

stresses or to the recent action of vegetation, are readily apparent.

The dinosaur field of Tendaguru is by no means yet worked out. One might almost say it has only been scratched. That future work will yield many duplicates of the species already found is only to be expected, but it would be a serious scientific loss to the world if the area were exploited on lines of only taking certain bones and abandoning all others to perish from exposure

simply because no immediate use can be made of the output. To cover up the bones again is not the same thing as leaving them untouched. In the circumstances, in view of the already considerable output, the preparation of which will take the British Museum some years, future field work at Tendaguru will be of a limited nature, and be carried on only in places where there is reason to believe in a possibility of different species being found.

Interionic Forces in a Completely Dissociated Electrolyte.¹

By H. HARTLEY, C.B.E., F.R.S.

ONE aspect of the solution problem which has lately come into prominence is the effect of the forces acting between electrically charged ions. Faraday was much impressed by what he called "the enormous electric power of each particle or atom of matter," that is, the large size of the ionic charge. Helmholtz in his Faraday Lecture gave a calculation showing that the attractive force between the electrical charges associated with equivalent quantities of oxygen and hydrogen is 71,000 billion times greater than the gravitational attraction between these masses. It would seem obvious that such forces as these must affect the behaviour of ions. However, the difficulties in the way of a mathematical analysis of the effects of the electrical forces between ions in solution were considerable, and the problem was not attacked successfully until thirty years later.

Sutherland in 1907 was the first to suggest that electrolytes were completely ionised at all concentrations and that the interionic forces were in part responsible for the change in equivalent conductivity with concentration. In 1909, Bjerrum found that the molecular colour of chromium solutions was independent of dilution in the absence of complex ions, and explained his results on the basis of complete dissociation. He pointed out that the old difficulty with regard to the Mass Law would be removed if the interionic forces were entirely responsible for the variation of the equivalent conductivity and of the molecular freezing-point depression with dilution, as there would be no question of any equilibrium between ions and molecules.

The theory was supported by the additive properties of solutions of electrolytes and by the small change in the heat of neutralisation of strong acids and bases with dilution. In 1912, Milner succeeded in calculating the freezing-point depression of an electrolyte at different concentrations on the assumption of complete dissociation, by taking into account the change in potential energy of the ions on dilution. He pointed out that as a result of the electrical forces between them they would be so distributed that on an average unlike ions would be closer together than like ions, and that consequently work must be done in separating them on dilution. His results showed that in dilute

solutions the change in the freezing-point depression with dilution could be ascribed entirely to the effect of interionic forces with a completely dissociated electrolyte.

In 1922, Debye and Hückel attacked the problem by fresh methods, starting from the same assumption of complete dissociation. By taking into account the unequal distribution of the ions, they were able to calculate approximately the freezing-point depression of salts of different valency types in very dilute aqueous solutions, although the calculated and observed values diverged at higher concentrations. But a matter of more immediate interest to us is their treatment of the conductivity problem on the basis of complete dissociation. They start from the same point of view as that of Milner, namely, that owing to the electrical forces between the ions there will be an excess of ions of opposite charge in the immediate neighbourhood of any single ion, as in the structure of a crystal of sodium chloride. Owing to the finite time which is necessary for the redistribution of the ions to take place round an ion that is in motion, there will always be an excess of ions of opposite sign in its rear, and hence it will be subject to a retardation when moving in an electric field. Further, as ions of opposite sign are moving in opposite directions and as both are supposed to carry with them a certain amount of solvent, the viscous resistance to the motion of the ions will be greater than if the solvent were at rest. Thus both these effects act in such a way as to reduce the speed of the ions. Assuming that at infinite dilution the ionic mobilities obey Stokes's equation, Debye and Hückel arrive at the expression

$$\frac{\lambda_o - \lambda_c}{\lambda_o} = \left(\frac{K_1}{D^{\frac{1}{2}}} w_1 + \frac{K_2}{D^{\frac{1}{2}}} w_2 b \right) \sqrt{vm},$$

where the term $\frac{K_1}{D^{\frac{1}{2}}} w_1$ represents the fall in conductivity due to the electrical retardation and $\frac{K_2}{D^{\frac{1}{2}}} w_2 b$ that due to the electrophoresis of the solvent.

K_1 and K_2 are universal constants for all solvents at the same temperature.

D is the dielectric constant of the solvent.

w_1 and w_2 are valency factors.

b is the average radius of the ions.

v is the number of ions per molecule.

m is the molecular concentration of electrolyte.

¹ Extract from the presidential address on "The Ionic Theory of Electrolytic Solutions," delivered at Oxford to the Science Masters' Association on Jan. 4.

