An application to electrolytes of the hydrate theory of solutions / by T. Martin Lowry.

Contributors

Lowry, T. Martin 1874-1936.
Royal College of Surgeons of England

Publication/Creation

Woking : Gresham, [1905]

UNCORRECTED PROOF.—Private, for Members only. 18

This paper may not be published until it has been read before the Faraday Society.

The Council invites members unable to be present at the reading of the Paper, to send their contributions to the discussion in writing to the Secretary, so that they may be communicated to the meeting.

AN APPLICATION TO ELECTROLYTES OF THE HYDRATE THEORY OF SOLUTIONS.

BY T. MARTIN LOWRY, D.Sc.

(A Paper to be read before the Faraday Society, Thursday, May 18, 1905.

During a period of nearly twenty years two rival theories have existed as to the nature of solutions, and especially of those solutions which are capable of conveying an electrical current by electrolysis. According to the hydrate theory, as developed by Mendeleef and by Pickering, the chief result of adding water to a salt is to produce a series of hydrates increasing in complexity with the amount of water added. Arrhenius, on the other hand, has suggested that the main result of the interaction is not the association of solvent and solute, but the dissociation of the solute into the ions into which it is resolved by electrolysis. The object of the present communication is to consider the possibility of extending the hydrate theory to electrolytes in such a way as to take account of the observations which form the experimental basis of the theory of electrolytic dissociation.

The hydrate theory postulates that an aqueous salt solution consists of a mixture of hydrates in equilibrium with the solvent and with one another. By crystallising under various conditions a limited number of these hydrates can be separated, but the solution probably contains many hydrates which cannot be isolated in this way. Amongst the hydrates that can exist only in solution there are probably included many compounds of greater complexity than those which separate when crystallisation takes place. But it must be supposed that even in solution there is a limit to the possibility of hydrate formation, so that ultimately a stage will be reached at which the molecule as such will be unable to combine with any further quantity of water.

According to the view now under consideration the ionisation of an aqueous electrolyte consists essentially in a further process of hydration whereby the fully hydrated molecule combines with an additional quantity of water to form two or more hydrated ions. The process of ionisation might thus be compared with the biological process of karyokinesis whereby the growth of a cell leads ultimately to the fusion of the individual and its resolution into two or more separated cells.

The possibility that the ions may be hydrated has frequently been discussed,[*] but this has usually been regarded as a secondary phenomenon, and

---

[*] See especially Kohlrausch, *Sitz. ber. Preuss. Akad. Wiss.*, Berlin, 1902, **26**, 579; Walden, *Zeit. phys. Chem.*, 1902, **39**, 539, where a large number of references are given, and a monograph, *Von der Hydraten in wässeriger Lösung*, Ahren's Sammlung, 1903, **8**, 466.

not, as is now suggested, a primary cause of the ionisation of aqueous electrolytes.[*] It is, moreover, an essential postulate of the theory that the ions should jointly be combined with a larger quantity of water than the molecule from which they are derived. That this is the case has been by no means generally conceded even by those who believe in the existence of hydrated ions. Thus Traube (*Phil. Mag.*, 1904, **8**, 158) has recently postulated that each ion is combined with a single molecule only of water, and Vaillant (*Comptes Rendus*, 1904, **138**, 1210) from a study of the density of aqueous solutions of electrolytes, has drawn the conclusion that the ions are for the most part anhydrous, but that the anions $\overset{-}{\mathrm{OH}}$, $\overset{-}{\mathrm{F}}$, $\overset{--}{\mathrm{S}}$, and $\overset{--}{\mathrm{CO}_3}$ are monohydrated. Lobry de Bruyn has recently shown (*Rec. trav. chim.*, 1904, **22**, 430) that there is no displacement of methyl alcohol during the electrolysis of aqueous silver nitrate, and this has been interpreted as indicating that the ions $\overset{+}{\mathrm{Ag}}$ and $\overset{-}{\mathrm{NO}_3}$ are anhydrous. Garrard and Oppermann (*Göttingen Nachr.*, 1900, p. 86), by studying the migration of boric acid during the electrolysis of a mineral acid, have been led to the conclusion that the sulphate ion is combined with $9H_2O$, the chlorine ion with $5H_2O$, the bromine ion with $4H_2O$, and the nitrate ion with $2{\cdot}5H_2O$, the hydrogen ion being assumed to be anhydrous. The coefficients of ionic hydration deduced by these observers do not appear to be adequate to account for the resolution of the molecule into its constituent ions, and it is probable that the actual values are considerably higher throughout. In the case of silver nitrate the alternative explanation, that the two ions are approximately equally hydrated, is to be preferred.

