DISCUSSION.

Mr. W. R. Bousfield, K.C., M.P. (*communicated*): The experimental investigation of the relation between hydration and ionisation can be approached along three converging lines. Each of these lines involves certain fundamental assumptions, and each depends for its successful quantitative application upon experimental work of a high order of accuracy. By combining these three lines of investigation it may be possible in the future to obtain a reliable estimate of the amount of water in combination with a solute under various conditions of temperature and concentration.

The first of these three lines of investigation is fully illustrated by Dr. Lowry in his reference to the work of Jones and Getman. The fundamental assumption involved in this method is that the relation between freezing-point depression and concentration (expressed in gramme-molecules per 1,000 grammes of solvent) obeys an exact straight line law. The exactitude of the law has not been fully demonstrated, and is, in fact, only claimed for very dilute solutions. Hence the method requires to be used with caution, and can only be relied on in combination with parallel lines of investigation. Dr. Lowry has shown that Messrs. Jones and Getman have made an unsound use of the data which they furnish, and his corrected figures show that their experimental data are not quite sufficiently accurate for exact quantitative deductions.

The second line of approach was foreshadowed by Dr. Lowry and myself in our recent paper on solutions of sodium hydroxide.* This method depends on the assumption, which has a high degree of probability, that the amount of contraction per gramme of solute which takes place in aqueous solutions is a measure of the amount of combination between solvent and solute.

If V be the "solution volume" of any solute, that is to say, the addition to

* Bousfield and Lowry, *Phil. Trans.*, 1905, **204**, p. 281.

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the volume of the water which ensues when one gramme of the solute is dissolved in a given volume of water, and if V_0 be the volume which one gramme of the solute would occupy in the liquid state, then the contraction resulting from the solution of 1 gr. of solute is $V_0 - V$. The solution volume V , which can be readily calculated from the density, is thus a measure of the contraction which takes place upon solution, and of the amount of water combination.

In that paper we gave a curve showing the gradual increase of contraction per gramme of solute with increasing dilution, and stated that the results indicated "that the process of hydration, on which the contraction of volume depends, proceeds continuously from the most concentrated to the most dilute solutions." We compared this increasing contraction with the increasing ionisation which takes place with increasing dilution, and pointed out that it "proceeds side by side with the process of ionisation, and does not cease until the latter is *almost* complete."

In a recent paper * I have further elaborated this method of investigation, and have given reasons which lead to the conclusion that the word "*almost*" in the above sentence should be eliminated, and that the hydration of the solute as evidenced by increasing contraction proceeds absolutely *pari passu* with increasing ionisation, until they both finally reach a limiting value together.

The third line of investigation, which I have dealt with at length in the same paper, is based upon a consideration of the variations of ionic size with temperature and concentration, as deduced by the application of Stokes' theorem as to the limiting velocity of a small sphere moving with small velocity in a fluid of known viscosity. Here is involved the assumption that Stokes' theorem is applicable to the dynamics of the hydrated ion, an assumption which I have endeavoured to justify in the paper. Proceeding upon this basis, I investigated the case of KCl, and arrived at the result that the volume of the hydrated ions for isothermal concentration variations at 18° C. was proportional to—

$$\left(1 + 3.33 H^{-\frac{2}{3}}\right) - 3$$

which expression holds accurately from about $H = 50$ to $H = \infty$. The values of the ionic volumes given by this expression are—

P. Percentage of KCl.	H. Total Hydration.	Ionic Volume.
0	∞	1.000
1	410	0.839
2	203	0.759
3	134	0.698
4	99	0.649
6	65	0.570

* "Ionic Sizes in Relation to the Conductivity of Electrolytes." An abstract of this paper appears in the *Proc. R. S.*, 1905, vol. lxxiv., p. 563. The full paper is in course of publication in the *Zeitschrift Phys. Chem.*

The ionic volumes are given in terms of the volume of the ions at infinite dilution as unity. This method only gives us the *relative* sizes, and hence the relative hydration at various concentrations. Moreover, the ionic volumes are not exactly proportional to the molecular hydration, as the volume of the nucleus of solute in the ions has to be subtracted in order to arrive at the volume of combined water.

The above results are arrived at solely from the conductivity and viscosity data for KCl, but I was able to correlate these results with those obtainable from the density data.

