INTRODUCTORY ADDRESS ON "THE ELECTROLYTIC DISSOCIATION THEORY."

By GEORGE SENTER.

The electrolytic dissociation theory was put forward by Arrhenius in 1887. Although at first the theory met with much opposition, due partly to misunderstanding, the striking verification of its consequences led in time to its general acceptance, and during the intervening period of over thirty years it has stimulated investigation to a remarkable extent and has contributed enormously to the progress of chemistry and the allied sciences, including physics, geology, and the biological sciences.

When Arrhenius first put forward his views it was clearly recognized that the ionisation theory raised many problems and certain difficulties for the solution of which much more experimental investigation was necessary. Among the difficulties was the fact that the so-called " strong " electrolytes did not follow the law of mass action, and also the observation of Ostwald and Arrhenius that whereas the catalytic activity of weak acids was diminished by the addition of neutral salts with an ion in common with that of the acid, in accordance with the law of mass action, the catalytic activity of strong acids was increased by the addition of salts with a common ion. Other problems were the exact determination of the degree of ionisation, including a comparison of the results obtained by osmotic and electrical conductivity methods ; the question of the mechanism of ionisation, which involved investigations with solvents other than water ; the question of " hydration " or, more generally, " solvation " of the ions ; the electromotive activity of the ions ; the chemical activity of the ions, and the relationship between colour (more generally absorption spectrum) and constitution of electrolytes. All these problems have now been brought much nearer solution, and some of them have been practically solved. Among the outstanding achievements in this field may be mentioned (1) Nernst's theory of electromotive force ; (2) the enunciation by J. J. Thomson and Nernst independently (1893) of the rule that the ionising power of a solvent is closely connected with its dielectric constant ; (3) the comprehensive investigations of Walden on the connection between ionising power and other properties of solvents ; (4) the admirable experimental investigations of A. A. Noyes, Washburn, and their collaborators in America on the exact degree of ionisation of strong electrolytes. In this paper it is only possible to deal briefly with two or three of the above topics.

Hydration in Solution.

In the earlier days of the ionisation theory the solvent was often regarded simply as a medium for ionisation of the solute and not as playing any direct part in the process of ionisation. As early as 1891, however, Van der Waals * had suggested that ionisation in aqueous solution is essentially a hydration process—that it is the affinity between ions and solvent which effects the rupture of the molecule and that the energy required for ionisation comes from the heat of hydration of the ions. It is now generally agreed that most ions in aqueous solution are associated with water molecules to a greater or less extent,† but there is still no conclusive evidence that hydration, or more generally solvation, is the determining factor in ionisation. Moreover, none of the many attempts made to obtain quantitative measurements of the degree of hydration of the ions has hitherto met with general acceptance. Most of the methods are based on the assumption that the deviation of some property of the solution from a simple law is due to association of solvent and solute, but no trustworthy evidence is brought forward to show that the whole of the deviation in question is due to this cause. Several

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* Van der Waals, *Zeit. phys. Chem.*, 1891, **8**, 215.

† For summaries of the evidence on this point see Baur, *Ahrens' Sammlung*, 1903, **8**, 466 ; Senter, *Trans. Faraday Soc.*, 1907, **3**, 24. Cf. also Philip, *Trans. Chem. Soc.*, 1907 **91**, 711.

investigators have attempted * to calculate hydration values from the mobilities of the ions by application of Stokes's law regarding the motion of a sphere in a medium of considerable resistance, but their conclusions are not in good agreement.

One of the most promising methods of investigation in this field is based on the determination of the amount of solvent transported with the ions during electrolysis. Washburn † used for this purpose a suitable non-electrolyte as reference substance, and Remy ‡ measured directly the changes in volume of the anode and cathode solutions. It is evident that this method in the first instance only affords information as to the *relative* ionic hydrations of anion and cation, and certain assumptions have to be made in order to obtain absolute values for the hydration of any one ion under definite conditions. For this and other reasons the results obtained cannot be regarded as conclusive.

The Deviation of Strong Electrolytes from the Law of Mass Action.

From its earliest days the ionisation theory was faced with the difficulty that the ionic equilibrium in solutions of so-called strong electrolytes did not follow the law of mass action, which applies so accurately to weak electrolytes (e.g. organic acids). The deviation from the dilution law is such that for uni-univalent electrolytes § the dissociation "constant" K of the equation

$$\frac{a^2c}{(1-a)}=K \quad \text{or} \quad \frac{C_i^2}{C_u}=K$$

(a=degree of dissociation; c=total concentration; C_i=concentration of ion; C_u=concentration of non-ionised part) increases rapidly as the concentration of the solution is increased. Otherwise expressed, the ionisation of strong electrolytes increases more rapidly with increased concentration than would be the case if the law of mass action were accurately followed. As is well known, a formula of the type $\frac{C_i^n}{C_u}=K$, where n is about 1·4, represents with a considerable degree of accuracy the variation of the dissociation of many strong electrolytes with the concentration.