It is believed that the theory of ionisation discussed in the present paper forms a natural and legitimate extension of the hydrate theory to the phenomena of electrolysis, and that it may help to remove the fundamental difficulty of Arrhenius's theory, to which Prof. Armstrong has especially called attention, namely the absence of a *motive* for electrolytic dissociation. Thus whilst it is true, as J. J. Thomson and Nernst have pointed out, that the electrical forces between the ions would be greatly reduced in a medium of high dielectric capacity such as water (S.I.C. = 80), this observation does not account for the separation of the ions, and some positive force must be applied if the influence of chemical affinity, as well as of electrical attraction, is to be overcome. The same criticism applies to the theory that an ionising solvent affords a protective menstruum which prevents the recombination of the ions, since, unless some disruptive force were also at work, such a menstruum could only slightly prolong the transient existence of the ions.

The evidence in support of the hydrate theory of ionisation may now be briefly stated.

I. In the first place it may be noted that this theory is in accord with the well-known fact that the best "ionising" or "dissociating" solvents are those

---

[*] Prof. Armstrong suggested some years ago that the association of the solvent with the negative radicle of the solute was the determining factor in electrolysis; he considered, however, that the positive radicle had no tendency to associate with the solvent, and that the process of ionisation did not involve the resolution of the molecule into separated ions. A somewhat similar suggestion has been made by Brühl (*Zeitschr. Phys. Chem.*, 1898, **27**, 319–322), who has associated the ionising properties of water with the presence of an unsaturated tetravalent oxygen atom. The clearest statement of the equilibrium between solvent and solute postulated by the hydrate theory of ionisation is, however, to be found in the course of a paper by R. Abegg, on "Valency and Molecular Compounds," which has recently appeared in the *Zeitschrift für anorganische Chemie* (1904, **39**, 330).

which are themselves most highly associated. Whilst Arrhenius laid special stress on dissociation as the characteristic feature of the process of ionisation, the hydrate theory emphasises an association of solvent and solute which accompanies, and is a primary cause of, the separation of the ions. Such an association with the solute may be expected to occur most readily in the case of solvents composed of molecules having a high coefficient of association. The actual degree of ionisation must, however, be dependent also on the mutual affinity of the ions, and on the readiness of the molecules of the solvent to separate from one another in order to combine with the solute.

II. In the second place, it may be noted that complete ionisation is possible only in presence of a very large excess of water, that is, under exactly those conditions which are most favourable to the formation of complex hydrates. At the same time there is no difficulty in accounting for the ionisation of concentrated solutions, since in accordance with the laws of mass action the more complex hydrates would still be present, though in greatly reduced proportions. It is remarkable that in its earliest form the theory of electrolytic dissociation actually postulated a minimum of hydration in the most dilute solutions, since under these conditions the salt was regarded as being completely resolved into anhydrous ions. A similar view has recently been advocated by H. C. Jones (*vide infra*).

III. The influence of temperature on ionisation is also in accord with the view that the process is essentially one of association with the solvent. As the temperature rises the proportion of water required to produce a given degree of ionisation steadily increases. This result may be attributed to the influence of temperature in decreasing the stability of all the hydrates in solution, but especially of the complex hydrates which constitute the ions. In the neighbourhood of the critical temperature the solvent ceases to be associated, and, as Hagenbach has shown (*Ann. Physik*, 1901 [5], **2**, 276), its ionising properties are reduced to a minimum.

