ELECTROLYTIC DISSOCIATION.

Professor Svante Arrhenius (The Nobel Institute, Stockholm) sent in a paper in which he summarized the present evidence in favour of the dissociation theory of solution.

1. *Evidence from Analytical Chemistry.*—There are four fundamentals upon which the idea of a dissociation of electrolytes (i.e. salts, acids, and bases) into their ions is built up. These four are the additive properties, the electric conductivities, the freezing-points, and the catalytic actions of electrolytes. That which has won the adhesion of most chemists is the rational explanation of analytical chemistry which is here given. All salts which belong to the group of chlorides give the same reactions which in olden times were said to be characteristic of chlorine. The most familiar of these reactions is that with any silver salt in aqueous solution—in most cases silver nitrate is used for analytical purposes— which gives a characteristic cheese-like precipitation of silver chloride. But it is not true that the said reaction is characteristic of all substances containing chlorine ; for instance, chlorates, perchlorates, a great number of inorganic chlorine-containing compounds of metals, examined by Werner and his school, as well as most organic chlorine compounds, do not show this characteristic reaction. All the chlorine compounds which show it are characterized thereby in that, on being electrolysed, they give chlorine as an ion ; the other chlorine compounds are either not conductors of electricity when dissolved in water, or, if they are, they do not give chlorine as an ion.

This peculiarity was absolutely inexplicable on the old chemical theories, and there is no other explanation than that salts, and in general electrolytes, when dissolved in water, alcohol, or another solvent, are partially decomposed into their ions, e.g. sodium chloride into sodium ions and chlorine ions, and that each ion has its own characteristic reaction.

Also a very well known fact of quantitative analytical chemistry speaks in favour of the dissociation theory. The characteristic reagents for barium salts are sulphates, which give a nearly insoluble precipitate, barium sulphate, when they are added to an aqueous solution of a barium salt. The analytical chemist, who wishes to precipitate the dissolved barium as completely as possible, adds his sulphate solution in excess. The barium sulphate is the less soluble the greater the content of sulphate ions in the solution. This behaviour can be explained only in the following manner. The barium ion and the sulphate ion in the mixed solutions give barium sulphate, with which they are in equilibrium. This barium sulphate is only soluble to a certain degree at a given temperature ; the excess becomes precipitated. This quantity of barium sulphate may exist in a solution in presence of a certain quantity of sulphate ions and

of barium ions, but the greater the quantity of the sulphate ions present, the less is the quantity of barium ions in the equilibrium. The barium ion is therefore precipitated by the sulphate ion the more completely the greater the quantity of sulphate ion added. Evidently this equilibrium between barium-sulphate barium-ion in the solution and sulphate ion cannot be understood if the barium ion and the common constituent of all sulphates, SO_4, are not free from each other.

In reality the theory of electrolytic dissociation has furnished analytical chemistry with a leading principle which it lacked before. The great practical importance of chemical analysis gives the strongest support to the theory of electrolytic dissociation.

2. *Additive Properties.*—The aforementioned behaviour of electrolytes is a special instance of the so-called additive properties of this important class of substances. These additive properties had for a long time attracted the attention of physico-chemists. Valson in 1870 showed that the capillarity and the specific gravity of a salt solution might be regarded as the sum of three characteristic magnitudes, the first having reference to the solvent—he used water as solvent—the second to the positive ion (metal) of the salt, and the third to its negative ion. Such additive properties have been investigated in great numbers, as may be seen from any text-book of physical chemistry, and in general it may be maintained that any property of a dilute solution is additive. The solution behaves as if it contained, besides the solvent, two independent substances—the metal ion of the salt and its negative ion (the rest of the salt).

Amongst these properties there was one which had interested chemists in a high degree, namely, the heat evolved on the formation of a salt in a mixture of the dilute solutions of the corresponding basis and acid. If these are strong, the said heat is 13·4 great calories per gram-equivalent. The well-known explanation of this fact was given in 1884 and favoured the acceptance of the dissociation theory in a high degree.