It might at first sight be supposed that the deviation from the law of mass action is due to inaccurate determination of the dissociation factor a. This is a very unlikely explanation, however, as Noyes and his collaborators have shown that for many of the most accurately investigated salts the values of a as determined by freezing-point and electrical conductivity methods—which are based on entirely different principles—are in very close agreement, and in neither case is the dilution law even approximately valid.

Within recent years much attention has been devoted to the elimination of errors in the determination of the degree of ionisation. As regards the conductivity method, two chief sources of uncertainty are the alteration of viscosity of the solution with varying concentrations and the effect of impurities in the solvent, usually water. The viscosity

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* Bousfield, *Zeit. phys. Chem.*, 1905, **53**, 301; Riesenfeld and Reinhold, ibid., 1909, **66**, 672; Remy, ibid., 1915, **89**, 467.

† *Tech. Quart.*, 1908, **21**, 288.

‡ *Zeit. phys. Chem.*, 1915, **89**, 529.

§ Both anion and cation univalent, e.g. KCl.

correction has been fully discussed by Kraus,* and it is shown that in many cases the formula

$$\alpha = \frac{\Lambda_v \eta}{\Lambda_\infty \eta_v}$$

(Λ_v=equivalent conductivity at dilution v, and Λ_∞ =limiting equivalent conductivity; η and η_v=viscosities of pure solvent and of solution) gives satisfactory results.

The effect of traces of impurity in the solvent gives rise to uncertainty as regards the values of Λ_v in dilute solution and particularly as regards the value of Λ_∞. This question has been very thoroughly discussed by Arrhenius.† After correcting for the slight conductivity of the solvent on the assumption that it is chiefly due to carbon dioxide, he arrives at the important conclusion that uni-univalent salts follow the dilution law in very dilute solution up to a concentration of 0·0002 molar, and that they all have the same ionisation constant (experimental data of Kohlrausch and Maltby). The correction to be applied for impurities in the solvent has also been discussed by Kraus and Bray,‡ by Wegscheider,§ by Bousfield,|| and very fully by Kendall,¶ and all agree that strong electrolytes obey the law of mass action in sufficiently dilute solution. This conclusion is a very probable one on general grounds, and, indeed, would appear to follow from thermodynamical considerations.

There is, however, a good deal of uncertainty in correcting for the conductivity of the solvent, and it would clearly be of great advantage to use solvents of such a high degree of purity that the correction in question becomes practically negligible in very dilute solution. This important advance has recently been made by Washburn.** Water of specific conductivity 0·05–0·07 $\times 10^{-6}$ reciprocal ohms at 18° was prepared by a method similar to that recently described by Bourdillon,†† a quartz distilling flash and receiver and block-tin condenser being used, and conductivity measurements with potassium chloride between the concentrations of 0·00001 and 0·001 molar under such conditions that the solutions came into contact only with quartz or platinum. The law of mass action was followed within the limits of experimental error up to a concentration of about 0·00007 molar, the dissociation constant K being 0·02; between 0·00007 molar and 0·001 molar, K increased regularly up to a value of 0·052 at the latter concentration. The results of further investigations on these lines will be awaited with great interest.

In connection with a possible explanation of the deviation of strong electrolytes from the dilution law, it is important to decide whether the abnormal behaviour is due to the ions, to the non-ionised molecules, or to both. In this connection it is instructive to consider the "active masses" or "activities" of the ions and molecules concerned, the activity being defined as the effective concentration which would enable the mass action law to hold accurately.‡‡ If we regard the ionisation formula

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* *J. Amer. Chem. Soc.*, 1914, **36**, 35; compare Bousfield and Lowry, *Proc. Roy. Soc.*, 1902, **71**, 48.

† *Medd. K. Akad. Nobelinstitut.*, 1913, **2**, No. 42.

‡ *J. Amer. Chem. Soc.*, 1915, **35**, 1413.

§ *Zeit. phys. Chem.*, 1909, **69**, 621.

|| *J. Chem. Soc.*, 1913, **103**, 310.

¶ *J. Amer. Chem. Soc.*, 1916, **38**, 1480, 2460; 1917, **39**, 9.

** Ibid., 1918, **40**, 106; Weiland, ibid., 1918, **40**, 131.

†† *J. Chem. Soc.*, 1913, **103**, 191.