IV. Striking evidence in favour of the hydrate theory of ionisation is afforded by a consideration of the mobilities of the different ions in aqueous solutions. The simple relationships that have been observed between the fluidity of a dilute aqueous solution and its electrical conductivity[*] are most readily explained by supposing that the resistance to electrolysis is mainly viscous or frictional in character, and depends rather on the size and shape of the migrating ions than on their chemical characteristics. From this point of view the following table of ionic mobilities is remarkable—

Li	Na	K	Rb	Cs
33·44	43·55	64·67	67·6	68·2

since it appears that the larger atoms yield the more mobile ions, and that the lithium ion (at. wt. 7) moves through the solution only half as rapidly as the rubidium ion (at. wt. 85) or the cæsium ion (at. wt. 133). Such a result affords the clearest possible evidence that the ions cannot be represented by the simple formulæ conventionally assigned to them, and strongly supports the view that in aqueous solutions the ions are present in the form of complex hydrates. Independent evidence that the lithium ion is more fully hydrated than the potassium or cæsium ion is given in the following sections.

The evidence afforded by the ionic mobilities that the kathion, as well as the anion, tends to form complex groups, is of importance in view of the

---

[*] Kohlrausch, *Ber. Preuss. Akad. Wiss.*, 1901, **42**, 1026; 1902, **26**, 572; *Proc. Roy. Soc.* 1903, **71**, 338–350. Bousfield and Lowry, *Proc. Roy. Soc.*, 1902, **71**, 42.

general tendency to regard the metallic radicles as being almost entirely devoid of residual affinity.

V. In the table of ionic mobilities the radicles H and OH occupy an altogether unique position, the mobility of the hydroxyl ion being more than double as great as that of any other anion—

$$\mathrm{OH} = 174,\ [\tfrac{1}{2}\mathrm{SO_4} = 68{\cdot}7],\ \mathrm{Br} = 67{\cdot}63,\ \mathrm{I} = 66{\cdot}40,\ \mathrm{Cl} = 65{\cdot}44,\ \mathrm{NO_3} = 61{\cdot}78,$$

whilst that of the hydrogen ion is nearly five times as great as that of any other kathion :—

$$\mathrm{H} = 318,\ \mathrm{Cs} = 68{\cdot}2,\ \mathrm{Rb} = 67{\cdot}6,\ \mathrm{Tl} = 66{\cdot}00,\ \mathrm{K} = 64{\cdot}67,\ \mathrm{Ag} = 54{\cdot}02.$$

The peculiar properties of these two ions are most readily explained by supposing that they are either anhydrous or are combined with a smaller proportion of water than any of the other ions. Confirmation of this view is afforded by at least two independent considerations :—

(1) The affinity of water molecules for the ions H and OH must be relatively slight, since otherwise liquid water, like fused salt or caustic soda, would be a good electrolyte. Actually, when freed from saline impurities, it forms a most effective insulator.

(2) Whereas nearly all sodium and potassium salts are good conductors, the acids from which they are derived vary very greatly in their electrolytic properties, and are often exceedingly poor conductors. This is readily accounted for if it be supposed that in the salts ionisation is brought about by the affinity of the solvent for both anion and kathion, but in the acids mainly by the affinity of the solvent for the anion. Similar considerations may be applied to the bases, which vary in their electrolytic properties far more than the chlorides derived from them. This case is, however, complicated by the fact that the bases have a much greater tendency than the acids to dissociate into water and a neutral anhydride, *e.g.*—