It was to be expected that the opponents of our theory would attack the doctrine of the additive properties. Thus, for instance, Eilhard Wiedemann in 1891 asserted that the heat of replacement of bromine in dissolved potassium bromide through chlorine introduced as gas is the same as the corresponding quantity for any dissolved bromide, e.g. hydrobromic acid. By means of the thermochemical data of Thomsen and Berthelot I showed that the deviations from additivity in Wiedemann's case are about seventy times as great as for the heats of neutralization.

Another such objection was raised by Kahlenberg, who urged that double decompositions between salts occur not only in aqueous solutions, which are conductors for electricity, thus indicating electrolytic dissociation, but as well in solutions of, e.g. benzene, which were said to be non-conductors. This last assertion was disproved by Allen, Cady and Lichtenwalter, who investigated the reactions indicated by Kahlenberg more accurately.*

3. *The Diffusion of Electrolytes.*—A property of great theoretical importance is diffusibility. Nernst showed that the diffusion constant of a salt may be calculated as the quotient between the moving force, which here is the osmotic pressure, and the sum of the frictional resistances of its ions, which was calculated by Kohlrausch from the electric conductibility of the salt's solutions. In this manner I determined,

* Compare N. Dhar, *Zeit. Elektrochem.*, **22**, 245, 1916 ; *Medd. Nobel Inst.*, **3**, 15, 1916 ; see also Partington's paper below.

for instance, the diffusion constant for $1\cdot04$ normal HCl at $12°$ to be $2\cdot09$, in agreement with Nernst's calculation. The constant increased on addition of chlorides such as NaCl, KCl, or NH_4Cl, and this increase is easily understood if we suppose that HCl as well as the salts is dissociated. If HCl is alone in the water, each H-ion is followed by a Cl-ion ; otherwise strong electric charges would appear, and cause forces producing this equality. The diffusion constant is, as said, $2\cdot09$ at $12°$, whereas if the H-ion moved independently its diffusion constant would be $6\cdot17$, and if the Cl-ion moved freely its diffusion constant would reach only the value $1\cdot26$ according to the figures of Kohlrausch. If NH_4Cl is added to the water in which the diffusion takes place, the H-ion moves more freely than when HCl is alone, for the positive charge of the diffusing H-ion may be compensated not only by means of the negative charge of a Cl-ion moving together with the H-ion, but also through the positive charge of an NH_4 ion moving in the opposite direction. I found that in $2N$. NH_4Cl the diffusion constant of the H-ion in $1\cdot04N$. HCl reaches the value $4\cdot50$, i.e. more than double the diffusion constant in water. The said change is characteristic for electrolytes, and agrees very well with an approximative calculation. On the other hand, the diffusion constant of the chlorine ion in the NH_4Cl solution becomes smaller than $2\cdot09$. If the added quantity of NH_4Cl were very much greater than the HCl present, the values $6\cdot17$ for the H-ion and $1\cdot26$ for the Cl-ion would be reached. This observation cannot be explained if we suppose that H and Cl are bound to each other. It may therefore be regarded as an *experimentum crucis* for the electrolytic dissociation theory.[*]

4. *Colours of Solutions.*—A very interesting and much discussed additive property is the colour of solutions of electrolytes. At very high dilutions, at which the degree of dissociation $a=1$, i.e. salts are completely dissociated, the colour of the solution is composed of the colour of the solvent, that of the cation and that of the anion. With an uncoloured solvent, as water, and the one ion uncoloured, all solutions of the salts with a common coloured ion, e.g. all permanganates, ought to have the same colour. This Ostwald showed to be the case.[†] He extended this theorem to indicators, in which case the acid or the basis is very little dissociated and gives a wholly different colour from that of its salts. This circumstance was for a time regarded as a strong proof in favour of the electrolytic dissociation. But Hantzsch has made it probable that here a case of isomerism occurs. Opinion then turned over to the other side. It was, for instance, said that we might expect that a concentrated solution of blue vitriol changed colour on dilution because its degree of dissociation increased in a very high degree, and the undissociated salt ought not to possess the same colour as the copper ion. In reality the change of colour is insensible. A very detailed examination of this circumstance was carried out by Robert Wright.[‡] He found that strong (nearly totally dissociated) acids exert the same absorptive power on light as their salts, whereas weak (little dissociated) acids often show a great difference in this respect from their salts. This is just what we ought to expect from the view-point of our theory.