‡‡ G. N. Lewis, *Zeit. phys. Chem.*, 1907, **61**, 129; *Proc. Amer. Acad.*, 1907, **43**, 259.

from this point of view, it is evident that, assuming that the relative concentrations of ions and molecules have been accurately determined, the increase of the dissociation "constant" k_1 with the concentration must be due to one of the following causes: (1) the activity of one or both of the ions must increase less rapidly than their respective concentrations; (2) the activity of the non-ionised molecule must increase more rapidly than its concentration; (3) a combination of both factors may occur. In sufficiently dilute solution the activity of an ion or molecule is of course proportional to its concentration, and the law of mass action holds.

It has now been shown by Noyes and his collaborators * that the product of the concentration of the ions of a saturated solution of a sparingly soluble salt increases slightly, and the concentration of the non-ionised salt diminishes considerably, when a salt with an ion in common with the sparingly soluble salt is added in progressively increasing quantity to the solution. It appears, therefore, that the deviation of strong electrolytes from the law of mass action is to be ascribed mainly to the abnormal behaviour of the non-ionised molecules. James Walker † has reached a similar conclusion on kinetic grounds. Since in the case of non-electrolytes the activity is proportional to the concentration, the different behaviour of non-electrolytes in salt solutions must be connected with the presence of ions. In this connection it is interesting to note that it is the total ion concentration in the mixture which primarily determines the degree of ionisation of uni-univalent salts. Another important conclusion, closely related to the above, is that the a values for all uni-univalent salts are nearly identical, from which the conclusion may be drawn that the cause which determines the deviation of strong electrolytes from the law of mass action is largely independent of the nature of the ions.

Recent investigations by Walden ‡ on the dielectric constants of dissolved salts lead him to consider the problem of strong electrolytes from a different standpoint. He finds that when salts are dissolved in solvents with small dielectric constants the magnitude of the latter property is considerably increased, and hence he draws the conclusion that salts increase the dielectric constant and the degree of dissociation of water, and therefore its ionising power. In favour of this view he cites the conclusion of Arrhenius that weak acids are more highly ionised in salt solutions than in water. McBain and Coleman § have shown, however, that the increased catalytic activity of weak acids due to the addition of salts, on which Arrhenius based his conclusions, can be more satisfactorily accounted for on the view that the undissociated strong acid, formed by interaction of the $H^\cdot$ ions of the weak acid and the anions of the salt, has also a catalytic effect (cf. p. 16). This conclusion, that the presence of neutral salts does not increase the ionisation of weak acids, is in harmony with the observation of Poma and Tanzi || that the ionisation of water is not increased, but in fact diminished, by the presence of neutral salts. McBain and Coleman discuss other evidence

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* A. A. Noyes and W. C. Bray, *J. Amer. Chem. Soc.*, 1911, **33**, 1643; A. A. Noyes, C. R. Boggs, F. S. Farrell, ibid., 1911, **33**, 1650; W. C. Bray and W. J. Winninghoff, ibid., 1911, **33**, 1663; W. C. Bray, ibid., 1911, **33**, 1643–1649.

† J. Walker, *B.A. Reports*, 1911, **81**, 349.

‡ *J. Amer. Chem. Soc.*, 1913, **35**, 1649; compare A. Sachanov, *Zeit. phys. Chem.*, 1914, **87**, 441.

§ *J. Chem. Soc.*, 1914, **105**, 1517.

|| *Zeit. phys. Chem.*, 1912, **79**, 55.

which has been advanced in favour of the view that salts increase the ionisation of weak acids and bases, and show that in no case is it convincing. These considerations appear to have some bearing on the equation deduced some years ago by Partington,* on the basis of a suggestion by Larmor that the ions in an electrolytic solution by their collision with neutral molecules may facilitate the dissociation of the latter. The experimental evidence does not appear favourable to the existence of the effect suggested by Larmor.

It is unnecessary to consider here the various formulæ which have been suggested from time to time to represent the relationship between degree of dissociation and concentration of strong electrolytes. The one which has met with most acceptance was put forward independently by McDougall † and by Kraus and Bray,‡ and is as follows:—

$$\frac{(\alpha c)^2}{(1-\alpha c)}=K+D(\alpha c)^m,$$

where K, D, and m are constants for any one electrolyte. This formula is very widely applicable to solutions in solvents other than water, but does not appear to give very satisfactory results for aqueous solutions.§

The main aspects of the problem of strong electrolytes have now been discussed. In addition to the proposed explanations already briefly mentioned, Jahn ‖ and G. N. Lewis¶ have put forward the view that the deviation from the mass law is to be ascribed to an increase in the ionic mobility with increasing ionic concentration. It has been suggested that the formation of complex ions may play a part in the phenomenon, but an explanation on these lines appears to be out of the question in the case of uni-univalent salts. Moreover, the fact that the deviations from the mass action law occur in such high dilutions would appear to be difficult to reconcile with any explanation based on association between solvent and solute.