$$\mathrm{NH_4OH = NH_3 + H_2O}$$
$$\mathrm{Zn(OH)_2 = ZnO + H_2O.}$$

VI. Independent evidence in favour of the hydrate theory of ionisation is to be found in a consideration of the freezing-points of dilute aqueous solutions. At extreme dilutions the molecular depression of the freezing-point reaches a maximum value corresponding very closely with that required by the theory of electrolytic dissociation. In less dilute solutions, however, values are obtained which cannot be accounted for in terms of this theory as originally propounded. Thus in a large number of cases the molecular depression, which might be expected to decrease continuously with increasing concentration, actually reaches a minimum value between N/10 and N/2, and then increases again with the concentration ;* the molecular conductivity, however, decreases steadily as the concentration increases, and does not reach a minimum value. This result was admirably explained by Jones and Chambers by assuming that "*there is combination between the molecules of the dissolved substances and the molecules of the solvent, thus removing a part of the solvent as far as the freezing-point lowering is concerned.*" No alternative theory has been suggested, and the explanation given is probably correct. Jones and Getman are of opinion that "*it is the molecules and not the ions that combine with water to form hydrates,*" † and that "*hydrates of any con-*

---

* Arrhenius, *Zeit. phys. Chem.*, 1888, **2**, 496. Jones and Chambers, *Amer. Chem. Journ.*, 1900, **23**, 89. Biltz, *Zeit. phys. Chem.*, 1902, **40**, 185.

† *Amer. Chem. Journ.*, 1904, **31**, p. 356.

siderable complexity do not exist" * in dilute solutions. It is, however, noteworthy that in many cases the molecular depression begins to increase at concentrations as low as N/10 to N/5. At these low concentrations the greater part of the salt must be in the ionised condition, and the experimental data are fully in accord with the view that combination with the solvent is characteristic of the ion even more than of the molecule. †

VII. The theory of electrolytic dissociation owes much of its acceptability to the readiness with which it lends itself to exact mathematical treatment. The whole theory can indeed be summed up in the single equation—

$$K = m\,a(u + v)\left\{\begin{array}{l} K = \text{specific conductivity} \\ m = \text{concentration} \\ a = \text{coefficient of ionisation} \\ u \text{ and } v = \text{ionic mobilities} \end{array}\right.$$

since this equation includes (1) the conception that only a part a of the solute is directly active in electrolysis and (2) the conception that each ion migrates independently and possesses a specific ionic mobility u or v. In the case of dilute solutions the constants in this equation can be determined, but the values for concentrated solutions are at present unknown.‡ The hydrate theory, on the other hand, has suffered because of the extreme difficulty of giving quantitative expression to phenomena that cannot readily be observed except in concentrated solutions. The essential constants of the hydrate theory are, however, quite as simple as those of Arrhenius's theory. For any given solution the chief constants are—(1) The *total hydration* (or, more briefly, the *hydration*), H, of the solution, which expresses the total number of molecules of water present per molecule of salt. (2) The *coefficient of combination*, β, which expresses the fraction of the total quantity of water that is actually combined with the salt to form hydrates. (3) The product of these two quantities will give the average composition of the hydrates in solution; these may be termed the *average molecular hydration*, or, more briefly, the "molecular hydration," of the solution and may be represented by the symbol h. Thus $h = \beta H$ may be regarded as the fundamental equation of the hydrate theory, and whilst the empirical composition of a salt solution may be expressed as $NaCl + H\,H_2O$, the average composition of the hydrates will be $NaCl + h\,H_2O$, and the proportion of combined water h/H.

Only two attempts appear as yet to have been made to determine the molecular hydration of dissolved salts. One of these is described by Jones and Getman in the paper quoted above. Assuming that the abnormally great molecular depressions of the freezing-point of salt solutions of moderate concentration were due to a combination of solvent and solute whereby the quantity of solvent water was reduced, they were able to compute the amount of solvent water remaining in the solution by comparing the observed molecular depression with that calculated from the coefficient of ionisation of the solution. No correction was made for the influence on the ionic mobility of the changing viscosity of the solution, and the results can therefore only be regarded as approximately correct. But in the absence of more reliable data the figures deduced for the weight of solvent water in

---

* *Ibid.*, p. 355.

