THE VARIATION OF ELECTRICAL CONDUCTIVITY OF ELECTROLYTES WITH INCREASE IN CONCENTRATION

Professor Alfred W. Porter, D.Sc., F.R.S., introducing his own paper on "The Variation of Electrical Conductivity of Electrolytes with Increase in Concentration," said: I think one of the outstanding features of the discussion so far is the importance of the failure of the law of dilution, and the next important feature is that any attempts to get over the difficulties raised by it are of purely an empirical character. I have dealt with this matter in the paper which I am communicating this evening.

1. The outstanding difficulty in connection with the dissociation theory is the failure of Ostwald's dilution law in even moderately dilute (though perhaps not in exceedingly dilute) solutions of strong electrolytes. If the failure arose only in highly concentrated solutions there would be no occasion for surprise; it would be explicable in any or all the ways which have been brought forward to explain the march of osmotic pressure and vapour pressure with concentration. But the failure of the law in even dilute solutions seems to shut the door to this way of escape, and we are obliged to assume that there is something fundamentally wrong in applying to dissociation (except in the case of weak electrolytes) the principles of mass action in the same exceedingly simple way as to a mixture of a dissociating gas and the products of its dissociation. Until the precise change required to be made has been put forward, there has been nothing to do except to make empirical changes in the dilution law so as to bring it into accord with experiment. Most of these changes consist in altering the indices or adding terms to the simple dilution law

$$\frac{C_v^2}{C_s} = K \text{ (Ostwald)}$$

and many examples of this process of transformation are given in Captain Partington's paper. The results are rather bewildering, although in many cases they are satisfactory from the empirical point of view. If, however, empirical correspondence with fact is all that is desired, it is possible to obtain much simpler equations by departing altogether from the general form of the usual dilution law.

If $\log(\mu_\infty - \mu)$ is plotted against $\log c$, where c is the volume concentration, the curve obtained is a straight line, in many cases, from dilutions of 10,000 litres/gr. equivalent to 1 litre/gr. equivalent. Curves are given for LiCl and ZnCl₂ in Fig. 1. It will be observed that in spite of the different valency of the metal in the two cases the slope is the same for both. Its value is almost exactly 1/3. (LiCl = .32, ZnCl₂ = .33, NaNO₃ = .33, Na₂SO₄ increases up to .38). This rectilinearity of the curve shows that we can write—

$$\mu_\infty - \mu = \text{constant} \times c^{\frac{1}{3}}$$

or equally well

$$(1 - \alpha) = \text{constant} \times c_1^*.$$

* As pointed out in the meeting, this equation was first given by Kohlrausch (*Wied. Ann.*, 26, 161 (1885)), and is used for extrapolations to infinite dilution. I doubt if it is generally realized through how large a range it is often true. As

2. Amongst the empirical equations which have been put forward a special value is attached to van't Hoff's equation $a^3/(1-a)^2=KV$, and to the general equation $a/(1-a)^n=KV^{1-n}$ (Storch), of which it and Ostwald's are special cases. As to how nearly van't Hoff's equation

FIG. 1.

fits is exhibited in Fig. 2. It is specially noteworthy that the index n (given by the slope on the logarithmic diagram) is practically the same for KCl as for Na_2SO_4 in spite of the difference in valency. Storch's

FIG. 2.—Test of van't Hoff's equation.

general equation is specially attractive because it is the correct form, according to the law of mass action, for a possible reaction. It is rather to whether it really holds to infinite dilution is full of doubt owing to the increasing uncertainty in the value of $1-a$ as the dilution increases. But it certainly holds well in the middle region.

124 VARIATION OF ELECTRICAL CONDUCTIVITY :

remarkable that the particular reaction which makes $n=2/3$ (van't Hoff) has not yet been identified in spite of the enormous attention that has been paid to the question. In the case of very dilute solutions the law of mass action should be expected to be valid whatever uncertainty naturally relates to concentrated solutions. In reality the degree of dissociation, α , diminishes with increasing concentration, but it does not diminish as fast as the simple law of mass action requires. Any straightforward introduction of the consideration of electric forces would tend the wrong way; for the attraction between the two ions will increase with increasing concentration, and encourage the formation of complexes. Presumably this is why those who introduce the consideration of the electric actions between the ions postulate complete dissociation. The diminished ionisation with increase in concentration is then wholly to be attributed to the attractions; the fact that it does not diminish as fast as the law of mass action does not matter, for the law of mass action does not come in at all. The only other way is to attribute a more indirect effect to these attractions. For example, the formation of complexes, such as Grothus chains may promote dissociation due to collisions. The increased tendency to form such chains as the concentration increases will favour the subsequent formation of ions; thus the proportion of molecules that are dissociated will be greater than it otherwise would be. This tendency on the part of strong electrolytes to form complexes might be the distinguishing feature between strong and weak electrolytes. If so, the ground is removed from under Arrhenius' objection against those who explain the deviations by introducing the consideration of electric forces, that they "have not taken into consideration that some weak acids obey Ostwald's law even in such concentrated solutions that they contain a greater number of ions per unit volume than solutions of strong electrolytes, which show strong deviations from the same law."

