

small as we please. Let us then make them so small that the duration  $\tau$  shall be but a small part of the duration  $1/\delta v$ . Then we are at liberty to substitute a single u f w with one definite wave-frequency, for the entire of the little group of u f w's of different wave-frequencies that furnish the rays that fall within any one of the foregoing degrees. To see this it is only necessary to proceed by successive steps which are so exactly analogous to those adopted in § 17, that it is unnecessary to repeat the procedure here. We thereby learn that—

### THEOREM XIII.

*When we have to consider in any problem what happens within a limited time, it is permissible to divide the wave-frequencies (or the corresponding wave-lengths) of the light with which we are concerned, into little groups and to substitute light of a single wave-frequency for each of these.*

It is important to bear in mind that this substitution can be effected whatever be the intensities, phases, and states of polarization of the individual undulations of the little group, inasmuch as it depends upon our pairing each member of the group with a *supposed* one which we are at liberty to conceive of as in the opposite phase, in the same state of polarization, and of the same intensity as that member of the group with which it is paired; and this can be effected however unrelated in these respects that member of the group may be to its colleagues.

22. The foregoing theorems (with perhaps a few additions such as the theorem which explains how to resolve a beam or pencil of light into its component u f w's) would be a sufficient foundation on which to proceed with the chamber study of optical phenomena by the new analysis. It will, however, be convenient to continue the study in conjunction with experiments which will afford assistance; and accordingly we intend next to inquire how to exhibit in optical instruments the resolution of light into its component u f w's, and how to employ this resolution as our guide in making and in interpreting experiments.

[To be continued.]

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XXV. *The Theory of Electrolytic Dissociation.* By W. C. D. WHETHAM, M.A., F.R.S., Fellow of Trinity College, Cambridge\*.

THE theory of the ionic dissociation of electrolytes, chiefly due to Arrhenius, was successful in explaining the electrical properties of aqueous solutions, and in co-ordinating

\* Communicated by the Author.

those properties with the phenomena of osmotic pressure and chemical activity. Hence there followed a general though not universal adoption of the theory, despite the opposition of some chemists. Lately, however, evidence has been offered to show that the general connexion between the properties of electrolytes, which seems to exist in the case of solutions in water, fails when other solvents are used, and that the exact numerical relations between, for example, conductivity and osmotic pressure, which were at one time thought to hold, are inexact at moderate concentrations even for aqueous solutions. It has hence been argued that the fundamental conceptions of the dissociation theory are erroneous, and that it should no longer be accepted as a valid explanation of the electrolytic phenomena. In the present stage of the discussion, it may be of interest to examine the foundations on which the theory rests, and to inquire how far they are affected by such criticism as we have indicated.

The conception of the complete independence from each other of certain parts of the dissolved molecules of electrolytes is attained by two distinct lines of research: (1) the examination of the electrolytic conductivity; and (2) the consideration of the thermodynamic theory of osmotic pressure and allied phenomena.

The appearance of the products of electrolysis at the electrodes, and at the electrodes only, indicates that the opposite parts of the solute must travel in opposite directions through the liquid under the influence of the electric forces, while Faraday's experiments show that the separation of a definite quantity of substance at the electrodes is always associated with the passage through the solution of a definite quantity of electricity, which is proportional to the valency of the ion. We are thus led to conclude that the process of electrolytic conduction is a kind of convection, in which the opposite ions are moved electrically through the liquid, and carry with them definite electric charges. This view of the phenomena was further developed by Kohlrausch, who showed that a calculation of the velocities with which the ions moved under a given electric potential gradient could be made from a knowledge of the conductivity of the solution and of the transport ratio, which had been investigated by Hittorf. The numerical values of the mobilities of different ions obtained by Kohlrausch's theory were confirmed by Lodge, Whetham, Orme Masson, and Steele, who have experimentally determined the velocity of certain ions by tracing their effect on an indicator, or by measuring the rate of motion of the boundary between two different solutions,

It is well known that a finite electromotive force is needed to effect electrolytic decomposition ; but, when the process is examined more closely, it is found that the reverse electromotive force of polarization exists only at the electrodes. If this reverse force is eliminated, by the use of alternating currents or otherwise, the conduction proceeds in conformity with Ohm's law, that is, the current is proportional to the electromotive force, so that any force, however small, causes a corresponding current. Thus within the liquid there are no reverse forces of polarization, and consequently no work is done by the current in causing reversible electrolytic separations. The freedom of passage indicated by the facts of electrolysis must therefore exist, whether a current flows or not ; the function of the electric forces is merely directive, and the only work expended is done against that frictional resistance to the motion of the ions which is called the ionic viscosity.

