

# Recent Views on Electrolytes

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## I

In the years around 1908, Hantzsch and I were simultaneously occupied with investigations upon the *light absorption of electrolytes*<sup>1,2</sup>. We both obtained the same experimental result, namely, that *the colour of many electrolytes within a considerable range of concentration is independent of the concentration*. The conclusions, which we drew from this result, were however rather different. Hantzsch considered that the ionization was without importance for the colour. If an acid showed a colour different from that of its salts, he assumed that it had a different constitution and called it a *pseudo acid*. According to my opinion, however, the constancy of colour could be only satisfactorily explained by assuming *complete* (or almost complete) *ionization*. If an acid showed a colour different from that of its salts, this was taken simply as an indication of incomplete ionization.

The idea of a complete ionization of many electrolytes has proved very profitable. Many properties of strong electrolytes can be explained as being due to an effect of the ionic charges of the completely ionized electrolyte. Only because this effect of the ionic charges was not sufficiently considered in the first decades of the dissociation theory, was the complete ionization of many electrolytes not discovered at that time.

In the calculation of the effects of the ionic charges the forces between the ionic charges themselves, the so called *inter-ionic forces*, must first be taken into account.

For these the validity of Coulomb's law is generally accepted:

$$K = \frac{\epsilon_1 \epsilon_2}{Da^2}$$

( $\epsilon_1$  and  $\epsilon_2$  the ionic charges,  $a$  the inter-ionic distance,  $D$  the dielectric constant of the solvent).

Secondly, the *forces between the ionic charges and the solvent* have to be taken into consideration. These forces are of special interest when the properties in different solvents are compared.

In the calculation, it is of course essential, to ascribe to the ions molecular properties, as possessed by molecules of non-electrolytes. In many cases, it is sufficient to treat the ions as rigid spheres with a constant diameter. If a more exact calculation is required, one can, with Born<sup>3</sup>, instead of a constant diameter, introduce *repulsive forces*, which are inversely proportional to a high power of the inter-ionic distance. For ions in a cubic lattice, Born rendered the exponent 9 probable. If a still more exact calculation is required, the *deformability* of the ions may be taken into consideration. An electrical force produces a dipole moment in a "soft" ion, the magnitude of which can be estimated by measurements of refraction or by spectroscopic investigations, and the presence of which produces forces, which can be taken into account in the calculation<sup>4</sup>.

## II

We will examine in further detail a few typical examples from the results obtained. Let us consider an *ionic vapour* of stable, monovalent positive and negative ions of radius 1 Ångström. At extremely high temperatures, only known in astronomy, of 100000° C and more, the ions will move almost independently of each other, the thermic movements being so strong that the inter-ionic forces exert little influence. The picture is quite different, however, when experimentally realizable temperatures, such as 2000° C are considered. The inter-ionic forces will here cause the ions to associate completely to pairs. This is conceivable, considering that the energy necessary to separate the ionic pairs is about 250 kcal per mole, and that the mean translatory energy of an ion at 2000° only reaches about 7 kcal per mole. In agreement with this, Nernst<sup>5</sup> has found normal vapour density for NaCl vapour. Further evidence of the extreme force by which the ions are held together in the pairs may be found in the fact that *the electrical conductivity of salt vapours is indeed very low*.

By further lowering of the temperature, a point will be reached where the inter-ionic forces, at a still very high temperature, will cause the ions to associate and form a liquid phase. In the condensed liquid, the association of ions assumes a character, which is quite different from that in vapour. The ions no longer form ionic pairs, but one ion is associated with several other ions at the same time. The whole fluid may be regarded as a single aggregate of ions. Under these conditions the association should not prevent the movements of the ions relative to

one another, which is confirmed by Arndt's<sup>6</sup> finding that many salts show a molar conductivity in the fluid state similar to that in aqueous solution.