5. *The Electric Conductivity of Solutions.*—The first germs of the electrolytic dissociation theory are found in my doctor thesis of 1884,

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[*] Compare Arrhenius, *Zeit. phys. Chem.*, **10**, 74, 1892.
[†] *Zeit. phys. Chem.*, **9**, 579, 1892.
[‡] *Journ. Chem. Soc., Lond.*, **103**, 528, 1913 ; **104**, 669, 1914.

There I conclude that the electrolytes consist of conducting and non-conducting molecules in such an equilibrium that in extreme dilution all molecules become conducting, and with increasing concentration the non-conducting molecules increase at the cost of the conducting ones. In this manner the increase of the molecular conductivity with increasing dilution was explained. Later (1887), this theory was precised so that the conducting molecules are dissociated into their ions. Hence the degree of dissociation, a, is calculated by means of the formula

$$a = \frac{\lambda_v}{\lambda_\infty}$$

in which λ_v is the molecular conductivity for the dilution v (1 gram-molecule in v litres) and λ_∞ the same quantity for infinite dilution. λ_∞ is a limiting value which may be calculated with the aid of extrapolation formulas given by Kohlrausch and others. This calculation of a was generally accepted and is still regarded as giving nearly reliable results.* It is also generally accepted that for higher concentrations a correction for viscosity should be introduced. Mostly it is supposed that this correction is proportional to the viscosity, so that we should introduce $\lambda_u \eta_u$ instead of λ_v, where η_u is the viscosity of the solution with the dilution v and η_∞ is the viscosity of pure water (at the temperature of investigation). For dilute solutions ($v > 10$) the said correction is for common salts, acids, and bases rather insignificant.

6. *Ostwald's Law.*—Now Ostwald, and at the same time van 't Hoff and Planck, tried to see if the law of Guldberg and Waage for chemical equilibria were not valid for the equilibrium between the dissociated molecules (i.e. the ions) and the undissociated ones. Van 't Hoff and Planck, who calculated the figures of Kohlrausch for salts and strong acids and bases, found no agreement between the theoretical demands of Guldberg and Waage's law and experience. Ostwald thereupon calculated some figures of his own regarding weak acids and found good agreement with the demands of the theory, and so he formulated "Ostwald's law" for weak electrolytes (1888). Bredig, a little later, stated that this law holds good also for weak bases. I drew the attention of van 't Hoff to the circumstance that weak acids offered a much better material than salts for investigating the validity of the laws of mass action in the case of electrolytic dissociation, whereupon he, together with Reicher, made a very careful examination of the behaviour of formic, acetic, butyric, monochloracetic, benzoic and shikimic acids within very wide limits of concentration, and found a wonderful agreement with the law of mass action (1888).

This agreement was rightly regarded as the most convincing proof of the validity of the dissociation theory. But still strong electrolytes made a very marked exception from the said law, and this exception has been one of the most difficult questions in this branch of science. Noyes (1892) rejected the method of determining the degree of dissociation, a, by means of the conductivity, and used for this purpose experiments on solubility of salts (see 1 above), and supposed that the law of mass action was absolutely exact for this case. As I showed immediately afterwards (1892), the values of a determined in this manner are subject to precisely similar disagreements in regard to the law of mass action as the a-values calculated from the figures of conductivity.