So far our results show that under all conditions the ions possess the freedom necessary for their passage through the liquid. That freedom may, however, on the facts enumerated, be secured by a possibility of interchange between the oppositely electrified parts of two dissolved molecules at the instant of collision, or to the successive formation and decomposition of molecular aggregates. Let us trace the consequences of such suppositions.

In accordance with the elementary principles which hold good for the chance encounters of a large number of moving particles, the frequency of collision, or the number of molecular aggregates formed per second, will be proportional to the square of the number of dissolved molecules. Now, on the view suggested, the motion of the ions, and therefore the average ionic mobility, will depend on such chance collisions, and be proportional to the frequency with which they occur. The velocity of the ions under a given potential gradient will thus be proportional, approximately at any rate, to the square of the concentration of the solution. The quantity of electricity conveyed per second under a given electromotive force, that is, the conductivity of the solution, must depend on the product of the relative velocity of the ions and the number of ions per unit volume. It follows that, on any hypothesis of molecular interchanges, the conductivity of a solution will be approximately proportional to the cube of the concentration. This result is quite contrary to observed facts. In dilute solutions, the conductivity is nearly proportional to the first power of the concentration, and, as the concentration increases, the conductivity usually

increases at an even slower rate. We are bound to conclude that no process which requires the conjunction of two molecules is involved, and that the ions move independently of each other through the liquid. It should be noticed that migratory independence from each other on the part of the ions is quite compatible with connexion between the ions and the solvent, whether such connexion is of the nature of definite chemical combination or more general physical influence. The electrolytic dissociation theory is quite independent of any particular view we may take of the nature of solution, which may be produced by actions analogous either to physical or to chemical processes.

Many other purely electrical phenomena indicate the same independence of the ions, and receive a ready explanation if that conclusion be accepted. Thus, Kohlrausch's specific coefficients of ionic mobility are definite constants for each ion in dilute solution, and do not depend on the other ion present. Again, when a layer of water is placed on the top of a solution of an electrolyte, owing to the diffusion of the two ions the water takes with reference to the solution a positive or negative potential, according as the positive or negative ion in that solution has the greater mobility. From a knowledge of the osmotic pressures and of the specific coefficients of mobility of the ions, Nernst has shown that it is possible to calculate the observed numerical values both for this difference of potential and for the rate of diffusion of the salt as a whole.

Let us now turn to the second series of observations which led to the development of the dissociation theory. The phenomena of osmotic pressure, and the laws to which those phenomena conform, can be deduced by the application of thermodynamics, either in the manner of van't Hoff and Lord Rayleigh, from the observed relations between the solubility of gases and their pressure, as formulated in Henry's law, or from the fundamental ideas of the molecular theory, as pointed out by Willard Gibbs, von Helmholtz, and Larmor. Adopting the latter method, it is clear that the osmotic pressure which a solution will exert against a solvent is measured by the rate of change of the available energy of the system when solvent is allowed to enter the solution reversibly through a semi-permeable membrane. On the molecular theory, we must imagine the solute to be distributed through the liquid as a number of discrete particles, each of which may affect, either by way of chemical combination or physical influence, a certain minute volume of the solvent lying round it. The nature of this influence is unknown, but, whatever