† The interpretation of the experimental data is discussed in the following section.

‡ For an attempt to determine the values of the constants in less dilute solutions, see Bousfield and Lowry, *Phil. Trans.*, 1905, **204**, 253–322.

1000 c.c. of solution may be taken as a first approximation to the actual values. The figures given for aluminium chloride are quoted in column iv. of the table.

The authors considered that "*the difference between this amount of water and* 1,000 *grams was the amount that had combined with one gram-molecular weight of the salt under the conditions present in the solution in question,*" and proceeded to determine the average molecular hydration by dividing this difference by 18. This method of calculation, the results of which are tabulated in the last column of the table, led to the remarkable conclusion that "*the amount of water combined with one molecule of the dissolved substance is greatest in the most concentrated solutions employed and becomes less and less as the dilution increases.*" Such a reversal of the normal laws of mass action suggests the existence of some serious flaw in the method used in deducing these values. Two errors appear to have been made. (1) The total weight of water in 1,000 c.c. is not 1,000 grams but a smaller quantity, as is shown in column iii. of the table. (2) The combined water in 1,000 c.c. is combined not with one, but with m, gram molecules of the salt. The actual weight of combined water in 1,000 c.c. is given in column v. of the table, and when this is divided by $18\,m$ it gives the average molecular hydration h, shown in column vii. The coefficients of combination $\beta = h/H$ are set out in column viii.

The corrected values show a regular increase of molecular hydration as the dilution increases, and are, therefore, in accord with the view that ionisation involves an increase, and not a decrease, in the hydration of the solute. The last three values show an abrupt drop in the molecular hydration, but this is to be attributed rather to the large effects produced in the case of dilute solutions by small experimental errors, than to a sudden reversal of the behaviour observed in more concentrated solutions.

TABLE I.

HYDRATION OF ALUMINIUM CHLORIDE IN AQUEOUS SOLUTIONS.

Concentration m.	Coefficient of Ionisation a.	Total Water in 1,000 c.c. W.	Solvent Water in 1,000 c.c. $W-w$.	Combined Water in 1,000 c.c. w.	Hydration H.	Molecular Hydration h.	Coefficient of Combination β.	Molecular Hydration (Jones & Getman).
2·124	0·177	917	150	767	24·0	20·6	0·84	48·1
1·593	0·237	943	228	715	33·0	25·0	0·78	43·7
1·434	0·253	950	253	697	36·9	27·1	0·73	42·0
1·195	0·312	959	331	628	44·8	29·3	0·66	37·2
0·876	0·388	971	460	511	61·6	32·5	0·53	30·0
0·657	0·435	979	568	411	82·8	34·8	0·42	24·0
0·531	0·476	983·5	642	341	103	35·7	0·35	19·8
0·398	0·529	990	754	236	138	[32·9]	0·24	13·7
0·299	0·570	992	872	120	184	[22·3]	0·12	7·1
0·200	0·620	994	942	52	262	[14·1]	0·05	3·3

A similar investigation of the molecular depressions of the freezing-points has been made by Biltz (*Zeitschr. Phys. Chem.*, 1902, **40**, 220). This author found that cæsium nitrate (which exhibits a minimum of hydration) behaved in a normal manner, and by assuming that other alkaline salts had a similar coefficient of ionisation he deduced for the molecular hydration of potassium chloride in solutions from N/10 to N/2 the values $h = 26$ to 15 H_2O, for sodium chloride $h = 25$ to 19 H_2O, and for lithium iodide $h = 40$ H_2O.