Values of w_1 and w_2 for different salt types in which the anion and cation have equal mobilities are given in the following table. w_1 varies with the relative mobilities of the two ions; w_2 is independent of them.

VALUES OF VALENCY FACTORS.

Salt Type.	w_1 .	w_2 .
KCl	1	1
K_2SO_4	4.24	1.41
$MgSO_4$	8	2

It will be seen that the above equation is in general agreement with the experimental results for strong electrolytes, as the fall in λ is proportional to the square root of the concentration, and is dependent on the dielectric constant of the solvent and on the valencies of the ions. The best test of the theory is to see how nearly the equation enables us to calculate the conductivity of a salt in different solvents. The observed and calculated

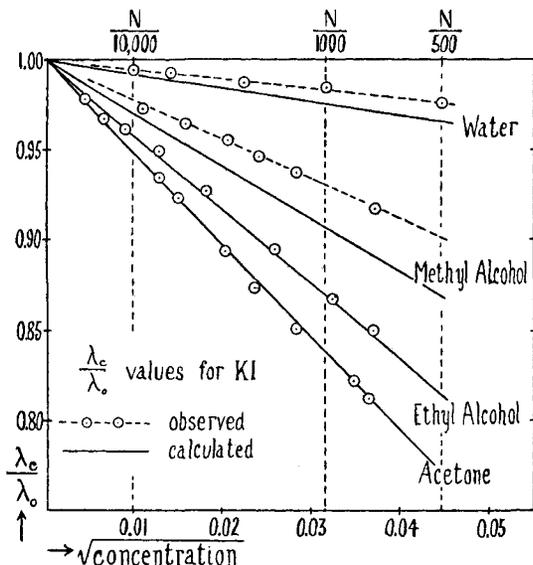


FIG. 1.

results for potassium iodide are plotted in Fig. 1, the values of b required being calculated by means of Stokes's equation from the mobilities of the ions at infinite dilution. In water and methyl alcohol the calculated slope of the λ_c/λ_0 curve is greater than the observed slope; in ethyl alcohol and acetone the agreement is very close. The salt was chosen at random; others would have given better agreement in some solvents and worse in others, but looking at the results generally,

it is a striking achievement that Debye and Hückel's theory is able to predict so closely the variation of the equivalent conductivity in dilute solutions in different solvents from a knowledge of the physical properties of the solvent and the mobilities of the two ions at infinite dilution.

The mathematical theory is not yet in a final form even for dilute solutions; it takes no account of the changes in the solvent due to the high pressures produced locally by the electrical attractions between the ions, or of the change in the dielectric constant with the concentration of electrolyte. There is, too, some uncertainty as to the exactness with which Stokes's equation is obeyed; nevertheless, in its present form it gives us ample support for the belief that strong electrolytes are completely dissociated in dilute solution, and that the interionic forces may be responsible for their changes in properties with dilution.

Even, however, in dilute salt solutions, specific chemical interaction between the ions may be of importance, in addition to the normal electrical attraction between them. It is true that in dilute aqueous solutions there is a surprisingly close agreement between the behaviour of salts of the same valency type, although the salts of mercury form a striking exception to the rest, but when we pass to non-aqueous solvents with a lower dielectric constant, the purely physical aspect of the ionic relationship becomes more limited in its application, while the specific interaction of the ions begins to play a more important part. For example, in water the slopes of the equivalent conductivity curves of uni-univalent salts are nearly the same, while in methyl alcohol the results are far less regular; most nitrates have a different slope from that of the chlorides, and the values for silver nitrate fall much more rapidly than those for any other salt.

These differences are too great to be accounted for, on Debye's theory, by differences in the sizes or relative mobilities of the ions; and they indicate in some cases incomplete dissociation owing to interaction between the ions. With divalent ions the discrepancies in non-aqueous solvents are still more marked. In methyl alcohol, calcium chloride and perchlorate are normal in slope while calcium nitrate behaves like a weak electrolyte; with zinc, on the other hand, the perchlorate and nitrate are normal while the chloride is abnormal. Whether this is due to the formation of complex ions or of molecules is not yet known, but it is evident that in dilute non-aqueous solutions the specific interactions of the ions—in fact, their chemical affinities—may dominate the situation.

Obituary.

SIR GEORGE GREENHILL, F.R.S.

THE death of Sir George Greenhill will be greatly regretted by some generations of Artillery officers who were instructed by him in the mathematics of their profession as they passed through the 'Advanced Class' of the school at Woolwich which has had several names but is now known as

the Artillery College. When the present writer joined that class in the spring of 1880, Greenhill had already been the mathematical professor there for several years. He went there after a short service at Coopers Hill and followed in succession Bashforth, Hirst, and Niven.

Good judges have been of opinion that Greenhill