If the ionic volume be represented by I_v , I showed that the relation between solution volume and ionic volume was—

$$V = 0.405 - 0.05 I_v$$

which at once gave a rational density formula for KCl, viz. :—

$$\frac{1}{\rho} = \frac{H v + e V}{H + e}$$

where ρ = density of KCl solution.

H = total hydration.

e = ratio of molecular weight of KCl to molecular weight of water.

v = volume of 1 gr. of water at 18°.

V = solution volume of 1 gr. of KCl.

This may be written—

$$\frac{1}{\rho} = \frac{H v + e (0.405 - 0.05 I_v)}{H + e}$$

$$\text{where } I_v = \left(1 + 3.33 H^{-\frac{2}{3}}\right) - 3$$

This density formula holds accurately for KCl from 0 to 6 per cent., and since the values of I_v which enter into it are based *solely upon the conductivities*, we get a complete correlation between the density law and the conductivity law, with the result that ionisation and hydration (as evidenced by contraction) are shown to proceed *pari passu*, and that complete ionisation is only attained at the same time that maximum contraction per gramme of solute is reached.

The results of these three lines of investigation, fragmentary though they are at present, appear to me to indicate the generalisation that the amount of combination of solvent with solute increases progressively and continuously with increasing dilution, and reaches its maximum only when complete ionisation is attained. The considerations urged by Dr. Lowry all seem to point to the same conclusion, which is indeed, as he indicates, the only one which can be reconciled with the law of mass action. According to the law of mass action, the amount of water combination should continue to increase up to the point at which the ions may be regarded as completely isolated by the solvent, so that there is no longer any competition among the ions for the molecules of the solvent. This is the point which we usually style "infinite dilution."

I observe that Dr. Lowry considers that the H and OH ions "are either anhydrous or are combined with a smaller proportion of water than any of the other ions." The latter is in my opinion the true view. The large variations in size of the H and OH ions, as shown by the great temperature variations of their mobilities, can, I think, only be accounted for by variations of size due to water combination. It is clear, however, that the amounts of

combined water can only be small. By the use of Stokes' theorem it can be calculated that at 18° C. the volume of the hydrated H ion is only $\frac{1}{33.8}$ that of the hydrated lithium ion, whilst the volume of the OH ion is about six times as great as that of the H ion. The hydration of both ions must therefore be very small compared with that of the lithium ion.

It was pointed out by Dr. Lowry and myself* that the viscosity temperature co-efficients and the conductivity temperature co-efficients for "water" were *practically identical*, and this might at first sight seem to support the view that the H and OH ions are anhydrous, since the identity of the co-efficients would be consistent with the view that the sizes of the conducting ions did not change with temperature. But further consideration displaces this view. If we assume for the moment that the minute conductivity of purified "water" is due to H and OH ions, we should have for the specific conductivity of water—

$$\kappa = m(u + v)$$

where m represents the concentration of the conducting ions and u and v the mobilities of the H and OH ions. The values of u and v are—

$$\begin{aligned} u &= 318(1 + 0.0154 T - 0.000033 T^2) \\ v &= 174(1 + 0.0179 T + 0.000008 T^2) \end{aligned}$$

where T stands for (temperature - 18°), and the temperature co-efficients of the H and OH ions are taken from Kohlrausch.†

The substitution of the values for u and v gives us

$$\kappa = m \times 492(1 + 0.0163 T - 0.00018 T^2)$$

Now the experimental temperature formula for "water" as given by Kohlrausch is

$$\kappa = \kappa_{18}(1 + 0.0251 T + 0.000130 T^2)$$

Thus we see that the actual temperature co-efficients *cannot be derived from those of the H and OH ions*, and we are driven to the conclusion that *these are not the ions upon which the observed conductivity of "water" depends.*

It is doubtful whether water possesses any autolytic conductivity whatever. Its observed conductivity probably depends upon a volatile organic impurity which it is almost impossible to separate entirely from water. In the continuous distillation of water into a platinum vessel I have observed a jelly-like organism growing freely in the continuously renewed distillate at a temperature of about 30° C., indicating that the organic food necessary for the growth of the organism was still present in a high-class distilled water. The temperature co-efficients given by an impurity of this kind might very well be almost identical with the viscosity temperature co-efficients. For instance, the temperature co-efficients of sodium valerate are very close to the required values. I do not think, therefore, that there is any evidence for regarding the H and OH ions as being anhydrous, and on the other hand the evidence furnished by their temperature co-efficients points the other way.