it may be, as soon as the solution becomes so dilute that, except for an inappreciable fraction of the time, these spheres of influence do not in general intersect each other, any further addition of solvent will only increase the separation of the spheres of action; it cannot change the internal condition of one of these spheres or affect the interaction between the solute particles and their surrounding solvent. The change of available energy produced by the entry of solvent must then simply be that due to the dilution of the solute particles, and cannot depend on any interaction between solute and solvent. The rate of change of available energy with dilution, that is, the osmotic pressure, must consequently be independent of the nature of the solvent, and will therefore have the same value if no solvent be present. Thus, in cases where this is possible, that is, for volatile solutes, it follows that the osmotic pressure must be equal to the gaseous pressure corresponding to the same concentration. We thus theoretically establish the gaseous laws for the osmotic pressure of volatile solutes, and, since volatility is probably only a matter of degree, it seems reasonable to extend this result to non-volatile bodies. Whether this extension be regarded as theoretically valid or not, there is abundant experimental evidence that it is practically justified, since the osmotic pressure of solutions of such substances as cane-sugar is well known to have the gaseous value.

When in solutions of electrolytes we examine the osmotic pressure or the correlated effects such as the depressions of the freezing-point, abnormally great values are obtained, and, by the course of reasoning given above, it follows that a number of solute particles greater than that indicated by the chemical formula must exist in the solution; that is, that dissociation must have occurred. To connect this result with the migratory independence of the ions of electrolysis, it is necessary to show that for solutions so dilute that the solute particles are beyond each other's sphere of influence, the number of ions indicated by the electrical behaviour is the same as the number of independent particles required to produce the observed osmotic effects. Thus for a dilute solution of potassium chloride, which yields two electrical ions, potassium and chlorine, the depression of the freezing-point should be twice as great as for a solution of cane-sugar of equivalent molecular concentration. For bodies yielding three ions, such as sulphuric acid or barium chloride, the freezing-point depression should similarly be three times the normal value. When the concentration of the solution is increased, the spheres of influence of the solute particles will intersect, and

the thermodynamic deduction of the gaseous value of the osmotic pressure ceases to be valid. Unless we know at what concentration this intersection begins to produce appreciable effects, and what its result will be both on the electrical and on the osmotic properties, we cannot infer that the decrease in equivalent conductivity will proceed in accordance with the decrease in the abnormal excess of osmotic pressure.

It has commonly been assumed, as a necessary consequence of the dissociation theory, that the number of ions indicated by the electrical conductivity must agree with the number of particles producing osmotic pressure both at extreme dilution, when the ionization is usually complete, and also when the concentration is increased to a moderate extent and some of the ions recombine. While it seems likely that the first of these relations should hold in cases where the ionization is known to be complete, it will now be evident that the second relation can only exist if the connexion between the ions, which is produced by increasing the concentration, affects equally both the conductivity and the osmotic properties. Such might be the case were the only result of increasing concentration to cause a certain number of ionic re-combinations to form electrically inactive molecules, each molecule producing the normal osmotic effect; but, if any other appreciable influence arises from ion to ion, it may possibly change the rate of variation of available energy with dilution, that is, the osmotic pressure, before it decreases the ionic mobility. The second relation then can only be expected to hold while the solute particles are beyond each other's sphere of action, and the experimental examination of the relation merely gives a means of estimating at what dilution this condition fails. The conductivity shows that ionization begins to be incomplete at very great dilutions. Even for monovalent salts, such as potassium chloride, the equivalent conductivity begins to diminish at concentrations of about  $10^{-3}$  gram-equivalent per litre, while, with salts containing divalent ions, it is doubtful if complete ionization is more than just reached at the greatest dilution which can be investigated experimentally, namely about  $10^{-5}$  gram-equivalent per litre. Incomplete ionization, however, does not necessarily connote inter-ionic influences except at the moments of collision and in the combined molecules, while for non-electrolytes, the gaseous value of the osmotic pressure is known to extend to much higher concentrations. It is possible, therefore, that the second relation suggested by the theory should hold good for a certain small range of concentration. Nevertheless, as

