

IONISATION AND THE MASS LAW.

Dr. H. M. Dawson (Leeds University) sent in a paper entitled
"Ionisation and the Mass Law."

The so-called anomaly of the strong electrolytes is not unjustly regarded as the *bête noire* of the ionisation theory as formulated by Arrhenius. No generally accepted interpretation of the behaviour of these substances has yet been put forward, and the difficulties presented by the very large deviations from the requirements of the mass law at moderate dilutions have led various authors—Sutherland,* Milner,† Ghosh ‡—to reject the theory that the strong electrolytes are ionised to an extent which depends on the concentration, and to substitute for this the hypothesis of complete ionisation. Whatever may be the merits of this hypothesis in its application to salts and similar substances, it fails to give an adequate explanation of the transition electrolytes. The polarity of electrolytes is not such as to permit of a sharp division into weak electrolytes, which apparently conform to the requirements of the mass law over a wide range of concentration, and strong electrolytes which exhibit widely divergent behaviour. On the contrary, the available evidence is in favour of the view that there is a gradual and continuous series of intermediate electrolytes which bridge the gap between the compounds of weak polar character and those of the salt group. For this reason, the writer is inclined to seek for an explanation of the anomalies of the salt group of electrolytes on the basis of the original ionic hypothesis.

In the measurement of the degree of ionisation of electrolytes, methods have been used which depend on the measurement of electrical conductivity, osmotic pressure (more particularly depression of freezing-point), contact potential, and of distribution between immiscible liquids. Without entering into a discussion of the relative merits of the different methods, it is sufficient for the present purpose to recognize that the conductivity method is the only one which has been used at all extensively, and that this is generally supposed to afford a trustworthy means of arriving at the degree of ionisation,

In regard to the method in question, the writer would refer to two points. The first of these is concerned with the accuracy of the measurement of conductivity by the Kohlrausch method. Since the introduction of the Lummer-Kurlbaum platinizing solution the method has been credited with a high order of precision, and recent improvements by American investigators are said to have raised the accuracy so as to give measurements in which the error is only about ± 0.01 per cent. Such measurements are said to have established the validity of the mass law for uni-univalent salts at very high dilutions, thus confirming the view previously expressed by Arrhenius on the basis of the suitably

* *Phil. Mag.*, 1902 [vi.], 3, 161, and subsequent papers.

† *Ibid.*, 1918 [vi.], 35, 214, 352.

‡ *J. Chem. Soc.*, 1918, 113, 449, 627, 707, 790.

corrected numbers obtained by Kohlrausch and Maltby. The validity of this conclusion is intimately bound up with the question of the degree of approximation of the best available conductance data to the true values. Reproducibility of results by the use of a particular form of apparatus affords no guarantee that such results represent the true values, and it is by no means certain that the Kohlrausch method is entirely free from errors of method. This point has quite recently been raised by Newbery,* who, by a method analogous to that employed in measuring the resistance of metallic conductors, has determined the conductance of a number of electrolytes and compared the results with those obtained by the Kohlrausch method. The differences revealed afford considerable support for the view that the conductivity of solutions cannot be measured with the accuracy which is commonly assumed.

It is not suggested that errors of experiment can be made responsible for the observed deviations of strong electrolytes from the mass law. In my opinion, these are mainly due to the changes which these highly polar compounds produce in the ionising power of the solvent medium. It is probable that the dielectric capacity of these compounds or of the compounds to which they give rise by interaction with the solvent is relatively very large. The addition of such compounds to a solvent of relatively low dielectric capacity will thus tend to make the polar solute more highly ionised than it would be if the ionisation were entirely due to the influence of the solvent. The magnitude of this auto-ionising influence may be expected to depend on the polarity of the solute and of the solvent, the effect of the solute being most clearly marked when the solute is a strongly polar compound and the solvent is practically non-polar. Sachanov's observations† on the behaviour of salts in solvents of low dielectric capacity show pretty clearly that electrolytes exert an ionising action on one another which is considerable in magnitude, and the accumulation of further data of this nature will probably serve to throw further light on the anomaly of the strong electrolytes

* *J. Chem. Soc.*, 1918, **113**, 701.

† *Zeit. phys. Chem.*, 1914, **87**, 441.