If the temperature is still further lowered, it is to be expected that the ions will associate to form an *ionic lattice crystal* and X-ray investigations by Bragg<sup>8</sup> and by Debye and Scherrer<sup>9</sup> have unambiguously shown that salts are really built up as ionic lattices. The ions have *lost their free mobility* in the ionic lattices. For this reason salts in the solid state are as a rule poor conductors. The physics of the ionic crystal lattices has especially been developed by Born<sup>3</sup>. He has shown, for example, that it is possible to calculate accurately the considerable hardness of many salts from the assumption that the ions in the lattice are held together only by the inter-ionic Coulomb forces. It is especially interesting that Born<sup>4</sup> together with Heisenberg has succeeded in calculating the *heat of vaporization of the alkali halides*. Table 1 shows how well the calculated values agree with the experimental values estimated by v. Wartenberg. In this calculation the work necessary for separating the ions, the so called *lattice energy*, was first determined. To obtain the heat of vaporization, the energy, liberated in the process of building up ionic pairs from the separate ions, was subtracted. Since the volatility is closely connected with the heat of vaporization, these calculations by Born and Heisenberg show that the low volatility of the alkali halides, built up of small ions, is completely explained by the existence of inter-ionic forces.

Table 1. Heat of vaporization (kcal per mole) theoretically calculated by Born and Heisenberg<sup>4</sup>. Figures in brackets experimentally found values of v. Wartenberg and co-workers

	F	Cl	Br	I
Na	61 (57)	43 (44)	39 (39)	32 (37)
K	51 (42)	40 (40)	36 (38)	32 (37)
Rb	41 (40)	37 (38)	34 (37)	30 (37)
Cs	41 (35)	31 (37)	29 (37)	26 (37)

For electrolytes built up of simpler ions, it is possible, as especially shown by V. M. Goldschmidt<sup>10</sup>, to predict the lattice form, and therefore also the crystal structure. For only slightly deformable ions, it is determined by the relative amounts and the ratio of the radii of the ions. For more strongly deformable ions, the influence of the deformability is added.

In conclusion we can say that typical properties of salts, like their power of crystal formation, their hardness, their high melting point and low volatility support the idea of their complete ionization in all three states of aggregation.

## III

Passing now to *aqueous solutions*, we must, with Nernst and J. J. Thomsen, take into account that the dielectric constant ( $D$ ) of water is about 80. In aqueous solutions, the inter-ionic forces are therefore about 80 times smaller than in ionic vapour, and hence in dilute solutions of not too small ions, the inter-ionic forces will give rise to no significant association of ions. However, this does not mean that the effect of the forces is negligible. An ion picked at random will, by virtue of *the long range of the inter-ionic forces*, have an appreciable effect on a great number of the surrounding ions, attracting those with opposite charges and repulsing those with charges of the same sign. As a result of this, the ion considered will be surrounded by a kind of atmosphere of ions with opposite charge. This situation was already perceived in 1913 by Milner<sup>11</sup> but first in 1923 Debye and Hückel<sup>12</sup> succeeded on this basis in formulating the laws for the effect of the inter-ionic forces.

The main problem is to find expressions for the empirical *coefficients* by which the changes with concentration of the conductivity, the osmotic properties, and of the active mass of the ions were registered after abandoning the use of a "degree of dissociation" as impracticable for this purpose (Bjerrum<sup>13</sup>).

A long series of experimental works by many authors has shown that the *formulae of Debye and Hückel* in an excellent way describe the conditions in sufficiently dilute solutions of electrolytes (the expression for the conductivity coefficient in fact only after a small alteration by Onsager<sup>14</sup>). The formulae given represent the limiting laws, approached with increasing dilution. In the case of dilute salt solutions, there remains no decrease in conductivity, osmotic effect or ionic activity, which can be ascribed to incomplete dissociation.

The *heat of dilution* caused some difficulties in the beginning. A negative heat of dilution was first expected, since it was argued that the overcoming of the inter-ionic forces in the process of dilution would absorb thermal energy from the solution. This is, however, not correct.

According to Debye<sup>15</sup> the dielectric properties are explained by the dipolar structure of the water molecule. Now, the dipoles of water have a *mutual potential energy* which depends upon the field of force. On dilution of an ionic solution, this potential energy decreases, and an amount of energy is released which is more than sufficient to overcome the inter-ionic forces. The total result is therefore a heat formation of about 3/10 of the heat absorption first expected (Bjerrum<sup>16</sup>). Recent, very exact measurements from Nernst's laboratory<sup>17 18</sup> together with experiments by Lange<sup>19</sup> and co-workers, clearly show an approach to this theoretical limiting law on increasing dilution. Table 2 gives a survey of the values for high dilutions, found in Nernst's laboratory.