* Compare Kraus, *J. Amer. Chem. Soc.*, **36**, 64, 1914.

These latter have also been generally accepted as being nearly exact for dilute solutions. Some authors, as v. Steinwehr (1901), Liebenow (1902), Malmström (1905), Kjellin (1910), and P. Hertz (1912), have tried to explain the deviations from the law of mass action as due to the electrical forces between the charged ions. These authors have been led to different results, and 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.

7. *Non-aqueous Solutions.*—With solutions in other solvents than water, the deviations from Ostwald's law are often very much more pronounced than for aqueous solutions. It even happens that the electrical conductivity increases more rapidly than in proportion to the concentration of the dissolved salt, which seems to indicate that the degree of dissociation decreases with increasing dilution. This appears to be absolutely untenable from the point of view of the mass action law.[*] Walden explained it as due to a dissociating influence of the salt molecules, depending upon their high dielectric constant, compared with that of the solvent. He has corroborated his opinion through a great number of measurements.

This dissociating action of the salt may be represented by the formula :

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

in which c is the concentration of the salt, K, k and m three constants. The dissociation constant increases proportionally to the nth power of the concentration of the ions—here for simplicity only two ions are supposed. For weak acids in water k is very small, so that it may be neglected, and Ostwald's law holds good. For strong acids or bases and for salts K may, except for extremely high dilutions, be omitted. We then get the formula of Rudolphi, or, if $m = \frac{1}{2}$, of van 't Hoff, which fits rather well with observation. Kraus and Bray have proved the validity of their formula for strong electrolytes dissolved in 26 different solvents.

8. *Ostwald's Law for Salt Solutions in Water.*—Kraus and Bray did not find the above formula applicable to aqueous solutions, which have been investigated in very dilute solutions by Kohlrausch and Maltby. This seemed to me very peculiar. I therefore re-examined these figures, which had been found through application of a correction for the conductivity of the water about as great as the conductivity of the dissolved salt itself. The conducting substance in water was indicated as dissolved carbonic acid from the air. Evidently an examination must be carried out, if the correction was right. This was possible by means of an older investigation regarding the equilibrium between any number of electrolytes in aqueous solution [†] and James Walker's determinations of the conductivity of carbonic acid in aqueous solution.[‡] The result was that the correction to be applied to Kohlrausch's and Maltby's figures never reached more than 0·08 per cent. and falls wholly within the errors of observation. In the interval between the concentrations 10^{-5} and

* This never occurs with aqueous solutions, if the conductivity is corrected for the viscosity (compare Sloan, *Journ. Amer. Chem. Soc.*, **32**, 946, 1910).
† *Zeit. phys. Chem.*, **2**, 296, 1888, and **5**, 1, 1890.
‡ *Journ. Chem. Soc. Lond.*, **77**, 5, 1900.

$2 \cdot 10^{-4}$ Ostwald's law is valid for $NaNO_3$ and NaCl with a value of $K = 0 \cdot 024$ (at $18°$ C.). The other four salts (KCl, LiCl, KNO_3 and $LiNO_3$) examined by Kohlrausch and Maltby in the same memoir possess nearly the same value of K.*

In a quite recent memoir † Weiland has determined the conductivity of potassium chloride, KCl, in extreme dilutions, with the highest possible care and " ultra-pure " conductivity water. He found the constant $K = 0 \cdot 02$, i.e. within the unavoidable errors equal to the value deduced by myself from Kohlrausch's and Maltby's figures. The law of Ostwald is valid at concentrations below 10^{-4}. Sixteen other uni-univalent salts treated by Noyes and Falk give the same value $K = 0 \cdot 02$ in the same interval.‡