Professor Porter (*communicated*): There are a few points on which I desire to say an extra word. I cannot bring myself to believe that a good case has been made out for the validity of Ostwald's law at extreme dilutions of strong electrolytes. The difficulties of the determination of the degree of ionisation in this region are so great that I share the scepticism of McBain, Dawson, Newbury, Philip, and others. Those who think that a good case has been made out for it have further to account for the transition from one law to another, when the concentration is increased. It certainly cannot be abrupt. Probably some law such as—

$$\frac{\alpha^2(1+b\alpha/V)}{(1-\alpha)(1+c(1-\alpha)/V)} = \text{constant}$$

would suit: where b and c are additional constants. This changes from Ostwald's form to van't Hoff's as V diminishes. I give it because it may suggest to some one the mechanism which is the source of all the trouble.

Dr. Lindemann thinks that it is the variation of the dielectric constant of the solution with increased concentration which disturbs the problem. But Ostwald's law certainly breaks down at concentrations in which the change in the dielectric constant is infinitesimal ($V=10,000$). Further, it appears to me that allowing for variation in the dielectric constant is only another way of taking into account the electric forces between

the ions which will tend rather to diminish ionisation below the mass-action value, instead of increase it, with increased concentration.

My objection to Mr. Bousfield's law of dilution is that it makes the degree of ionisation depend upon the absolute quantity of solution taken and not upon the concentration only, which we know to be the case. In this it sins in the same way as Rudolphi's equation (of which it is a modification), viz. :—

$$a^2/(1-a) = K(V)^{\frac{1}{2}}.$$

It was apparently this defect which made van 't Hoff look for and find a modified form which is free from it.

Such an equation cannot possibly be true. I have no objection against his modifying terms. The law of mass action in its simple form is only true for perfect gases or for particles which simulate the behaviour of perfect gases; and as the concentration increases the particles of solute differ more and more from this specification.

In regard to the evidence for or against hydration, I do not consider it safe to rely on the identity of the temperature variation of conductivity as an indication of it (Kohlrausch). The variation of viscosity with temperature is *roughly* an exponential law for most substances. To the fluidity I have fitted a curve of the type $(A+B/T)^n$ similar to Bertrand's equation for vapour pressures. Such a formula holds for substances as diverse as water and quasi-solid pitch, with the same index in both cases. Moreover, if we were considering the motion of large spheres in the solution the effective viscosity would be the same for different spheres provided that the liquid came to rest in contact with them in all cases. The problem of ions is much harder to discuss, and consequently it is harder to make any safe inference from Kohlrausch's observation.

I agree with Professor Philip that the identity of van 't Hoff's equation for both binary and ternary electrolytes is one of the most striking, and at the same time mysterious facts in the whole subject.

Jahn's name has been mentioned. I am rather surprised that explicit attention has not been called to his application of the thermodynamic potential,* in which allowance is made for mutual action between the two ions and between them and the solvent. The final form (approximate) is

$$\frac{n_i^2}{N-n_i} \exp. \left[-\frac{aN}{n} + n_i \left(\frac{2c-b}{n} \right) \right] = K$$

where n is the amount of solvent and the constants a , c , b , arise from mutual terms. The agreement with experiment is perhaps not as good as might be expected from the introduction of (effectively) two additional constants, but the equation only professes to be approximate. The values of K calculated for values of N , ranging from .3386 to .0254 for KCl are

.169 .166 .169 .179 .200 .203 .203* .187 .187 .206 .178 .172

The degree of success attained warrants one in expressing the hope that if we knew how to allow exactly for all the mutual actions (not only the electrical ones) that all the difficulties would vanish.

* *Grundriss der Electrochemie*, 2nd edit., p. 159.