

ride and hydrochloric acid as calculated according to this principle are shown to furnish a better agreement with the measured values than are those based on the isohydric principle.

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GHOSH'S THEORY OF ELECTROLYTIC SOLUTIONS.

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1. Introduction.

The so-called "anomaly" of solutions of strong electrolytes has been one of the outstanding problems of chemistry almost since the inception of the Ionic Theory. Attempts which have been made to account for the behavior of these solutions from a theoretical standpoint have not met with marked success. In most instances such theories have been designed to account for only a limited number of the characteristic properties of electrolytic solutions and they have rarely been extended to include non-aqueous solutions.

In a series of articles¹ Ghosh has recently advanced a theory of electrolytic solutions which is very comprehensive in its scope, and which is founded upon somewhat novel assumptions with regard to the nature of electrolytes and their solutions. He has developed relations to account for nearly all important properties of electrolytic solutions in different solvents and has compared the consequences of his theory with existing experimental data. Therefrom he draws the conclusion that his theory is fully substantiated.

If Ghosh's theory is correct, it will be necessary to alter greatly the present day treatment of the properties of electrolytic solutions. Since, ultimately, the soundness of any theory must be judged by the degree of correspondence between the experimental data and the consequences resulting from the theory, a consideration of the postulates and assumptions upon which the theory of Ghosh is founded may be deferred until this theory has been examined from an experimental point of view.² The question to be answered is: To what degree of precision is Ghosh's theory able to account for the experimental data? If the theory is correct in its essential details, as Ghosh believes it to be, then it should render substantial account of the experimental results. Systematic deviations, between the consequences of the theory and the experimental facts should

¹ Ghosh, *J. Chem. Soc.*, **113**, 449, 627, 777, 790 (1918).

² Partington (*Trans. Faraday Soc.*, **15**, 111 (1919-20)) has criticized certain features of Ghosh's theory and Ghosh has replied to the same (*ibid.*, **15**, 154 (1919-20)). This discussion, however, has left many points in an uncertain state.

appear only under conditions not included within the scope of the theory as postulated.

2. Method of Testing the Equation.

In examining a theory of this kind, whose purpose is to account for the relation between a dependent and a number of independent variables, it is practically necessary to resort to graphical methods, for in no other way is it possible to comprehend at a glance the degree of correspondence between theory and experiment, as one or another of the independent variables is subjected to change. The only graph which has a decided value for this purpose is one which leads to a linear relation between the independent and the dependent variables under consideration. Where the equations involving the variables in question are complex, other variables must be chosen such that a linear relation exists between them, which, in some cases, renders the problem difficult, since various undetermined constants may be involved. In the case of the Ghosh Equation, however, a comparison by graphical method is both simple and conclusive, since a linear relation exists between the experimentally determined variables themselves. The conductance is expressed as a function of the concentration by means of the equation

$$\log \Lambda = \log \Lambda_0 - \frac{\beta C^{1/3}}{DT} \quad (1)$$

where

$$\beta = \frac{NE^2 (2N)^{1/3}}{2.3026 mR}.$$

Here N is Avogadro's number, 6.16×10^{23} , E is the electrostatic unit of charge, 4.7×10^{-10} e.s.u., R is the value of the gas constant in absolute units, and m is a factor depending upon the number of ions n produced from a single neutral molecule and upon the number of charges associated with a single ion, as well as the manner of distribution of these ions in the solvent medium. It is evident that, for a given solvent at a given temperature, the logarithm of the equivalent conductance is a linear function of the cube root of the concentration. Any systematic deviations between the experimental and the theoretical values will at once be apparent if the experimental values of $\log \Lambda$ and of $C^{1/3}$ are represented graphically. This method of treatment, moreover, obviates any assumption with respect to the values for the constants Λ_0 and β , since, if the theoretical equation holds, the experimental values will follow a linear relation from which the values of the constants may be uniquely determined.