9. *The Freezing-point of Aqueous Solutions.*—In 1885 Raoult showed that the freezing-point is an additive property changing from $2 \cdot 0$ for univalent negative ions, e.g. Cl, NO_3, etc., to $0 \cdot 8$ for bi- or poly-valent positive ions, such as Ca, Ba, Al, etc. There are many exceptions; e.g. weak acids, as HCN, CH_3COOH, give only about half the normal value. In 1887 I calculated all figures of Raoult under the assumption that the molecular depression of the freezing-point is $1 \cdot 85$, as demanded by the theory of van 't Hoff, for all kinds of molecules or ions. The agreement was very satisfactory, and thereby a very strong support was given to the electrolytic dissociation theory. Some figures of Raoult were not concordant with the theoretical demands ; these cases were re-examined by myself in 1888 and the exceptions found to depend upon errors of observation. The theoretical demands are completely fulfilled in ex-tremely dilute solutions. For more concentrated solutions the deviations may reach considerable values, specially for substances which are known to have a great affinity for water, such as LiCl, $MgCl_2$, $CaCl_2$, etc. A thorough examination by Noyes and Falk § gave the result that for solutions that are not more concentrated than $0 \cdot 1$ normal the difference between the observed figures and those calculated from the electric con-ductivities does not reach more than 2 per cent. for electrolytes consisting of two univalent ions. The same is true for potassium sulphate and lead nitrate. Hygroscopic salts with divalent positive ions show much greater deviations, the lowering of the freezing-point being greater than the calculation demands.

10. *Deviations in Concentrated Solutions.*—In general the lowering of the freezing-point is greater in concentrated solutions than the theo-retical value. Exception make solutions of copper sulphate, zinc sulphate, cadmium iodide, and similar salts in which double or complex molecules have been proved to exist Some authors, as Bjerrum, have therefore expressed the opinion that such electrolytes as KCl are wholly dissociated in solution, and that the observed deviations from the theoretical value are due to electric attraction between the ions.‖ Milner has calculated the said effect of the electric charges, and Bjerrum finds it agree rather well with the observations for KCl. According to Adams's measure-ments,¶ which are in best accordance with those of Bedford and Jahn, the observed freezing-points of dilute solutions (up to $0 \cdot 1$ normal) of KCl agree with the values calculated from the conductivity within

* *Medd. Nob. Inst.*, **3**, 42, 1913.
† *Journ. Amer. Chem. Soc.*, **40**, 131, 1918.
‡ Washburn, *Journ. Amer. Chem. Soc.*, **40**, 155, 1918.
§ *Journ. Amer. Chem. Soc.*, **34**, 455, 1912.
‖ *Fysish Tidsshrift*, **15**, No. 2, 1917.
¶ *Journ. Amer. Chem. Soc.*, **37**, 495, 1915.

$0\cdot0001°$ C. Hence the idea of Bjerrum that the electrolytic dissociation of KCl and other salts is complete seems not to agree very well with experience. Much more peculiar is the hypothesis proposed by Snethlage that the salts, and in general strong electrolytes, should not be dissociated at all,* which has aroused a great deal of discussion.

It should be remembered that in higher concentrations the values of the molecular conductivity and of the molecular lowering of the freezing-point are dependent upon the unit in which the concentration is expressed. Thus, for instance, the great deviations from van 't Hoff's law for the molecular lowering of the freezing-point for cane sugar, which occur if the concentration is expressed in gram-molecules per litre, nearly wholly disappear if the calculation is based on molar concentration. The still remaining disagreement may be explained by the rather probable hypothesis that each molecule of sugar binds five molecules of water.† Through the investigations of Washburn and others it is very probable that the ions bind rather great quantities of water, which must be taken into consideration when molar concentrations are used, which seem to give the best results. Here rather much work remains to be done before a clear idea can be formed regarding the exact magnitude of the deviations at higher concentrations.