The theoretical values given are calculated according to the following expression:

$$U_c = 418 \frac{\sqrt{c}}{1 + 0.327 a \sqrt{c}}$$

In this expression, the ionic diameter  $a$  was taken as 4 Ångström.  $U_c$  is the heat of dilution for one mole of salt at 18° C on diluting from  $c$  to 0.

Table 2. Heats of dilution after Naudé<sup>18</sup> at 18° C, the values expressed in *gal. per mole*

From	0.004 <i>N</i>	0.0133 <i>N</i>	0.1 <i>N</i>	0.333 <i>N</i>
to	0.002 <i>N</i>	0.0067 <i>N</i>	0.002 <i>N</i>	0.0067 <i>N</i>
theoretically	6.7	10.9	76	107
LiCl	7.7	8.6	83	128
NaCl	5.0	8.1	41	10.6
KCl	—	7.6	—	5.4
NaNO <sub>3</sub>	6.5	0.2	—10	—154
KNO <sub>3</sub>	4.0	—2.5	—94	—353

For concentrated aqueous solutions — whereby often must be understood solutions above 0.01 *N* — it has so far been impossible to carry out satisfactory calculations of the ionic coefficients and the heats of dilution. Firstly, we do not know with what  $D$  we have to reckon. The experimental determination of  $D$  of salt solutions is so difficult, owing to the conductivity of these solutions, that it has so far not been possible to obtain agreement with regard to the change in  $D$  of water upon addition of salt (*cf.*<sup>20</sup>). Besides, in more concentrated solutions the conditions prevailing in the vicinity of the ions play an important role, and it is for this reason necessary to take into account the ionic radii. Debye and Hückel have deduced an expression for the activity coefficient, in which the radius of the ions is introduced, and which in many cases leads to radii of the expected size. It follows, however, from their mathematical treatment that the expressions cannot be correct for small ions (Bjerrum<sup>21</sup>). It is possible to proceed further by distinguishing between the ions which are in the immediate proximity of each other and the rest of the ions<sup>21</sup>. Such a distinction between *associated* and *free* ions is, however, only to be considered as a mathematical artifice, with no chemical meaning, and neither this treatment, nor the use of elaborate graphical integration (H. Müller<sup>22</sup>), nor integration by power series (Gronwall, La Mer and Sandved<sup>23</sup>) met with definite success. The physical basis for all these calculations is, namely, the validity of Coulomb's law:  $K = \epsilon_1 \epsilon_2 / Da^2$ ; and for ions in close proximity to each other, it is certainly not permissible to introduce in this equation the macroscopically determined  $D$  of the solvent. For this reason