VIII. The results obtained by studying the freezing-points are complicated by the fact that both molecules and ions may enter into combination with the solvent. It may, however, be noted that the abnormality decreases in the series Li, Na, K, Rb, Cs, indicating that the hydration reaches a maximum in the case of lithium and decreases as the molecular weight increases. This result is confirmatory of the conclusions arrived at from a study of the ionic mobilities of the series. Collateral evidence is also afforded by the data for the molecular elevation of the boiling-point and the molecular lowering of the vapour pressure, which, likewise, exhibit minimum values.*

Indications analogous to those resulting from a study of the freezing-points of aqueous salt solutions are afforded by the determination of the influence of dissolved salts on the solubility in water of neutral solids and gases. But, whilst the results are of considerable interest, the phenomena are too complex to permit of exact deductions as to the nature of the hydrates present in solution.

IX. Extension of the theory to fused salts. Autolytic and heterolytic conductivity.

Whilst the hydrate theory of ionisation applies primarily to aqueous electrolytes, it can be used, without any substantial alteration, in all cases of heterolytic conductivity in which the electrolytic properties of a solution are due to the interaction of the solute with an ionising solvent. Thus in non-aqueous solutions it is probable that complexes are formed in which molecules of ammonia, sulphur dioxide, etc., plays the same part as the water in the hydrates referred to in the preceding part of the paper. Ionisation may therefore again be attributed to the superior combining power of the ions as compared with the molecules of the dissolved salt.

Some slight modification of the theory is necessary to render it applicable to the case of autolytes which become conductors when merely fused. No method is at present known of determining the coefficient of ionisation of fused salts, and Whetham † has pointed out that it is possible in this case to apply the old Grotthus theory of electrolysis, according to which free ions do not exist in the liquid, and the coefficient of ionisation is therefore zero. Various reasons may, however, be urged in favour of the view that the mechanism of electrolysis is similar to that which obtains in solution, and that only a part of the fused salt is directly active in electrolysis. Thus :—

(1) Polymerisation appears to be an essential characteristic of autolytic salts. Volatile compounds and compounds which are liquids at ordinary temperatures, and are therefore but slightly associated, are usually insulators except when associated with an ionising solvent. The acids are therefore heterolytes, whilst the salts derived from them are autolytes. Again, stannic chloride is in an insulator, whilst stannous chloride is a conductor when fused. Mercuric chloride is a poor conductor, but the silver haloids, which are insoluble and non-volatile, though readily fused, conduct even better than such liquids as 30 per cent. sulphuric acid, which exhibit the maximum conductivity obtainable in composite electrolytes (*see* Armstrong, *Proc. Royal Soc.*, 1886, **40**, 280).

(2) Definite proof of the polymerised character of fused salts has been obtained by J. F. Bottomley (*Trans. Chem. Soc.*, 1903, **83**, 1421–1425), who has found the coefficients of association of sodium and potassium nitrates, as determined from measurements of surface tension, to be 10·68 and 8·73 respectively. He concludes that "the conductivity of fused salts is to be

---

* A. Smits, *Zeitschr. Phys. Chem.*, 1902, **39**, pp. 385–432.

† *Proc. Far. Soc.*, June 30, 1903.

explained on the same hypothesis as that which furnishes an explanation of the conductivity of solutions, namely, that in order to prevent the equalisation of ionic charges, a protective menstruum is necessary, and it appears that this menstruum may be furnished by the same substance as that which also undergoes ionisation." If, however, the ionisation of aqueous solutions be explained in terms of the hydrate theory as due to the association of the ions with the molecules of the solvent, the analogous explanation for fused salts would be that the ions are associated with the neutral molecules of the salt. Thus in the case of fused potassium chloride the liquid would contain ions such as

$$\overset{+}{\mathrm{K}}(\mathrm{KCl})_x \quad \overset{-}{\mathrm{Cl}}(\mathrm{KCl})_y$$

corrresponding to the hydrates

$$\overset{+}{\mathrm{K}}(\mathrm{H_2O})_x \quad \overset{-}{\mathrm{Cl}}(\mathrm{H_2O})_y$$

postulated in aqueous solutions. The effective cause of ionisation would therefore again be found in the tendency of the simple ions to associate with the molecules of the solvent, and the extent of ionisation would be determined by the relative stability of the molecular and of the ionic complexes.