Dr. Larmor has pointed out to the writer, there is reason to believe that the gaseous laws would fail at much smaller concentrations in solutions of electrolytes than in those of non-electrolytes. If, as is most likely, the forces between the dissolved molecules are electrical in nature, the effect of two non-ionized bipolar molecules on each other will be analogous to that between two short magnets: the force will vary inversely as the fourth power of the distance. On the other hand, with two isolated charged ions, the force will be that between two small electrified bodies, and will vary as the inverse square of the distance. Thus, beyond a certain minute range, the inter-molecular forces will rapidly become insensible, and solutions of non-electrolytes will then conform to the gaseous laws. Electrified ions, however, will produce sensible effects on each other at ranges much beyond these inter-molecular spheres of action, and, even at great dilution, will diverge from the ideal conditions. Such divergence will certainly change the quantity of work done on dilution, and thus affect the osmotic properties. It is not clear, however, that it will also diminish the migratory freedom necessary for electrolysis: the inter-ionic forces will, on the average, be equal in all directions, and may not influence the mobility of the ions under an electromotive force. As a conclusion, then, it follows if we accept the dissociation theory that, in those solutions which are known to be fully ionized at great dilutions, the limiting values of the osmotic properties and of the electrical conductivity should indicate the same number of ions to the molecule; when the concentration increases and the ionization of such solutions ceases to be complete, it is possible, but not necessary, that, throughout a small range, the two methods should give identical values for the coefficient of ionization; the concentration at which such identity ceases should probably indicate the point at which inter-ionic forces begin to prevent further conformity with the gaseous laws; and finally, for the case of solutions in which complete ionization is not shown by the equivalent conductivity, we cannot assume that any exact relation between the two lines of research will be found.

We must now see how far the experimental facts bear out these theoretical conclusions. The equivalent conductivity of electrolytes reaches a definite limit at a dilution which can only be experimentally examined with accuracy in solutions of simple salts, such as potassium chloride, which contain two monovalent ions. In these cases alone, then, can we look for the verification of the ideal relations. At the present time, the best known of the osmotic properties is the depression

of the freezing-point, and in Raoult's book on *Cryoscopy* are given the following results obtained by Loomis for the molecular depressions at a concentration of 0.01 gram-molecule of salt in 1000 grams of water, as in themselves trustworthy and in accordance with the best of other results published before the year 1901.

*Group I.*

Potassium hydrate ...	3.71	Nitric acid .....	3.73
Hydrochloric acid ...	3.61	Potassium nitrate .....	3.46
Potassium chloride ...	3.60	Sodium nitrate .....	3.55
Sodium chloride .....	3.67	Ammonium nitrate ...	3.58

*Group II.*

Sulphuric acid .....	4.49	Calcium chloride .....	5.04
Sodium sulphate .....	5.09	Magnesium chloride...	5.08

*Group III.*

Magnesium sulphate...	2.66	Zinc sulphate .....	2.90
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In the first group are substances which are shown by their electrical properties to yield in solution two monovalent ions. On the dissociation theory, therefore, the osmotic pressure effects should, at high dilution, have double their normal value. The normal value for the molecular depression of the freezing-point is 1.857, calculated from the osmotic theory, and confirmed by experiments on dilute aqueous solutions of non-electrolytes. Twice this value is 3.714, a number to which all the observed molecular depressions of substances in Group I. closely approximate. The electrical behaviour of bodies in the second group similarly indicates dissociation into three ions, which would produce a molecular depression of 5.57. The experimental numbers differ from this value by about 10 per cent., but the error is in the right direction, since the electrical conductivities at the concentrations used show that the ionization is still far from complete in salts with divalent ions. The corresponding error is yet greater in salts of the third group, which give two ions both divalent; the molecular depression should be again 3.714, a number exceeding the observed values by about 30 per cent. All discrepancies are thus of the kind to be expected from a consideration of the electrical phenomena; and the salts of the first group, which are about 95 per cent. ionized at the concentration used in the cryoscopic experiments, yield very concordant results.