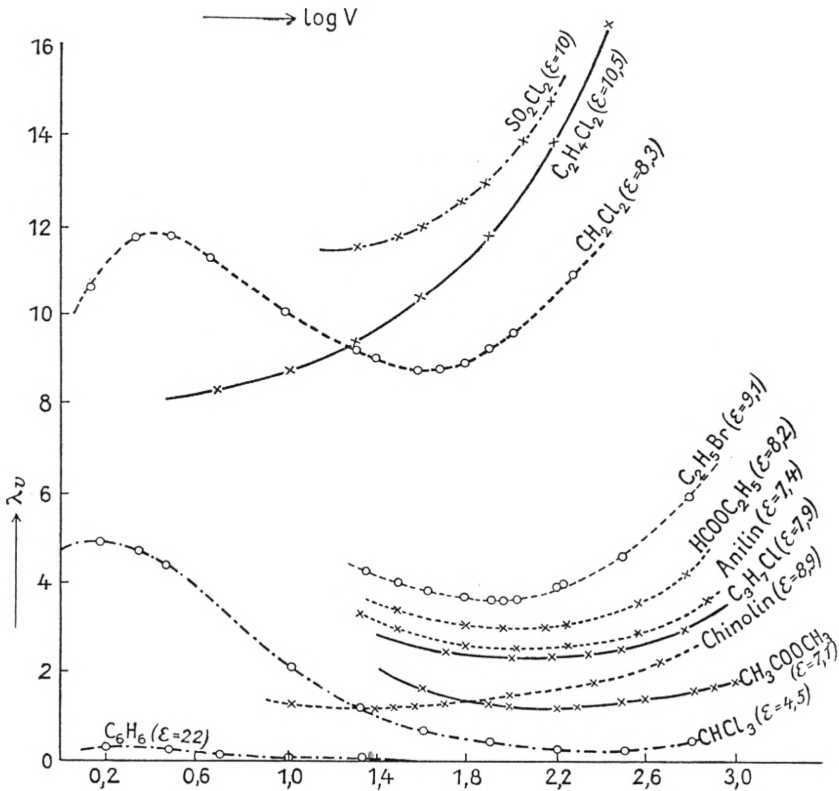


Fig. 1. Curves for the molar conductivity  $\lambda_v$  as a function of the dilution  $V$  and the nature of the solvent (after Walden<sup>25</sup>).

we cannot consider the ionic radii so far calculated as the true ionic radii. In agreement with this conclusion they are extremely dependent on the temperature. That in many cases, ionic radii of reasonable sizes have been calculated, is, in my opinion, partly a result of an accidental compensation of several disturbing factors. In case of the heats of dilution, large deviations from the theory appear even at very small concentrations (comp. table 2). No compensation occurs here.

Passing from water to solvents with lower dielectric constants, the inter-ionic forces increase and the above difficulties for an exact theory appear at even smaller ionic concentrations than in water. The Debye-Hückel limiting laws have, however, also proved useful here (Schreiner and Frivold<sup>24</sup>).

In solvents with very small dielectric constants the molar conductivity as a rule has a rather anomalous course. Fig. 1 shows according to Walden<sup>25</sup>, the molar conductivity of tetra-amyl-ammonium iodide in a series of solvents with  $D < 10.5$ . The conductivity first decreases normally with decreasing dilution, but

then passes a minimum and begins to rise again. The smaller the  $D$ , the smaller as a rule is the conductivity at the minimum, and the earlier is the minimum reached. This minimum has been the cause of much speculation and it has, a little unjustly, been considered an argument against the validity of modern electrolyte theories (Kraus<sup>26</sup>). In fact it should have been possible to predict the existence of this minimum from the new conceptions. In the vicinity of the minimum we have mainly binary ionic association, similar to that in salt vapour, and consequently a small conductivity. With decreasing concentration, the ions associate to a lesser degree and hence they conduct better. But also with increasing concentration does the conductivity rise, since here the ionic association becomes more general, ion aggregates of increasing size being formed as we approach the state of melted tetra-amyl-ammonium iodide, which shows the high conductivity characteristic of molten salts (*cf.*<sup>21</sup>).

Unfortunately it has so far been impossible to overcome the mathematical difficulties in developing a quantitative theory for these phenomena. The same is true of the quantitative calculation of the influences of inter-ionic forces on the properties of large colloid ions with many charges. But we can deduce qualitatively the laws of ion absorption on large colloid ions and the inhibitory effect of their charges upon coagulation, on the basis of the conception of the inter-ionic forces as put forward here.

#### IV

The explanation of the phenomenon of *solubility* is one of the most important problems in recent theories on electrolytes. The solubility is closely connected with the heat of solution and according to Fajans<sup>27</sup> the heat of solution in water can be expressed as the difference between the heat of hydration of the ions and the lattice energy of the solid salt. The lattice energy is the work expended in the dissolution of the ionic lattice into its individual ions, and the heat of hydration — or as I prefer to call it — the *heat of solution* of the ions is the heat evolved in the transfer of the separated ions to water.

This idea of Fajans can be further developed by combination with some expressions put forward by Born<sup>28</sup>.

On transferring a sphere of radius  $r$  and charge  $z\epsilon$  from vacuum to a dielectric, work is gained since the sphere is attracted by the dielectric. This work is equal to:

$$\frac{(z\epsilon)^2}{2r} \left( 1 - \frac{1}{D} \right).$$

Born now identifies this work with the experimental heats of solutions of the ions, and calculates their radii on this basis. Table 3 gives for 11 ions the experi-

mentally found heats of solution ( $W$ ) in water (Fajans's values, recalculated by Born) and the ionic radii calculated from these ( $r$  is given in Ångström). Below are the radii estimated by V. M. Goldschmidt<sup>10</sup> from measurements of crystals ( $r$  observed). Although the agreement between the calculated and the observed radii is not complete (the calculated values are on an average about 0.6 Å too large), it seems justifiable to explain the large heats of solution of the ions in water in terms of an effect of their electrical charge.