3. Aqueous Solutions of Potassium Chloride.

In Fig. 1, values of $\log \Lambda$ are plotted as ordinates and those of $C^{1/3}$ as abscissas for solutions of potassium chloride in water at 18° , the data

being due to Kohlrausch and Maltby,³ and to Washburn and Weiland.⁴ According to Ghosh, β should have the value 3.620×10^3 for binary electrolytes in water, C being expressed in mols per liter. In the figure the straight line drawn, passing through the point $C^{1/2} = 0.2154$, corresponds to Ghosh's equation. Ghosh assumes a value of 122.5 for the conductance of potassium chloride at 0.01 N , in determining the value of Λ_0 . The value due to Kohlrausch, however, is 122.37. For the purpose of comparison, therefore, the straight line corresponding to Ghosh's equation has been drawn through this point at an angle corresponding to the value of β assumed by Ghosh, namely, $\beta = 3.620 \times 10^3$.

In the following table are given the calculated and observed values of Λ for solutions of potassium chloride in water at 18°, together with the differences between the observed and the calculated values.

TABLE I.
COMPARISON OF OBSERVED AND CALCULATED VALUES OF Λ FOR POTASSIUM CHLORIDE
IN WATER AT 18°.

	$\Lambda_0 = 132.06.$		$\beta = 3.620 \times 10^3.$			$T = 291.$	$D = 81.$	
V	5×10^4	2×10^4	10^4	5×10^3	2×10^3	10^3	5×10^2	
$\Lambda_{\text{calc.}}$	130.80	130.35	129.90	129.35	128.40	127.47	126.30	
$\Lambda_{\text{obs.}}$	129.51	129.32	129.00	128.70	128.04	127.27	126.24	
$\Lambda_{\text{obs.}} - \Lambda_{\text{calc.}}$..	-1.39	-1.03	-0.90	-0.45	-0.36	-0.20	-0.06	
V	2×10^2	10^2	50	20	10	5	2	1
$\Lambda_{\text{calc.}}$	124.31	122.37	119.97	116.9	112.1	107.4	99.7	92.7
$\Lambda_{\text{obs.}}$	126.24	122.37	119.90	115.6	111.8	107.5	101.3	96.5
$\Lambda_{\text{obs.}} - \Lambda_{\text{calc.}}$..	+0.03	=0.00	-0.07	-0.3	-0.3	-0.1	+1.6	+3.8

The conductance values, as determined by Kohlrausch and by Washburn and Weiland have a relative precision greater than 0.1%. In all likelihood the mean error does not exceed 0.05%. At the higher concentrations the conductance is measurably affected by the viscosity change of the solution due to the added salt. Since Ghosh subsequently employs conductance values corrected for viscosity,⁵ these corrected values have been employed in the comparison whose results are given above. It is evident that the observed values of Λ diverge from the theoretical curve at concentrations above approximately $2 \times 10^{-2} N$ and below $10^{-3} N$. These deviations greatly exceed the probable experimental error. The experimental curve is concave toward the axis of concentrations in dilute solutions and convex toward this axis in concentrated solutions with an inflection point at an intermediate concentration. The curve resulting from Ghosh's equation is very nearly tangent to the experimental curve in the neighborhood of the inflection point. Whether

³ Kohlrausch and Maltby, *Wiss. Abh. phys.-tech. Reichsanstalt*, **3**, 210 (1900) Noyes and Falk, *THIS JOURNAL*, **34**, 454 (1912).

⁴ Washburn and Weiland, *ibid.*, **40**, 137 (1918).

⁵ Ghosh, *Trans. Faraday Soc.*, **15**, 154 (1919-20).

this coincidence possesses a real significance or is merely an accidental result may be determined by an examination of non-aqueous solutions. It is well known that at lower concentrations the ionization curves for aqueous solutions of different binary electrolytes are practically identical and consequently what is true of solutions of potassium chloride will be true of other solutions of binary salts in water.