Since the date of Raoult's book, the most important and



accurate determinations of freezing-points are those undertaken by Dr. E. H. Griffiths by the methods of platinum thermometry. The results as yet obtained were announced to the British Association in the year 1901. From concentrations 0.0005 to 0.02 normal, the molecular lowering of the freezing-point of water produced by cane-sugar was found to be 1.858, while that produced by potassium chloride slowly increased with the dilution, till, in a solution of 0.0003 gram-equivalent per litre, it reached 3.720. Thus the non-electrolyte gave the theoretical result, and the binary electrolyte twice the molecular depression of the non-electrolyte, within extraordinarily narrow limits of experimental error. At this concentration the conductivity indicates that the ionization is about 99.7 per cent. Thus the evidence at present available goes to support the accuracy of the first relation of Arrhenius' theory in the case of aqueous solutions; the observed depressions never appreciably exceed the theoretical values, and the discrepancies in the other direction are readily explicable by incomplete ionization.

Passing to solutions in solvents other than water, we find that sufficient data are not available to decide whether the same relation between the electrical and the osmotic phenomena holds good. The difficulties of experiment are much increased, and no observations on osmotic effects seem to have been made on solutions in which the dilution was carried far enough to secure complete ionization. In many aqueous solutions, such as those of acetic acid and ammonia, complete ionization cannot be experimentally attained; and, without definite evidence, we cannot assume that it is in general reached by possible dilution in another solvent. For reasons already indicated, measurements on stronger solutions are of little use in this connexion. Moreover, for non-aqueous solutions we usually have little knowledge of the general electrolytic behaviour, and of such electrical constants as the transport numbers, so that it is not safe to conclude that the ions are of the same nature as those of the corresponding solutions in water. In alcoholic solutions, at any rate, what little evidence is forthcoming suggests that complex ions are very numerous, even at moderate dilutions, and any such complexity will diminish the number of solute particles and consequently the osmotic effects. Kahlenberg finds that solutions of diphenylamine in methyl cyanide show abnormally low molecular weights, and yet are non-conductors of electricity. Such a result perhaps indicates a dissociation yielding products which are not electrically charged, or a non-electrical double decomposition with the solvent. Until

further experiments have been made, it is impossible to say whether or not the first relation suggested by the dissociation theory holds for non-aqueous solutions. In fact, however great be the likelihood of the general similarity of all conduction in solutions, we have not sufficient knowledge of electrolysis in non-aqueous media to conclude that the nature of the process is the same as in aqueous solution. It is not yet certain that we can here apply Faraday's laws, Ohm's law, and Kohlrausch's theory of ionic velocity, though, for alcoholic solutions, a certain amount of evidence in favour of this view has been accumulated.

The second relation enunciated by Arrhenius suggests that, when the dissociation is incomplete, the coefficient of ionization measured electrically should agree with the value calculated from the osmotic effects; but, as we have seen, such a relation can only hold for certain cases, and then only within very narrow limits of concentration. In order to obtain a valid basis for exact comparison with cryoscopic determinations, it is necessary to measure the electrolytic conductivities at the freezing-point. When this is done, it is found that the two values of the ionization, though they approach each other with decreasing concentration, only actually coincide at the most extreme dilution reached in the cryoscopic experiments. Thus, in a full discussion of the subject which will be found in a treatise on the 'Theory of Solution' lately published by the present writer, it is shown that the disturbing causes we have indicated become appreciable at concentrations considerably smaller than hitherto believed; but it is now evident that the discrepancies that then arise are not conclusive evidence against the general truth of the explanations advanced by the dissociation theory. Such discrepancies merely afford useful information about the nature of the disturbing influences, and about the value of the concentration at which these influences begin to be appreciable.

Passing as before to solutions in solvents other than water, we again find the phenomena more complicated, even if the general nature of the conduction should prove to be the same as in aqueous solutions. Complex ions seem to be common, and other disturbing factors appear to be present. Kahlenberg has called attention to cases in which the boiling- or freezing-points of conducting solutions indicate molecular weights equal to or greater than the normal, and this suggests that no dissociation occurs. Until the specific ionic mobilities in these solvents are known, we have no means of estimating what percentage ionization is required to give the observed

conductivity ; if the mobilities are high, it is possible that a small value would be enough. In any case, such observations may be explained by association of the non-ionized solute molecules, or by the existence of complex ions.