Table 3

	H+	Li+	Na+	K+	Rb+	Cs+	Tl+	Ca++	Cl-	Br-	I-
$W$ (kcal)	262	110	103	82	73	74	82	344	77	68	57
$r$ calc.	0.625	1.49	1.59	2.00	2.24	2.22	2.00	1.91	2.13	2.41	2.88
$r$ obs.	0	0.78	0.98	1.33	1.49	1.65	1.49	1.06	1.81	1.96	2.20

In the case of an electrolyte composed of two  $z$ -valent ions with radii  $r_1$  and  $r_2$  the ionic charges determine a work of solution of the magnitude:

$$\left( \frac{(z\epsilon)^2}{2r_1} + \frac{(z\epsilon)^2}{2r_2} \right) \left( 1 - \frac{1}{D} \right) K_1$$

We have taken the approximate nature of Born's expression into account by introducing a coefficient  $K_1$ . According to the data in table 3 this coefficient, for most ions in water, lies between 0.75 and 0.5.

The lattice energy of the salt is:

$$\frac{2(z\epsilon)^2}{r_1 + r_2} K_2$$

where  $K_2$  is a coefficient somewhat less than 1 and dependent upon the nature of the lattice.

Typical binary electrolytes can crystallize in three different lattices like those of cesium chloride, sodium chloride and zinc sulphide (zincblende). The structure of these three lattices is shown in fig. 2. According to Born the coefficient  $K_2$  is for the CsCl lattice 0.783, for the NaCl lattice 0.777 and for the zincblende lattice 0.72.

The work of solution due to the ionic charges, or as it can also be expressed, the *affinity of solution* due to the ionic charges, is given by:

$$\left( \frac{(z\epsilon)^2}{2r_1} + \frac{(z\epsilon)^2}{2r_2} \right) \left( 1 - \frac{1}{D} \right) K_1 - \frac{2(z\epsilon)^2}{r_1 + r_2} K_2$$