Ghosh's equation reduces to the form $\Lambda_0 - \Lambda = AC^{1/2}$, at very low concentrations. This equation is one of the empirical functions employed by Kohlrausch for representing the equivalent conductance of electrolytes as a function of their concentration. Ghosh looks upon this as lending support to his theory. It may be noted, however, that, as Kohlrausch himself pointed out, the cube root function yields a curve concave toward the axis of concentrations at low concentrations.⁶ In determining the value of Λ_0 , therefore, Kohlrausch employed a corre-

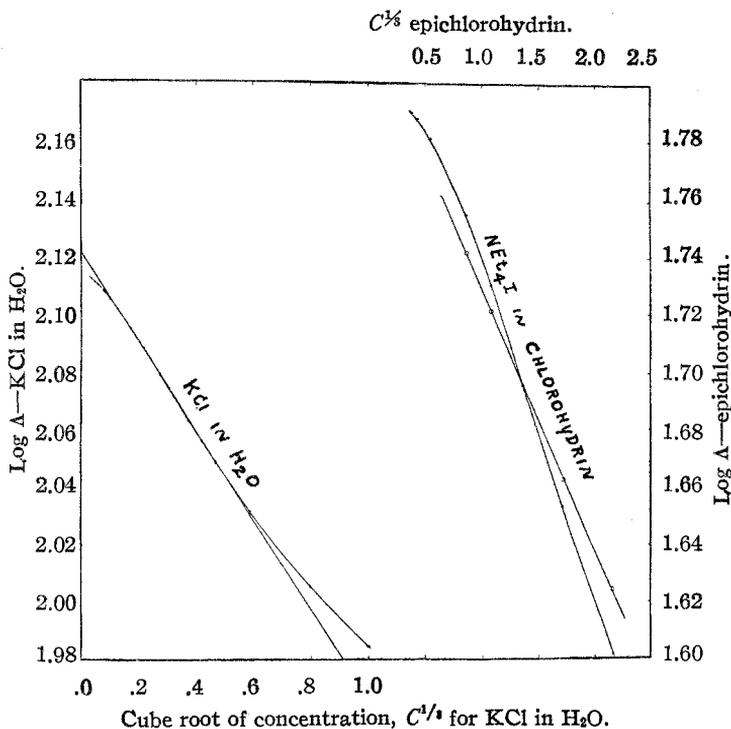


Fig. 1.—Curves for KCl in H_2O and NEt_4I in epichlorohydrin.

sponding extrapolation function in which the concentration appears with the exponent $1/2$ in place of $1/3$. This result of Kohlrausch is in entire accord with the results as plotted in Fig. 1, where the experimental curve is markedly concave toward the axis of concentrations at low concen-

⁶ Kohlrausch and Maltby, Ref. 3., p. 218.

trations. It is clear that the equation of Ghosh cannot be looked upon as exact. However, in view of the fact that the theoretical curve coincides in slope with the experimental curve in the neighborhood of the inflection point, it will be necessary to examine solutions in other solvents than water in order to determine whether or not Ghosh's theory contains in it certain elements of truth.

4. Application to Freezing-Point Data.

Before proceeding to a consideration of the conductance curve in non-aqueous solutions, we may examine the results of Ghosh's theory as applied to the freezing points of aqueous solutions of electrolytes. For the value of the van't Hoff factor i , Ghosh obtains the equation⁷

$$i = n \left(1 - \frac{1}{2} \log \frac{1}{\gamma} \right), \quad (2)$$

where n is the number of ions into which the electrolyte dissociates, and γ is the ionization, as calculated from Ghosh's Equation 1. According to the usual ionic theory, the value of i is given by the equation, $i = 1 + (n-1)\gamma$, where, as before, n is the number of ions into which the electrolyte dissociates and γ is the degree of ionization as calculated from conductance measurements, the value of Λ_0 being extrapolated by means of empirical functions.