The development of the hydrate theory of ionisation may possibly do something to modify the views of Lord Kelvin and others who have hitherto held out against the current views. They have revolted against the idea that a naked ion of sodium (for instance) could be floating about in water without decomposing the water and uniting with OH. A calculation based on the

* Bousfield and Lowry, *Proc. R. S.*, 1902, lxxi., p. 48.

† *Preuss. Akad. Wiss. Berlin, Sitz. Ber.*, 1901, xlii., p. 1031.

relative mobilities shows that the volume of the sodium ion at 18° C. and "infinite dilution" is nearly 400 times that of the H ion and about 60 times that of the OH ion. If, therefore, we suppose the sodium ion to be combined with n molecules of water, it may well be that the combination $\text{Na}(\text{H}_2\text{O})_n$ is a more stable combination than NaOH. An examination of this matter from the thermodynamic point of view would be interesting.

Much accurate work remains to be done in order to determine the physical constants to which the hydrate theory of ionisation necessarily leads, and I hope that the weight of evidence in its favour which Dr. Lowry has brought to bear in this paper, will lead to this work being systematically undertaken.

Dr. F. G. Donnan (*communicated*):—I was surprised to find no mention of the name of Werner in Dr. Lowry's interesting *résumé*, although our present concepts concerning the part played by "hydration" (or combination with the solvent) in ionisation-phenomena are very largely due to Werner's researches. Twelve years ago (*Zeitschrift für Anorganische Chemie*, vol. iii. p. 294, 1893) Werner expressed the view that ionisation is preceded by combination with the solvent, and showed for the first time how it was possible to bridge over the gap between the "Hydrate" and "Ionisation theories." The work of Werner, taken in conjunction with the masterly researches of Abegg and Bodländer, has shown very clearly that what is ordinarily termed normal or simple ionisation may be to a very large extent a "complex" ionisation, in which the solvent molecules play an essential part.

I scarcely think that Dr. Lowry has put the historical development of these ideas in a sufficiently clear light.

Mr. G. T. Beilby said that all who were interested in the theory of solution must be grateful to Dr. Lowry for his clear exposition of the latest developments by himself and by other workers of the hydrate theory. For his own part he believed that while association and dissociation play vitally important parts in the phenomena of *solutions*, yet they are not in themselves the true cause of *solution*. He was much interested in the author's views regarding conduction in the Nernst filament, but he did not agree that the Nernst mixture remained permanently in the vitreous state, for microscopic examination showed that after heating to the working temperature, the filament became crystalline. According to the phrase theory of the amorphous and crystalline states this was to be expected.

Mr. H. D. Law: Although the theory of hydrated ions is by no means new, hydration, as the direct cause of ionisation, is introduced by Dr. Lowry for the first time. The subject has been treated in such a broad manner that very few points are left open for discussion, and these for the most part increase rather than detract from the value of the theory. A few points, however, deserve a more careful study than has been given to them by the author. Assuming the theory to be correct, both water and methyl alcohol will produce ionisation in a similar manner. As these two liquids are strongly ionising media there will be attached to any ions present in a mixture, amounts of water and methyl alcohol roughly proportional to the quantity of each solvent present. Thus in the experiment of Lobry de Bruyn the number of silver ions containing water and those containing alcohol will be roughly proportional to the quantity of each solvent present. Thus in the solution there are two kinds of silver ions, one loaded with water molecules and the other containing methyl alcohol molecules. On electrolysis both will pass to the electrodes and the relative proportion of water to alcohol will in no way be disturbed during the process. If, however, a solvent had been chosen which has no marked ionising effect on silver nitrate, or, one which is

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in no way related to water, a displacement might have been expected. Thus, in the case of a mixture of pyridine and water—two entirely dissimilar substances—containing silver nitrate, a marked displacement has been observed in electrolysis (Livingston Morgan and Kanolt, *Zeitsch. für Physik. Chemie*); a direct attempt has been made to determine the amount of water attached to each ion by Bruni and Manuelli (*Zeitsch. für Elek. Chemie*). The chlorides of cobalt, manganese, and copper were dissolved in urethane, which is a non-ionising medium. Small quantities of water were then added, and the depression of the freezing points showed that in each case the undissociated molecules of the salts contained water attached to them. In the next experiments the same salts were dissolved in acetamide, which is a strongly dissociating medium. Water was again added in small quantities, but the molecular depressions showed only small irregularities. This, however, may be easily accounted for in consideration of the fact that both solvents will produce ionisation in the same manner. Thus it may be supposed that in the first place each ion contains its load of solvent—acetamide—and therefore in the addition of small amounts of water, paying due regard to the law of mass action, only a small portion will be used up for ionisation, and only small irregularities are to be looked for. These were actually found, especially in the case of copper chloride, and a simple calculation shows that the amount of water attached to each ion is extremely large. This, however, is only very slender evidence in favour of the theory and requires confirmation.