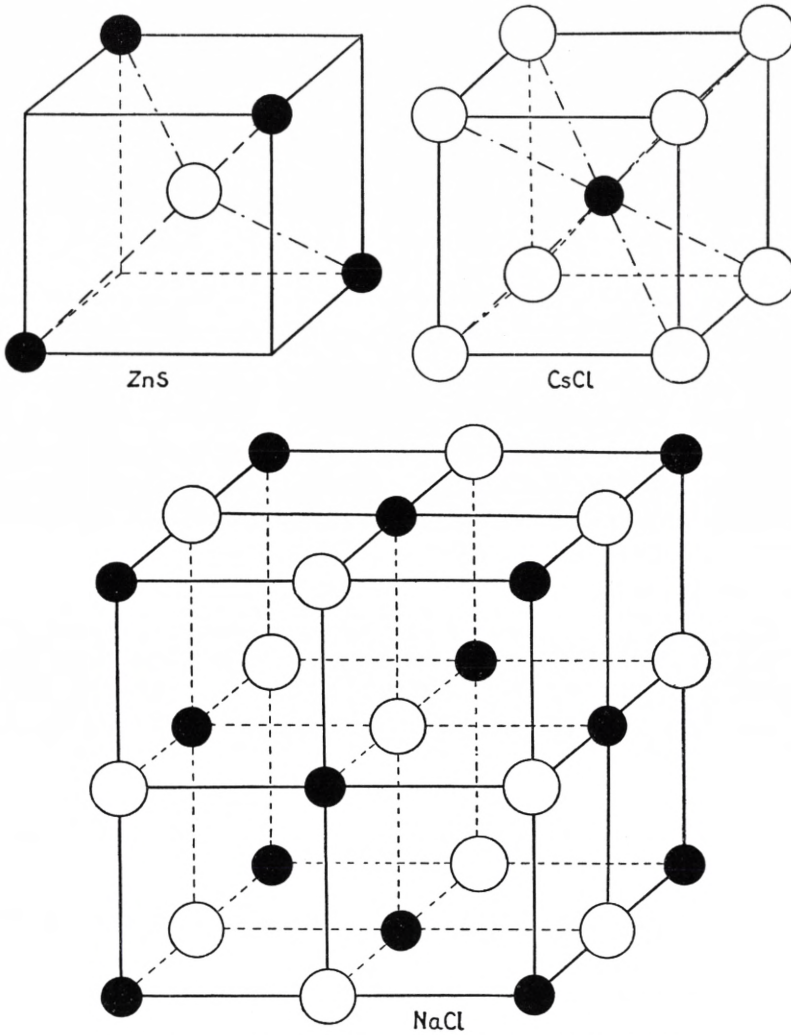


Fig. 2. Crystal lattices of CsCl, NaCl and ZnS (zincblende).

For water  $1 - \frac{1}{D}$  is approximately equal to 1. In this formula therefore the work of solution appears as a small difference between two large, insufficiently known figures, and hence it is difficult in this way to obtain a value for the electrical affinity of solution, which is accurate enough to enable an estimation of the solubility.

However, the formula is very valuable, all the same. The fact that its two terms are approximately of the same size for aqueous solutions explains the old

observation that *water is a good solvent for most salts*. In solvents with  $D$  less than that of water, the work of solution of the ions will be less than in water. Therefore with decreasing  $D$ , these solvents will have a decreasing capacity to dissolve salts.

If we confine ourselves to calculating the *relative solubilities in different solvents* (partition coefficients) the lattice energy is cancelled and only the variations of the work of solution of the ions have to be considered. If we assume that the ionic charges alone determine the solubilities, we arrive at the following expression<sup>29</sup>:

$$p = \log \frac{C_{\text{H}_2\text{O}}}{C_A} = \frac{z^2 \cdot 1.5}{r} \frac{D_{\text{H}_2\text{O}} - D_A}{D_A}$$

( $p$  partition exponent,  $C_{\text{H}_2\text{O}}$  and  $C_A$  solubilities in water and in A,  $z$  and  $r$  valency and radius (mean value in Ångström) of the ions,  $D_{\text{H}_2\text{O}}$  and  $D_A$ ,  $D$  of water and of A).

For potassium chloride in alcohol ( $z = 1$ ,  $r = 1.55\text{Å}$ ,  $D = 26$ )  $p$  is found equal to 2.0 against the experimental value 3.3. Considering that in the deduction of the formula we have neglected  $K_1$  and its variations, a better agreement can scarcely be expected. According to the formula the solubility of salts composed of ions with higher valencies should be especially diminished on passing from water to alcohol. This is also known to be the case, as the slight solubility in alcohol of sulphates and most other salts of di- and polyvalent ions would call to mind. We are at present carrying out investigations with the purpose of testing the above formula extensively. In these investigations, we take into consideration in the following way the presence of molecular forces other than those due to the electrical charges: we add to the above expression for the partition exponent  $p$  a term:

$$\log \frac{C_{\text{H}_2\text{O}'}}{C_{A'}}$$

in which  $C_{\text{H}_2\text{O}'}$  and  $C_{A'}$  are the solubilities in water and in A of a substance composed of particles similar to the ions, but uncharged. For the alkali and halogen ions, which have an electronic configuration like that of the inert gases, we may reckon with the solubilities of the corresponding inert gases, for a quaternary ammonium ion  $\text{NR}_4^+$  with the solubility of  $\text{CR}_4$  ( $\text{SiR}_4$  or  $\text{SnR}_4$ ), for large organic ions  $\text{R.COO}^-$  with the solubilities of the undissociated acids  $\text{R.COOH}$  etc.

As regards the difference between the solubilities of different salts only little indication of regularity has been found so far. Ephraim<sup>30</sup> and Fajans<sup>27</sup> have, however, both observed that *salts composed of ions of approximately the same size are comparatively slightly soluble*. Ephraim came to this conclusion by detailed

studies on complex salts, and Fajans by consideration of the solubility of alkali halides. In table 4 the solubilities of the alkali halides are surveyed. If we look at the solubilities of the potassium and rubidium salts, minima occur at KCl and RbBr, corresponding to the similar sizes of  $K^+$  and  $Cl^-$  and of  $Rb^+$  and  $Br^-$ . The least soluble of lithium and sodium salts are the fluorides, and of cesium salts the iodides, all in agreement with the Ephraim-Fajans's rule.

