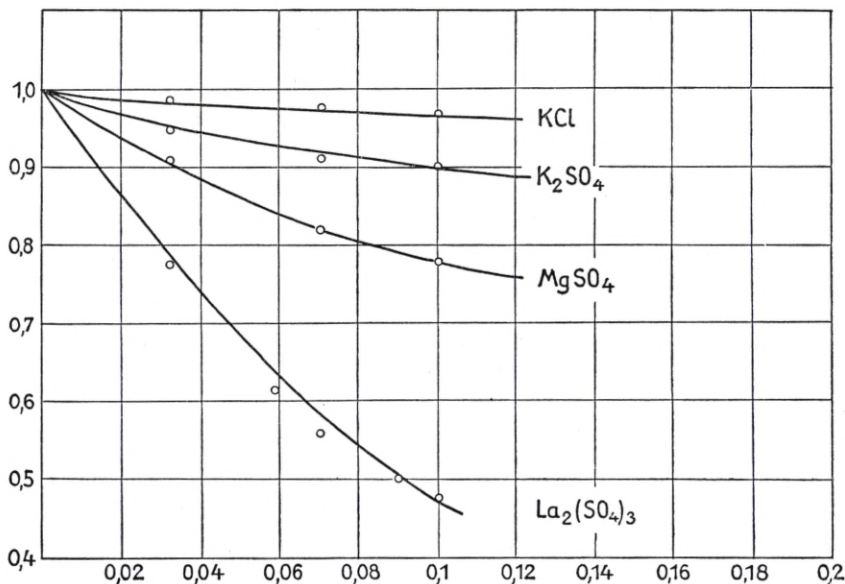| Salt | KCl | CsNO$_3$ | K$_2$SO$_4$ | Ba(NO$_3$)$_2$ | MgSO$_4$ | CuSO$_4$ | La$_2$(SO$_4$)$_3$ |
|------|-----|----------|-------------|----------------|----------|----------|---------------------|
| *a* in Å | 2.32 | 2.32 | 1.09 | 1.01 | 2.22 | 1.59 | 3.00 |

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*Fig. 4. The dependence of the osmotic coefficient on $\sqrt{\mu}$, after Rodebush and Hovorka.*

Figs. 4 and 5 show that it is also possible to understand the osmotic behaviour of the ions if it is assumed that there is no perceptible amount of undissociated molecules in the salt solutions examined.

This also appears in an interesting manner from a recently published paper by Schreiner and Frivold[14] on the freezing-point lowering of lithium chloride in cyclohexanol.

As regards the conductivity the theory is more complicated, but also in this case Debye and Hückel's theory can account for the conditions in dilute solutions of strong electrolytes without the assumption of incomplete ionization.

12. As well known, it has previously[15] been concluded that the so-called strong electrolytes are practically completely dissociated. This was indicated especially by the results of investigations on the optic and catalytic properties of salt solutions and by the peculiar uniformity of the degrees of dissociation of all strong electrolytes as calculated according to classical methods. These degrees of dissociation are mainly determined by the electric properties of the system (the charge and concentration of the ions, the dielectric constant of the solvent). Through the investigations by Debye and Hückel the hypothesis of the practically complete ionization of strong electrolytes has now become a fact which can hardly be questioned.

With our present knowledge it must be considered very unfortunate in the case of a strong electrolyte to consider the conductivity coefficient, $\mu/\mu_\infty$, as a degree of dissociation and to try to apply the law of mass action to it.
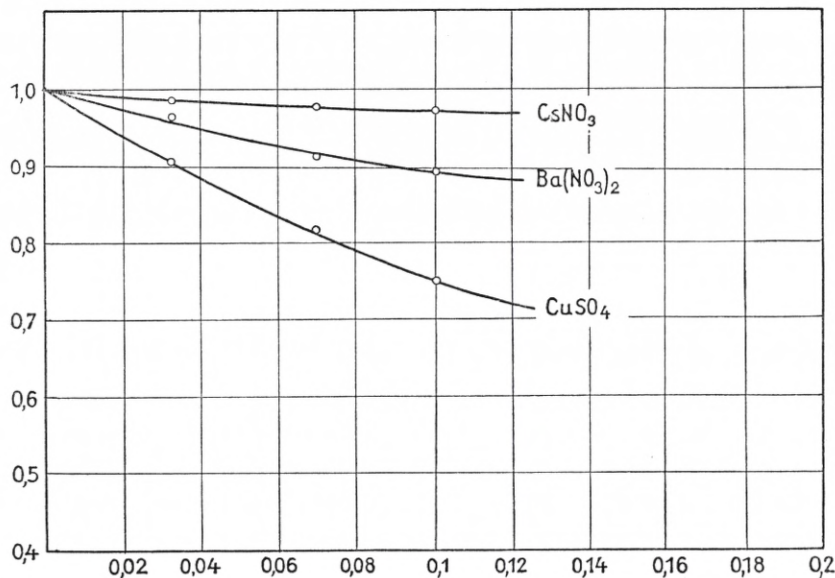
*Fig. 5. The dependence of the osmotic coefficient on $\sqrt{\mu}$, after Rodebush and Hovorka.*