The author assumes that in the case of hydrogen and hydroxyl ions none or only small quantities of the solvent became attached, to explain, of course, the great mobility of these substances. This greatly weakens the theory and is quite unnecessary. In a recent number of the *Zeitschrift für Elektrochemie* it was shown that the undissociated molecules of any substance increase the mobility of its ions enormously. Thus the $\text{O}\cdot\text{CH}_3$ ion wanders to the electrodes with extreme rapidity in presence of methyl alcohol, and further, the velocity of H ions is by no means abnormal in solvents other than water or allied solvents. It is here supposed that the conduction takes place actually through these undissociated molecules rather than by the more roundabout way of the solvent. This also partially explains many curious results obtained in the case of strongly dissociated electrolytes, especially if considered in conjunction with the hydration theory.

Although this theory of Dr. Lowry's throws much light into many seemingly irregular phenomena, the conduction of solid substances is still shrouded in mystery. In the case of the Nernst lamp, for example, we have the conduction of a solid salt where rapid diffusion is impossible, and still apparently no polarisation at the electrodes takes place. There is also the still more familiar example of the copper wire. Up to the present time no ionic theory of solutions is capable of extension to these cases.

Dr. C. H. Desch said that they were greatly indebted to Dr. Lowry for the lucid manner in which he had stated his views. One of the principal reasons of the vogue enjoyed by the ionic dissociation hypothesis was the readiness with which it lent itself to mathematical treatment, and the simplicity of the relations thus obtained, at least in the case of dilute solutions, and this outweighed the obvious physical objections to the hypothesis. He hoped that Dr. Lowry would turn his attention to this side of the question, and show them how to treat solution problems mathematically from the point of view of the hydrate theory.

He was struck by two difficulties in the hydrate hypothesis, or perhaps by one difficulty, expressed in two ways. Firstly, why should a hydrated

molecule break up into hydrated ions; and secondly, why should a solution containing such ions conduct electricity? He might perhaps be allowed to refer to a paper by Mr. E. C. C. Baly and himself (*Trans. Chem. Soc.*, 1905, **87**, 766), in which use was made of the conception of the atom as a system of electrons. Professor Hartley's work on the absorption spectra of metallic nitrates had shown that even in highly dilute solutions, which on the usual hypothesis were completely ionised, a physical connection must still exist between the two ions. When sodium and chlorine combined to form sodium chloride, a negative electron left the sodium atom and attached itself to the chlorine atom, thus establishing a Faraday tube of force between the two—the equivalent of the chemist's single bond of affinity. The action of ionising solvents was due to the pull which they exerted on the two halves of the molecule, tending to lengthen the Faraday tubes. When the lengthening was sufficiently great, interchange of ions between two neighbouring molecules would become possible, and in this condition the solution would conduct electricity. The degree of conductivity would be a measure of the relative number of molecules in the solution at any moment which were undergoing interchange. This number would be a function, amongst other things, of the relative "affinities" of the solvent for the dissolved molecules and for the ions, and in that way the theory would come into line with that proposed by Dr. Lowry.

Mr. H. J. Bluman asked the author whether the fact that in electrolyzing aqueous solutions of lead nitrate the vicinity of the cathode becomes depleted of lead ions, owing to the deposition of oxide on the anode, supported the results obtained by Messrs. Lorenz and Fausti, and mentioned by him regarding the behaviour of fused lead chloride solutions, or whether this was explained by a probable intermediate formation of plumbic acid.

Mr. F. S. Spiers asked the author whether he could give any explanation of the fundamental assumption made in his theory, namely, that the ions have a greater affinity for the solvent than have the undissociated molecules. With regard to electrolytic conduction by solids, were such conductors always *mixtures* of oxides, or was it possible even for a perfectly pure oxide so to conduct electricity?

The Chairman asked how the author would explain hydrolytic dissociation by means of the hydrate theory. For example, what would be the explanation of the hydrolysis of potassium cyanide, where free hydrogen cyanide is produced? The explanation is quite simple if we suppose water to contain H' and OH' ions; does the hydrate theory admit of these being present?