(3) Direct evidence of the tendency, which exists even in aqueous solutions, to form ionic complexes of the type formulated above, has been obtained by Abegg and Bödlander and other workers in the field of "Electro-affinity." As a result of their investigations it has become clear that double salts and complex ions are formed, not only in the case of substances such as the ferrocyanides, argenticyanides and platinichlorides

$$4\mathrm{KCN} + \mathrm{FeC_2N_2} \rightleftharpoons \mathrm{K_4FeC_6N_6} \rightleftharpoons 4\overset{+}{\mathrm{K}} \mid \overset{----}{\mathrm{FeC_6N_6}}$$

$$\mathrm{KCN} + \mathrm{AgCN} \rightleftharpoons \mathrm{KAgC_2N_2} \rightleftharpoons \overset{+}{\mathrm{K}} \mid \overset{-}{\mathrm{AgC_2N_2}}$$

$$2\mathrm{NaCl} + \mathrm{PtCl_4} \rightleftharpoons \mathrm{Na_2PtCl_6} \rightleftharpoons 2\overset{+}{\mathrm{Na}} \mid \overset{-\ -}{\mathrm{PtCl_4}}$$

but also in the case of divalent chlorides, such as those of mercury, cadmium, calcium, etc.:

$$2\mathrm{NaCl} + \mathrm{HgCl_2} \rightleftharpoons \mathrm{Na_2HgCl_4} \rightleftharpoons 2\overset{+}{\mathrm{Na}} \mid \overset{-\ -}{\mathrm{HgCl_4}}$$

$$2\mathrm{KCl} + \mathrm{CdCl_2} \rightleftharpoons \mathrm{K_2CdCl_4} \rightleftharpoons 2\overset{+}{\mathrm{K}} \mid \overset{-\ -}{\mathrm{CdCl_4}}$$

$$2\mathrm{KCl} + \mathrm{CaCl_2} \rightleftharpoons \mathrm{K_2CaCl_4} \rightleftharpoons 2\overset{+}{\mathrm{K}} \mid \overset{-\ -}{\mathrm{CaCl_4}}$$

It has further been shown that aqueous solutions of single salts may behave in a similar manner and yield complex rather than simple ions thus:—

$$2\mathrm{CoCl_2} \rightleftharpoons [\mathrm{CoCoCl_4}] \rightleftharpoons \overset{++}{\mathrm{Co}} \mid \overset{-\ -}{\mathrm{CoCl_4}}$$

$$2\mathrm{CdCl_2} \rightleftharpoons [\mathrm{CdCdCl_4}] \rightleftharpoons \overset{++}{\mathrm{Cd}} \mid \overset{-\ -}{\mathrm{CdCl_4}}$$

$$2\mathrm{CuCl_2} \rightleftharpoons [\mathrm{CuCuCl_4}] \rightleftharpoons \overset{++}{\mathrm{Cu}} \mid \overset{-\ -}{\mathrm{CuCl_4}}$$

The formation of such complexes, which are of exactly the same type as those postulated in the case of fused salts, affords the only satisfactory explanation of a number of instances in which a metal travels during electrolysis in the opposite direction to the current. It may be added that the formation of complex ions also affords an explanation of the fact that ionisation is not always accompanied by an abnormally great osmotic pressure;

thus in the three instances quoted above two neutral molecules give rise to two ions, and the molecular depression of the freezing-point due to the ionised salt would be the same as that due to the un-ionised molecules (*see* F. G. Donnan and Bassett, *Trans. Chem. Soc.*, **81**, 1902, 944).