For very weak electrolytes $\mu/\mu_\infty$ should on the other hand be considered a degree of dissociation. For in this case the ionic concentration is so small that we may neglect the effect of interionic forces and assume the mobility of the ions to be constant.

For electrolytes of medium strength it is possible (as already shown in 1916 for picric acid in alcohol[16]) to calculate the actual degree of dissociation from the conductivity coefficient by correcting the latter for the influence of the interionic forces. The stronger the electrolyte the greater this correction and the more uncertain the calculated degree of dissociation.

13. As we have now discussed the importance of the interionic forces to the activity of the ions, it will be of interest to return to the importance of these forces to the velocity of the ionic reactions.

It has already previously been mentioned that it is possible by means of the interionic forces to explain why a negative ion, as e. g. the hydroxyl ion, has a smaller effect on a group in a negative ion than on the same group in a neutral molecule or a positive ion. We shall now consider another aspect, namely *the influence of the ionic concentration on the velocity constant.*

Holmberg has in a very interesting series of papers shown that a number of reactions, in which *hydroxyl ions* or other negative ions react with *ions with a negative charge*, is catalyzed by the addition of salt and is particularly accelerated by salts with polyvalent cations (cation catalysis). As stated by Holmberg[17] in

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1921 this must, on the basis of the hypothesis on the complete dissociation of the salts, be explained by the fact that the interionic forces increase the velocity of reaction, although this author has not attempted any further elaboration of the idea.

Brønsted[18] has in 1922 in a very interesting paper shown that the influence of the salt concentration, not only on the ionic reactions dealt with by Holmberg, but also on other ionic reactions examined, may be formulated in the following equation:

$$k = k_o \frac{f_1 f_2}{f_{12}} \tag{10}$$

Here $k$ and $k_o$ are the velocity constants in the salt solution considered and at an infinitely small ionic concentration, respectively, $f_1$ and $f_2$ are the activity coefficients of the interacting ions (molecules) and $f_{12}$ is the activity coefficient of an ion the charge on which is equal to the sum of the charges on the interacting ions. As regards the derivation and meaning of this important formula Brønsted and I do not agree completely, but none of us have any doubt that numerically the formula gives a correct explanation of the influence of the salt concentration on the velocity of the ionic reaction.

When Debye and Hückel's expression for the activity coefficients according to formula 9 is substituted in Brønsted's formula, the latter will assume the following form:

$$\log \frac{k}{k_o} = 0.50 \frac{2 z_1 z_2 \sqrt{\mu}}{1 + 0.327 \sqrt{\mu} a} \tag{11}$$

($z_1$ and $z_2$ being the number of electrical charges, with the correct sign, on the two interacting complexes).

14. The influence of the ionic concentration is perhaps most clearly realized through the following considerations (as an example we shall use one of Holmberg's cation catalyses). We shall consider the influence of hydroxyl ions on the anion of dibromopropionic acid, $CH_2BrCHBrCOO^-$. Close to this ion the concentration of hydroxyl ions will, due to interionic forces, be smaller than elsewhere in the liquid. Assuming that the point of the molecule which is attacked is the β-bromine*) and that the distance of this atom from the negative charge is $r$ Å, we find that the concentration of hydroxyl ions in the vicinity of the β-bromine is

$$e^{\frac{E^2}{kTDr}} = 10^{\frac{3.1}{r}}$$

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*) After the reading of this paper Professor Holmberg informed me that the point of attack is probably the α-hydrogen, and I quite agree with this view. Hereby the tenor of the reasoning is not altered, however.

times lower than elsewhere in the solution. When the ionic concentration of the solution increases, the electric force emanating from the dibromopropionate ion will alter the distribution not only of the hydroxyl ions, but of all ions present. The greater the number of ions present the smaller the effect on the individual ion and the larger the concentration of hydroxyl ions in the vicinity of the dibromopropionate ion. The influence of the salt can thus be ascribed to a reduction of the electrostatic effect. A quantitative calculation will show that in dilute salt solutions the effect of the salt is independent of $r$, provided that $r$ is not too large.