He thought that Dr. Lowry's Paper was of much value, in that it attempted to put the ionic theory, which was, if not in a somewhat chaotic condition, at any rate in some respects rather contradictory and nebulous, on a sound basis. There was no doubt that the extreme adherents of the ionic theory had been too prone to bend and contort experimental incompatibilities in order to get them to fall into line with their pet hypothesis.

By collecting together and carefully digesting and co-ordinating a large amount of scattered information the author had performed a very real service, and by his modification of the ionic hypothesis and his endeavour to bring it into line with experimental facts he had given food for reflection. Such Papers were often far more useful than the mere piling up of detached experimental data, which the authors endeavoured to make agree by means of formulæ and equations which often bristled with unknowns. He asked the meeting to accord a hearty vote of thanks to Dr. Lowry for his useful and suggestive Paper.

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Dr. Lowry, in reply, said that he claimed little originality for the theory that he had described. The main ideas had been 'in the air' for a considerable time, but were so far unfamiliar that he felt justified in making a statement in extension of the somewhat narrow and faulty accounts of the ionic theory that were still current in the text-books.

In reference to the application of Stokes' Law to the migration of the ions, he believed that in the case of the less mobile ions there was complete experimental proof of a direct proportionality between the fluidity of the medium and the mobility of the ion. In the case of the smaller and more mobile ions this direct proportionality ceased and the relationship

$$u = a f \text{ (} u = \text{mobility, } f = \text{fluidity)}$$

should be replaced by

$$u = a f - b f^2,$$

the factor b increasing with the mobility of the ion. Thus in the case of hydrogen an increase of 4 per cent. in fluidity produced an increase of only 3 per cent. in the mobility. The strict application of Stokes' Law in this case led to the improbable assumption that the size of the hydrogen ion and its power of combining with water actually increased with considerable rapidity when the temperature was raised.

The difference between the temperature coefficients for the conductivity of "water," and those for the mobilities of the hydrogen and hydroxyl ions, was of great importance as for the first time affording proof that the conductivity of water must be attributed to impurities, and cannot possibly be due to ionisation of the water itself. The futility of the conventional calculations of hydrolytic dissociation based upon an assumed "ionisation constant" for water was thereby fully demonstrated. He did not deny that amongst the many constituents of a salt solution small numbers of these ions might perhaps co-exist, but even if this were so the proportions would vary for each different solution.

The difficulties to which Dr. Desch and Mr. Spiers had referred did not appear to be at all serious, since there was abundant evidence for the existence of the forces postulated by the hydrate theory of ionisation. Any difficulty that might be felt was due to a lack of appreciation of the forces classified under the term "residual affinity"; the magnitude and importance of these forces was only now beginning to be realised, and the dissociating effects produced by the chemical affinity between the molecules of the solvent and the constituent radicles of the solute would be largely reinforced by the mass-action of the solvent. Superposed on the purely chemical forces there might perhaps be a physical force favouring the aggregation of the solvent round the charged ions rather than round the neutral molecules of the solute.

A solution containing such charged ions, whether solid, liquid, or gaseous, would necessarily be a conductor, provided that the ions were free to move under the influence of the electrical forces. Until recently he had advocated the view that electrolytic conductivity in the case of solids was only possible when these were isotropic in character. Mr. Beilby had shown that the crystalline state was frequently less rigid than the amorphous, and might therefore offer less resistance to ionic motion. But he believed that the definite molecular structure of a crystal was, on the whole, inconsistent with the balanced molecular forces and labile molecular structure so characteristic of electrolytes, and that a crystal could only become an electrolyte by passing, either for the moment or permanently, into the amorphous state. The

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conduction in a Nernst lamp-filament might thus proceed through amorphous material, though the filament itself might contain a large proportion of crystal. It would be of interest to know whether electrical forces, like mechanical strain, could condition the passage from the crystalline to the amorphous state.

Mr. Law's suggestion of the rapid passage of an ion through the molecules of which it was a component was very similar to the theory of autolytic conduction that the author had put forward in conjunction with Mr. Bousfield (*Phil. Trans.*, 1904, 204, 256). At the same time he believed that the mobility of the hydrogen and hydroxyl ions was mainly due to the small affinity between the solvent and its own ions, resulting in the formation of exceptionally small ionic aggregates.