The most logical way of dealing with the problem would appear to be the systematic investigation of possible disturbing effects, including the influence of the ions on each other and on the non-ionised part of the molecules, as well as the mutual influence between ions and solvent, and, as we have seen, considerable progress has already been made along these lines. It would appear from the foregoing considerations that the influence of the ions on the undissociated part of the molecules is of special importance in this connection.

Chemical Activity of Ions and Non-ionised Molecules.

For many years after the enunciation of the electrolytic dissociation theory it was assumed by the supporters of the theory that, at least as far as electrolytes are concerned, only ions enter appreciably into reaction. Evidence that when electrolytes (acids, bases, salts) enter into chemical reaction either the ions or the undissociated molecules or both simultaneously may undergo chemical change was put forward independently and almost simultaneously by the author ** (April, 1907) and by

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* *J. Chem. Soc.*, 1910, **97**, 1158.

† *J. Amer. Chem. Soc.*, 1912, **34**, 855.

‡ Ibid., 1913, **35**, 1315.

§ Washburn, loc. cit.

‖ Jahn, *Zeit. phys. Chem.*, 1900, **33**, 545.

¶ G. N. Lewis, *J. Amer. Chem. Soc.*, 1912, **34**, 1631.

** Senter, *J. Chem. Soc.*, 1907, **91**, 460.

Acree and Johnson [*] (September, 1907). In the author's paper just cited the methods which may be used to decide as to the relative part taken in the total change by the ions and non-ionised molecules are described and applied to the case of an acid and of a salt. As an example, the reaction between bromopropionic acid and water, represented by the equation

$$CH_3CHBrCOOH + H_2O \longrightarrow CH_3CHOHCOOH + HBr,$$

may be considered,[†] the question being whether the reaction proceeds by interaction between water and the $CH_3CHBrCO_2{}'$ ion, between water and the undissociated molecule $CH_8CHBrCO_2H$, or in both ways simultaneously. The rate of interaction of the undissociated acid with water may be obtained by adding to the solution excess of hydrobromic acid, which diminishes the ionisation of the bromopropionic acid to such an extent that the effect of the $CH_3CHBrCO_2{}'$ ion is negligible. The reaction velocity of the $CH_3CHBrCO_2{}'$ ion with water can be obtained by observations with the sodium salt, and it is found that the rate of the reaction between the acid and water can be *quantitatively* accounted for on the assumption that both ions and undissociated molecules react. In the author's first paper on the subject it was also shown that a salt may react simultaneously with water and with OH' ions. Many other illustrations are given in communications by the author and by Acree, and the important conclusion that ions and undissociated molecules may simultaneously undergo chemical change may be regarded as established.

A different aspect of the same subject is met with in considering the catalytic activity of acids. On the basis of the earlier investigations of Arrhenius it was long assumed that only the $H^{\cdot}$ ions are catalytically active, but the fact that neutral salts increase the catalytic activity of strong acids remained unexplained. Lapworth [‡] was the first to apply the above considerations regarding the chemical activity of non-ionised molecules to this particular instance. He suggested, but without adducing experimental evidence, that the effect of neutral salts on the catalytic activity of strong acids could be accounted for on the assumption that the non-ionised constituent of the acid also takes part in the change. Later, experimental evidence in favour of the view that the non-ionised acid as well as the $H^{\cdot}$ ions play a part in the catalytic activity of strong acids has been adduced by Goldschmidt,[§] Bredig, with Miller, Braune and Snethlage,[||] Arrhenius,[¶] Taylor,[**] Dawson,[††] and others, and it is now generally accepted.

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[*] Acree and Johnson, *Amer. Chem. J.*, 1907, **38**, 258.

[†] Senter, *J. Chem. Soc.*, 1909, **95**, 1827; Senter and Porter, ibid., 1911, **99**, 1049.

[‡] *J. Chem. Soc.*, 1908, **93**, 2187; cf. ibid., 1915, **107**, 857.

[§] *Zeit. Elektrochem.*, 1909, **15**, 6; Goldschmidt and Thuesen, ibid., 1912, **18**, 39.

[||] Ibid., 1912, **18**, 535, 539; *Zeit. phys. Chem.*, 1913, **85**, 211.

[¶] *J. Chem. Soc.*, 1914, **105**, 1424.

[**] *Medd. K. Vetenskapsakad. Nobelinst.*, 1913, **2**, Nos. 34, 35, and 37; 1914, **3**, No. 1.

[††] Dawson and Crann, *J. Chem. Soc.*, 1916, **109**, 1262, and previous papers.

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