For large salt concentrations and large values of $r$ the magnitude of $r$ will, however, be significant, and it will be impossible to use the simple formula 11. It will probably be possible in the case of substances with a high value of $r$ (i. e. great distance between charge and reacting group) to ascertain that the ratio of the velocity of reaction in a medium with a small number of ions to that in a medium rich in ions will, with increasing ionic concentration, approach the limiting value $10^{\frac{3.1}{r}}$. In that case it will also be possible to determine the molecular dimension $r$ in this way.


## III.

15. It has sometimes been considered possible to contest the new views on strong electrolytes by proving the existence of undissociated molecules in some strong electrolyte or other. This opinion is, however, unjustified.

It might beforehand be expected that in nature we could meet with all the transition forms from the 100 per cent dissociated strong electrolyte through medium-strong and weak electrolytes down to the typical non-electrolytes.

That the green dichlorochromic chloride contains undissociated chloride may be ascertained by means of silver nitrate. That concentrated solutions of cupric chloride contains chloro-complexes is seen from the colour.

Particular interest is attached to the degree of dissociation of the hydrogen halogenides. As regards hydrogen chloride Schreiner[19] has, from its catalytic action in alcohol, calculated the dissociation constant in alcoholic solution to be about $10^{-2}$, and as the dissociation constant of acids in water is usually about $10^6$ times larger than in alcohol, he has concluded that it must be about $10^4$ in water. According to Schreiner, the index of refraction of concentrated hydrochloric acid also suggests an incomplete dissociation, and in this way he has calculated a dissociation constant of about $10^6$. A third method for an approximate estimation of the dissociation constant of hydrogen chloride has been devised by Ebert[20]. By extrapolating from the series $C_3H_7Cl$, $C_2H_5Cl$, $CH_3Cl$ to HCl he

calculates the solubility of undissociated hydrogen chloride in water. As the vapour pressure of hydrogen chloride, e. g. over 1 normal hydrochloric acid, is known, it is now possible for Ebert to calculate the concentration of undissociated hydrogen chloride in this acid and thus the dissociation constant of hydrochloric acid. The result he finds in this way is about $10^7$. On account of the nature of the extrapolation this method must, however, as emphasized by Ebert, produce a result which is too large.

Along different ways we have thus reached the result that hydrochloric acid is not completely dissociated, but even in 1 normal hydrochloric acid the amount of undissociated hydrogen chloride is only small (about $10^{-5}$ to $10^{-6}$ moles per litre).

Measured by means of the conductivity coefficient $\mu/\mu_\infty$ HCl, HBr, and HJ are all equally strong, but measured according to Ebert the ratio of the dissociation constants are $1:100:250$. Such a great difference agrees very well with the considerable differences in the "acid" properties of these substances when anhydrous, as ascertained by Hantzsch[21]. When the dissociation constant of hydrogen iodide is about 250 times that of hydrogen chloride, this means that the difference in strength between hydrogen chloride and hydrogen iodide is greater than between acetic and monochloroacetic acid.

While the dissociation constants of strong electrolytes previously calculated from the conductivity were not at all specific and were chiefly determined by the valency of the ions, the new dissociation constants distinguish themselves by their specificity, their variation from electrolyte to electrolyte, which is such a characteristic property of chemical equilibrium constants.

I ascribe great importance to the fact that the new views have drawn our attention towards the problem of *determining the dissociation constants for almost strong electrolytes* and thus obtaining a measure of the true strength also of these electrolytes.

Interesting problems are in this connection presented by sulphuric acid and the sulphonic acids.

As a last example of a strong electrolyte which is hardly completely dissociated, I shall mention *sodium hydroxide*. The activity of the hydroxyl ion is in solutions of sodium hydroxide considerably lower than in potassium hydroxide solutions\*). If the dissociation were complete, it should be the other way round as the activity of the ions in sodium salts is usually greater than in potassium salts, in accordance with the fact that the sodium ion is hydrated and consequently larger than the potassium ion. I therefore assume that the small activity of the hydroxyl

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\*)   Measurements by Miss A. Unmack, not yet published. Harned [22] has shown that the activity of sodium hydroxide is smaller than that of potassium hydroxide.

ion in sodium hydroxide may be explained by an incomplete dissociation in aqueous solution of sodium hydroxide. Harned has drawn a similar conclusion from his measurements[23].