Table 4. Solubility of alkali halides. Moles per 1000 g  $H_2O$  at  $18^\circ C$ . If the solid salt contains water, its water content is given in parenthesis

	Li	Na	K	Rb	Cs
F	0.11	1.06	15.9 (2 aq)	12.7 (?)	24.2 (1.5 aq)
Cl	18.5 (1 aq)	6.14	4.6	7.34	10.9
Br	19.7 (2 aq)	8.6 (2 aq)	5.6	6.4	5.8
J	12.1 (3 aq)	11.9 (2 aq)	8.35	7.2	2.9

This rule of Ephraim-Fajans can be derived from our general expression for the electrical affinity of solution. If  $r_1 + r_2$  is kept constant, the work of solution of the ions is minimum and the lattice energy maximum for  $r_1 = r_2$ . Consequently the solubility must also be minimum when the ratio of the radii is equal to one.

That the work of solution of the ions is minimum when  $r_1 = r_2$  follows mathematically from the fact that it is in the form  $(1/r_1 + 1/r_2)$ . That the lattice energy reaches its highest value for  $r_1 = r_2$  is seen from the fact that preference is then given to the CsCl lattice which has the greatest lattice energy ( $K_2 = 0.783$ ). When  $r_1/r_2$  diverges from 1, first the NaCl lattice ( $K_2 = 0.777$ ) and later the zincblende lattice appears ( $K_2 = 0.72$ ). For  $r_1 + r_2$  constant, the lattice energy becomes smaller the more  $r_1/r_2$  deviates from 1. The connection between the lattice type and ratio of the radii has been pointed out mainly by V. M. Goldschmidt<sup>10</sup>.

In conclusion it can be stated, I think, that all the more general features of the solubility of strong electrolytes can be freely deduced from their ionic structure. Before, however, a direct calculation of the solubilities of the individual salts is possible there is much to be done. Firstly we must be able to take into account the more or less hypothetical solubility of the ions deprived of their charge, secondly the deformability of the ions in the lattices must be taken into consideration and thirdly, we must obtain a more detailed knowledge of the coefficient  $K_1$  in the expression for the electrical work of solution of the ions.

## V

Besides the strong electrolytes, the properties of which indicate complete dissociation, there are a large number of *weak electrolytes*, for which incomplete

ionization has to be assumed. In order to describe their properties, we use at the same time chemical degrees of dissociation and *physical coefficients*, which express the effects of the ionic charges.

Thus we write for the conductivity:

$$\frac{\mu}{\mu_{\infty}} = \alpha f_{\mu}$$

where  $\alpha$  is the degree of dissociation and  $f_{\mu}$  a coefficient accounting for the inter-ionic forces. For the active mass (the activity) we write:

$$\frac{A}{c} = \alpha f_A$$

where  $A$  is the active mass of the ion,  $c$  the concentration of the electrolyte,  $\alpha$  the degree of dissociation and  $f_A$  a coefficient accounting for the inter-ionic forces.

This treatment has been used since 1916 in my laboratory with good results<sup>13</sup>.

In the case of weak electrolytes, we therefore use at the same time a physical and a chemical method. It is difficult to draw a *completely sharp boundary* between the ranges of application of these two methods. As long as the physical method has only been slightly developed, we must be content with the more *summary chemical method*, even when it is probable that the physical treatment will later on be carried through. It was in such a boundary case, that I myself<sup>21</sup>, some years ago resorted to the *introduction of a degree of association* for nitrates and other salts. A similar case it is perhaps when Nernst in his recent paper on the heat of dilution of salt solutions, assumes the *existence of undissociated molecules* in the alkali chlorides and nitrates<sup>31</sup>.

In their interpretation of the refraction and light absorption in concentrated ionic solutions, Fajans<sup>32</sup> and v. Halban<sup>33</sup> have encountered difficulties in distinguishing between physical and chemical phenomena. Their investigations show that we have to expect the interionic forces to exert a considerable influence on the refraction and light absorption of the ions in concentrated solutions, and it has not been possible to distinguish with certainty between these influences and the effect of a possible incomplete ionization.