(4) Precisely similar evidence of the formation of complex ions has recently been obtained in the case of fused salts by Lorenz and Fausti (*Zeitschr. Elektrochem.*, 1904, **10**, 630–633). These authors have shown that, in fused mixtures of lead chloride with sodium and potassium chlorides, the transport values prove that the lead is present in the form of a complex anion which travels in the opposite direction to the current. Their observations also indicate that the kathion is associated with neutral molecules of potassium chloride. These measurements, therefore, afford direct evidence of the presence in the fused salt of ionic complexes, positive and negative, of the types formulated above in the case of fused potassium chloride.

(5) It has recently been shown (Bousfield and Lowry, *Phil. Trans.*, 1905, **204**, 289) that in the case of caustic soda and certain other autolytes, the intrinsic conductivity (*i.e.*, the molecular conductivity divided by the fluidity of the solution) exhibits a minimum value at intermediate concentrations. At lower concentrations the conductivity is mainly heterolytic, and increases with the proportion of solvent present. At higher concentrations the conductivity is mainly autolytic and increases with the concentration of the solute. This result is best explained by supposing that whilst the heterolytic conductivity is due to the interaction of the solute with the solvent, the autolytic conductivity depends on a precisely similar interaction of the solute with other molecules of the same substance, as postulated above. It is also noteworthy that an analysis of the conductivity-temperature curves (*ibid.* pp. 307–308) indicates that the rate of decay of ionisation with rising temperatures is greatest in the case of concentrated solutions in which the conductivity is mainly autolytic. This observation affords strong confirmation of the view that autolytes, whether fused or in solution, are only partially ionised. It is indeed possible that in spite of their high conductivity, fused salts may have a relatively low coefficient of ionisation, since the ionic complexes are probably smaller than in solution, and the ionic mobility would therefore be relatively great.*

(6) *The Nernst Lamp.* Special interest attaches to the mechanism by which the current is conveyed in the filament of the Nernst lamp. This filament consists of a mixture of oxides, which becomes a conductor only when the temperature is raised, and is best regarded as a glass of very high melting-point. As such it exists in the state of an isotropic solid, which softens and melts only after reaching a temperature of brilliant incandescence, and does not crystallise when again allowed to cool. Like glass, it has the composition of an electrolyte, but behaves as an insulator until the temperature has been raised sufficiently to permit ionic migration to take place. Temperature-conductivity curves for filaments of very various compositions have been plotted by Reynolds (*Dissertation*, Göttingen, 1902), and are very similar in form to those for glass (Bousfield and Lowry, *Proc. Roy. Soc.*, 1902, **71**, p. 45), or for overcooled, concentrated, aqueous solutions of calcium chloride or sulphuric acid (Kunz, *Zeitschr. Phys. Chem.*, 1903, **42**, 591–596).

Further evidence that the current is conveyed by electrolysis is to be found in the isothermal conductivity-concentration curves plotted by

---

* A similar explanation applies in the case of solutions in liquid ammonia. In this solvent the ionisation is usually less than in water, but owing to the high values of the ionic mobility the actual conductivity is often greater.

Reynolds for various mixtures of oxides. These are similar in form to the curves for mixtures of acetic acid and water, but the maximum conductivity is reached at somewhat lower concentrations than is the case in aqueous solutions. An even more striking resemblance is, however, to be seen between the family of curves given by Reynolds for the conductivity of mixtures of ZnO_2 and Y_2O_3 at 900°, 1,000°, 1,100°, 1,200°, and 1,300° C. and the isothermal conductivity-concentration curves for mixtures of sodium hydroxide and water at 0°, 18°, 50°, and 100° C. (Bousfield and Lowry, *Phil. Trans.*, 1905, **204**, p. 321). Although the curves for the heated filaments are complicated by the occurrence of hysteresis and other disturbing factors, the appearance of the two series curves is such as to warrant the conclusion that the mechanism of conduction is essentially the same in the two cases.

130, HORSEFERRY ROAD,
WESTMINSTER.

The Gresham Press,
UNWIN BROTHERS, LIMITED,
WOKING AND LONDON.