When considering the similarity in structure between $H_2O$ and $OH^-$, it is quite obvious that an ion, as the sodium ion, which tends to form hydrates can also combine with hydroxyl ions. Indeed a parallelism between the hydration of the cations and the weakness of their bases might be expected. In this connection I should like to point out that both Kolthoff[24] and Gjaldbæk[25] have recently shown that magnesium hydroxide is incompletely dissociated in solution. For the second dissociation constant of magnesium hydroxide Gjaldbæk finds a value of about $10^{-2.1}$ when assuming the first dissociation constant to be infinite.

A number of determinations of the conductivity of magnesium methylate and various magnesium salts in methyl alcohol carried out by L. Zechmeister in my laboratory, but not published, show that magnesium methylate in methyl alcoholic solution is also rather incompletely dissociated as its conductivity is much lower than that of magnesium chloride and similar ternary electrolytes in methyl alcohol. The magnesium ion thus combines not only with $H_2O$ and $OH^-$, but also with the $CH_3O^-$-ion which is related to $H_2O$.

16. In his otherwise excellent book: *The Properties of Electrolytically conducting Systems*, New York 1922, Ch. A. Kraus has attacked the modern views on electrolytes chiefly for the following reasons: He is of the opinion that the interionic forces cannot explain the great variations of the conductivity coefficient $\mu/\mu_\infty$ with the concentration, which is observed even in very strong electrolytes in a solvent with a very low dielectric constant, e. g. in water at high temperatures approaching the critical temperature. It appears to him to be particularly impossible to explain why the conductivity coefficient in media with a very low dielectric constant at high concentrations increases in an abnormal manner — and often increases considerably — with the concentration.

Actually it is possible by means of the interionic forces also to account for this behaviour, if the *ionic association* produced by these forces is duly allowed for.

It is immediately evident that ions of opposite charges will, due to interionic forces, more frequently be found close together than will neutral molecules, provided the concentration is the same. The former attract each other, which the latter do not. In order to estimate the significance of this fact, a quantitative consideration should, however, be made.

An elementary consideration shows that the number of neutral molecules in a given solution between which the distance varies from $r$ to $r + dr$ for small values of $r$ (small compared with the average distance between the molecules) may be assumed to be proportional to $r^2dr$. For ions of opposite charges the

corresponding number is proportional to $r^2dr\ \mathrm{e}^{\frac{E^2}{kTDr}}$ and for ions of like charges it is proportional to $r^2dr\ \mathrm{e}^{-\frac{E^2}{kTDr}}$.

The curves plotted in fig. 1 on page (109) shows the frequency of molecular pairs without charge (I), of ionic pairs with like charges (III) and of ionic pairs with opposite charges (II) in aqueous solution at ordinary temperature. The abscissa is the distance between the components of the pairs (in Ångström), and the ordinate represents the frequency of pairs with this distance.

In the curve applying to ionic pairs consisting of ions of opposite charges (II) a pronounced minimum is observed at 3.5 Å. A similar minimum will of course occur in other solvents. It will always be located at the distance at which the work of separating the ions amounts to $2kT$, i. e. is equal to 4 times the average kinetic energy per degree of freedom. Ionic pairs with this distance are less frequent than those with greater or smaller distances. When in a solution the ions are so small that they can get perceptibly closer to each other than this, the frequency of closely associated ionic pairs will according to the figure increase considerably, and to obtain a correct picture of the influence of the interionic forces due regard must be had to this association. In aqueous solutions of sodium chloride and potassium chloride the charges of the ions cannot approach each other so closely. But when the ions are considerably smaller or have several charges, or if the dielectric constant of the solvent is considerably smaller than that of water this will be the case.

In Debye and Hückel's formula sufficient allowance has not been made for this association. I have tried to perform a more exact calculation by applying special considerations to the ions between which the distance is smaller than the distance corresponding to the minimum in the association curve and omitting to include them among the free ions. It seems actually possible to proceed along this line, which I shall endeavour to show elsewhere; it is particularly interesting that according to this point of view it is possible to account for the fact that the interionic forces can reduce the active mass of the ions, the osmotic effect and conductivity of their solutions to a tiny fraction of the values which would apply to perfectly free ions.