When, however, Kossel<sup>34</sup> considers even the *sulphate ion as a physical aggregate* of four negative oxygen ions and one positive sulphur ion, it is certainly going too far. In the sulphate ion, the properties of oxygen and sulphur ions have almost completely disappeared. Not only the reaction to light, which implies the configuration of the outer electrons, but also the reaction to X-rays, which implies the configuration of the inner electrons, show that the sulphur in the sulphate ion does not possess the properties of an independent positive sulphur ion. The K and L levels in the sulphur atom of the sulphate ion correspond

more nearly to those in sulphide, and do not at all possess the values which would have been expected for a free positive sulphur ion. The electrons from the oxygen ions in the sulphate ion must therefore in their penetration approach the positive sulphur nucleus almost as much as the eight external electrons in the sulphide ion<sup>35</sup>.

It is quite natural that the recent conquest by physicists of regions which had previously belonged to chemists, gives rise to the thought that the use of chemical methods is only an indication of the limitation of our physical understanding. The more able the physicists, the further they extend the boundaries of

Table 5. Equivalent conductance of the chlorides of the elements of the main groups at the melting point (after W. Biltz and W. Klemm<sup>37</sup>).

HCl ~ 10 <sup>-8</sup>					
LiCl 166	BeCl <sub>2</sub> 0.086	BCl <sub>3</sub> 0	CCl <sub>4</sub> 0		
NaCl 133.5	MgCl <sub>2</sub> 28.8	AlCl <sub>3</sub> 15.10 <sup>-6</sup>	SiCl <sub>4</sub> 0	PCl <sub>5</sub> 0	
KCl 103.5	CaCl <sub>2</sub> 57.9	ScCl <sub>3</sub> 15	TiCl <sub>4</sub> 0	VCl <sub>4</sub> 0	
RbCl 78.2	SrCl <sub>2</sub> 55.7	YCl <sub>3</sub> 9.5	ZrCl <sub>4</sub>	NbCl <sub>5</sub> $\kappa = 2 \cdot 10^{-7}$	MoCl <sub>5</sub> $\kappa = 1.8 \times 10^{-6}$
CsCl 66.7	BaCl <sub>2</sub> 64.6	LaCl <sub>3</sub> 29.0	HfCl <sub>4</sub>	TaCl <sub>5</sub> $\kappa = 3 \cdot 10^{-7}$	WCl <sub>6</sub> $\kappa = 2 \cdot 10^{-6}$
			ThCl <sub>4</sub> 16		UCl <sub>4</sub> $\kappa = 0.34$

physics and the less remains for the chemists. I believe, however, that the situation is not so unstable. The contrast between the rigid or slightly deformable ions of the strong electrolytes, and the ionic rudiments in complex ions, such as the sulphate ion, is so sharp that it is possible to maintain that there is a natural distinction between the two fields.

For salt vapours Franck and his co-workers<sup>38</sup> have been able, on the basis of absorption spectra, to distinguish clearly between the vapour of the alkali halides, which is composed of ion pairs, and that of silver halide, which is not composed of ions.

In table 5, the molar conductivities of the molten chlorides of the elements of the main groups are presented (after Biltz and Klemm<sup>37</sup>).

By looking at the table, it is easy to see, as Biltz himself stresses, that the chlo-

rides fall into two big groups, the ionic fluids with high conductivity and the molecular fluids with low conductivity.

Also in crystal lattices, we can seldom be in doubt as to whether an ionic lattice or a lattice of atoms or molecules is present, and in the same way the chemists are able in most cases to distinguish with considerable certainty between ionized double salts, such as the alums, and complex compounds, such as the iron cyanides.

Even in solution where the distinction is perhaps most difficult, the error in the determination of the degree of ionization seldom exceeds a few per cent.

On the other hand, I do not wish to maintain that it is impossible to describe the formation of a chemical compound from ions as a continuous, *physical process*. Water for one thing may be continuously transformed into vapour without our abandoning, for this reason, the clear distinction between liquid and vapour under normal conditions. In the same way it will certainly also be possible in the future to distinguish physical aggregates of ions from chemical compounds between ions.

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