11. *Velocity of Reaction.*—As early as in 1884 it was pointed out that those acids are the strongest which are dissociated in the highest degree. Ostwald showed that the catalytic action of different acids in hydrolysing cane sugar or ethyl acetate is nearly proportional to their electric conductivity. In 1889 I examined this question more closely, and found that the catalytic activity was proportional to the quantity of H-ions present, and further, that foreign substances, especially electrolytes, but also other substances, exerted an accelerating influence on the catalytic process; in this case the inversion of cane sugar was observed. This influence is so great that an addition of a neutral salt not only not diminishes the velocity of reaction of a strong acid, which we might expect as a consequence of the diminution of the degree of dissociation of the catalysing acid through the presence of the salt, but even increases it. Most authors therefore suppose that the undissociated molecules of strong acids such as HCl react more rapidly than their H-ions. If the problem is regarded in this manner, it is found that the quotient of the activity of the undissociated molecule to that of the H-ion is the greater the higher the dissociation constant of the acid, so that for weak acids the activity of the undissociated molecule may be neglected.

There is also another method of explaining the action of foreign substances. The velocity of reaction is proportional to the osmotic pressure of the reacting substance. In the case of inversion of cane sugar, the pressures of the H-ion and that of the cane sugar come into consideration. Now, it is well known that the freezing-point of an aqueous solution containing sugar and a salt is lower than the sum of the freezing-points of the sugar alone and of the salt alone in the same volume of water. The same is the case with a solution of ethyl acetate and salt.‡ Hence, also, the osmotic pressure of the mixture is greater than the sum of the osmotic pressures of its components. The difficulty is to say how much the osmotic pressure of each component has increased. In one case this is possible, namely, for the osmotic pressure of H-ions from $0\cdot1$ N. HCl

* *Zeit. phys. Chem.*, **85,** 211, 1913.
† Compare Fraser and Myrick, *Journ. Amer. Chem. Soc.*, **38,** 1907, 1916.
‡ Rivett, *Medd. Nobel Inst.*, **2,** 9, 1911.

in presence of different quantities of KCl.* That this action may suffice for the explanation of the action of neutral substances I have tried to prove on the observations published hitherto.†

The dissociation of weak acids decreases very much through addition of their salts. This causes a proportionate diminishing of their velocity of reaction, in full agreement with theory. On the other hand, the addition of salts of strong acids (such as HCl) increases the velocity of reaction of weak acids. This effect is also predicted by theory.‡ The degree of dissociation of indicators becomes also strongly increased through the addition of neutral salts.

Goldschmidt and Thuesen § have investigated the velocity of re-action at the formation of esters through the action of organic acids on methyl alcohol in which they are dissolved. This action goes on very slowly, but is accelerated by addition of stronger acids, such as HCl or picric acid. They found that the velocity is nearly proportional to the concentration of the hydrochloric acid and not to the number of H-ions present. At the experiments with picric acid the addition of a picrate ($0·15$ N. to $0·1$ N. picric acid) does not diminish the velocity of reaction in such a high degree as might be expected—$1:6$ instead of the theoretical value $1:11$. The authors are thereby carried to the conclusion that the undissociated parts of the acids play an important rôle as catalysers—Snethlage used this material for his deductions (see § 10) For the weaker trichlorbutyric acid the agreement with the theoretical values is very satisfactory.

These circumstances remind rather much of those occurring in aqueous solutions, and the deviations from the theoretical values seem to be of the same order of magnitude in both cases. The different factors are not so well known for the alcoholic solutions as for the aqueous ones. We therefore want still more experience before strict conclusions can be drawn. On the whole, it may be said that the dissociation theory corresponds as well with experience as may be expected in the present state of our knowledge.

STOCKHOLM,
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* Harned, *Journ. Amer. Chem. Soc.*, **37**, 2460, 1915.
† Arrhenius and Andersson, *Medd. Nobel Inst.*, **3**, 25, 1917.
‡ Arrhenius, *Zeit. phys. Chem.*, **5**, 1, 1890.
§ *Zeit. phys. Chem.*, **81**, 30, 1913.