By applying this method of calculation we make the modern picture of an electrolytic solution approach the classical picture, as we are dealing with a degree of association which resembles the old degree of dissociation.

It must not, however, be forgotten that the separation between free and associated ions is so to speak of a calculatory nature, and does not possess the sharpness which characterizes chemical transformations. On the other hand it is not without interest that this new picture explains why the classical picture with its degree of dissociation does not become completely useless under conditions where the

interionic forces result in extensive association, but on the contrary seem to obtain increased applicability.

The applicability of the picture of ions associated in pairs does not, however, continue to increase with the above mentioned external "associating" factors (large charge on the ion and high concentration, small dimensions of the ion and low dielectric constant). When the association in pairs is extensive, the interionic forces will namely also necessarily produce association into higher complexes, unless the solution is extremely dilute. This explains the high degree of association ascertained by Walden for strong electrolytes in media with very low dielectric constants.

In case of pronounced association *in pairs* the conductivity of the ions will be very small. In solvents with a very low dielectric constant the ions will probably, theoretically speaking, be free, not associated, in case of infinite dilution, but at the lowest measurable concentrations (0.0001–0.01 molar) the association in pairs will be very extensive and the conductivity consequently low. In more concentrated solutions the interionic forces may under such circumstances set up a conductivity increasing with the concentration. With increasing concentration the ionic pairs will approach each other, the interaction between them will tend to loosen them, ternary and higher products of association will become more frequent, and this will increase the conductivity. With increasing concentration we are approaching the state which is characteristic of melted salts, in which the ions are no doubt highly associated, but not in pairs, and thus able to move about and conduct the electric current.

The diagrams below give a schematical representation of the condition in a dilute, ionized solution with association in pairs (diagram I), that in a melted salt with high association, but not in pairs (diagram III), and an intermediate state in a relatively concentrated solution.

```
  I:    + —           + —                        + —
 II:    + —     + —     + —        + —     + —
III:    + — + — + — + — + — + — + — + — + — + — + — + —
```
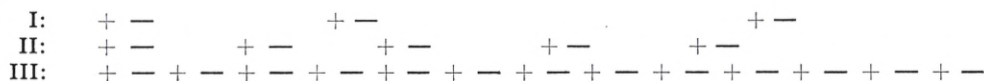
Within a range in which association in pairs prevails the conductivity will be low and the osmotic effect comparatively high. When the association is of a higher order (multi-ionic complexes), a considerable conductivity may occur simultaneously with low osmotic effect.

17. A summary of the above will give the result that *the property which characterizes strong electrolytes* is not the freedom of the ions. In a potassium chloride crystal the ions are very closely attached to each other, but also in crystalline condition potassium chloride is a typically strong electrolyte. Nay — the strong electrolytes are characterized by the fact that the combination of their ions into

chemical molecules is not accompanied by any considerable change in the properties of the ions. *On the contrary, their ions can approach each other very closely without the occurrence of perceptible deformation. An ideal strong electrolyte* would, according to my view, be an electrolyte the ions of which do not cause any mutual deformation. It is for such electrolytes that endeavours have recently been made to formulate a theory and compare the latter with experience.

As Kossel and many other scientists — especially physicists — have assumed, a *smooth transition* may be expected to occur from large, slightly deformable and slightly associating ions, through smaller ions which are to some extent associating and deformable, to small ions which form typical chemical complexes while altering their properties considerably. According to this we should find a smooth transition from the practically non-associating KCl, through the somewhat associating $KNO_3$, to complex ions as $Cr(CNS)_6^{---}$ and so on to $SO_4^{--}$ in which the hexavalent positive sulphur ion is assumed to be linked to four divalent negative oxygen ions. On the basis of the available experimental material it appears to me, however, to be more probable that there is a more or less sharp line of demarcation between *products of association* of only slightly deformable ions on one hand and more or less stable *chemical complexes*, built up of highly deformed or completely vanished ions on the other hand.

Presumably the formation of chemical complexes is associated with a change in the arrangement of certain electrons which after having been attached to one nucleus will become common to two nuclei. As far as I can see, it is most probable that such a change does not occur gradually, but when an electron in a certain state suddenly jumps from its original orbit into a new one associating it with both nuclei.

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