Summing up the results of our inquiry as far as we have gone, we may say that, in those cases for which the theory indicates exact relations, the experimental evidence is in favour of their existence, while all discrepancies are either suggested by the theory itself, or else occur under conditions where the experimental knowledge is too fragmentary for valid conclusions to be drawn.

We must now turn to other deductions from the theory, towards which considerable criticism has lately been directed. In the first place, the mass law of chemical action, which can be established thermodynamically for dilute systems, has been applied to electrolytic dissociation by Ostwald with complete success in the case of aqueous solutions of weak acids; but the law fails when applied to strong acids and other highly ionized electrolytes, and this failure has been regarded as one of the great objections to the dissociation theory. It is probable, however, that the explanation is to be sought in that difference in the law of the variation of the force with the distance which we have already pointed out must exist between solutions containing non-ionized bipolar molecules and those containing dissociated electrified ions. The thermodynamic basis of the mass law is only valid for dilute systems, and, as we have seen, even at small concentration, the forces between dissociated ions may be quite sensible and produce disturbing effects.

The dissociation theory has also co-ordinated the electrical ionization of aqueous solutions and the coefficients of chemical activity. There is no such definite theoretical deduction of this relation as of that between the conductivity and osmotic effects ; the connexion of electrical ionization with chemical activity is a matter of observation, and the conclusion that, in the rapid chemical actions characteristic of electrolytes, it is the ions which alone are active, rests on the evidence of this connexion alone. The numerical relations given by Arrhenius, and the many deductions from this hypothesis which have been verified for aqueous solutions, have led to the idea that a similar explanation of the nature of all rapid chemical action might be given, whatever the solvent and whatever the conditions. There seems, however, no valid theoretical reason which necessitates such an extension, and it is possible that, in other solvents and for gaseous systems,

rapid chemical change may be brought about by non-electrical double decomposition. This idea is supported by an observation of Kahlenberg on the instantaneous production of a precipitate of copper chloride when hydrochloric acid is passed into a non-conducting solution of copper oleate in benzene. It is evident that such an observation indicates that, in the particular solvent used, chemical action may occur which is not correlated with electrolytic conductivity, but it does not in the least weaken the electrical and osmotic evidence which we have adduced above in favour of the theory of the ionic dissociation of the aqueous solutions of electrolytes.

### XXVI. *Notices respecting New Books.*

*Annuaire pour l'An 1903, Publié par le Bureau des Longitudes.*  
Avec des Notices Scientifiques. Paris: Gauthier-Villars (55 quai des Grands-Augustins). Pp. viii+808. Price 1 fr. 50 c.

THIS important annual contains, besides the usual astronomical, physical, and chemical tables, a number of specially contributed articles, the most important of which are:—"Shooting-Stars and Comets," by R. Radau; "Science and Poetry," by J. Janssen; "On the Work carried out at the Mont Blanc Observatory," by J. Janssen; and the speeches delivered by a number of distinguished French scientists as a tribute to the memory of the late A. Cornu and that of H. Faye.

*Compte Rendu du deuxième Congrès International des Mathématiciens, tenu à Paris de 6 au 12 Août 1900. Procès-verbaux et Communications, publiés par E. DUPORCQ.* Paris: Gauthier-Villars, 1902.

ALMOST every department of mathematics, pure and applied, is touched on in this volume; and a mere glance through its pages cannot fail to be instructive to mathematicians of all classes. Cantor contributes a paper on the Historiography of the science; Volterra an interesting estimate of the careers and labours of Betti, Brioschi, and Casorati. Hilbert discusses at considerable length the future problems of mathematics; Poincaré the rôle of intuition and logic; and Mittag-Leffler reproduces, with comments, some important letters of Weierstrass to Sophie Kowalewski. Then follow some thirty papers of various lengths upon the theory of numbers, analysis, geometry, dynamics, history, and methods of teaching. At one of the meetings some discussion arose in regard to the proposed adoption of Zamenhof's artificial language *Esperanto* as a universal language in science and commerce; but although the growing disadvantages attending the publication of scientific papers in so many different languages were fully recognized, the motion carried was that of Vassilief, that Academies and Societies study the means for remedying the evil at present existing.