It is a well-known fact that for dilute solutions of many electrolytes, such as potassium chloride, for example, the value of i , as determined from freezing-point measurements, agrees within the limit of experimental error with the value as determined from conductance measurements on the basis of the usual ionic theory. It follows, therefore, that the values of i , as calculated from Equation 2, cannot be in agreement with the experimentally determined values of i . In the following tables are given the values of i as calculated according to the equations of Ghosh, assuming the constants given in Table I, together with the experimentally determined values of Adams⁸ and the values calculated from conductance measurements in the usual way.

TABLE II.
COMPARISON OF THE EXPERIMENTALLY DETERMINED VALUES OF i WITH THOSE CALCULATED ACCORDING TO GHOSH'S EQUATION AND THOSE CALCULATED ACCORDING TO THE IONIC THEORY.

$C \times 10^3$	2.	5.	10.	20.	50.	100.
i_{Ghosh}	1.970	1.960	1.949	1.936	1.913	1.891
i_{Adams}	1.969	1.961	1.943	1.922	1.888	1.861
$i_{\text{cond.}}$	1.971	1.956	1.941	1.918	1.889	1.860

From the table it is evident that, at concentrations above 0.01 N , the values as calculated from Ghosh's equation deviate systematically

⁷ Ghosh, Ref. 5, p. 707.

⁸ Adams, THIS JOURNAL, 37, 481 (1915).

from the determined values by amounts which are in excess of the experimental error. These deviations exceed 1% at 0.1 *N*. Another fact which argues strongly against the adequacy of Ghosh's equation is the fact that the values of *i* as determined from freezing-point measurements differ for different electrolytes at higher concentrations. Since the value of *i* as calculated from Ghosh's equation is the same for all electrolytes of the same type, it follows that the observed variation in the experimentally determined values of *i* are not accounted for by his theory. In the following table are given values of *i* for a number of binary electrolytes at a concentration of 0.1 *N*.

TABLE III.

VALUES OF *i* AT 0.1 *N* CONCENTRATION FOR DIFFERENT ELECTROLYTES IN WATER.

Salt.	KCl.	KNO ₃ .	KIO ₃ .	NaIO ₃ .	LiCl.	KOH.	HCl.
<i>i</i>	1.861	1.787	1.764	1.772	1.901	1.865	1.917

The values of *i* for the first four electrolytes are derived from the very exact determinations of Adams⁸ and of Hall and Harkins,⁹ while the remaining values are taken from the tables given by Noyes and Falk.¹⁰ It is seen from this table that the extreme variation in the value of *i* is from 1.764 to 1.917. This variation in the value of *i* for different electrolytes at higher concentration cannot be ascribed to experimental error. It represents, in fact, a real difference in the properties of the solutions of these substances. Ghosh's theory, being founded upon the assumption that all electrolytes are completely ionized, is obviously unable to account for the divergence in the properties of different electrolytes of the same type. In the case of aqueous solutions, as has already been pointed out, the ionization curves for different electrolytes do not differ very greatly, but it is evident that the freezing-point curves differ to a much greater extent. We shall see that, in non-aqueous solvents, solutions of electrolytes of the same type differ very largely as regards their ionization values according to the conductance method also.

5. Non-Aqueous Solutions.

The most extensive material for testing the applicability of Ghosh's theory is found in conductance data relating to solutions in non-aqueous solvents. That Ghosh experienced some difficulty in attempting to apply his equations to solutions in non-aqueous solvents is evidenced by the fact that he was forced to assume more or less arbitrary types of ionization for solutions of simple binary salts. In the case of solutions of tetraethyl-ammonium iodide, for example, he assumes a ternary ionization of the type $(MX)_2 = M_2^{++} + 2X^-$. No independent evidence exists in support of this assumption. As we shall see below, this assumption

⁸ Hall and Harkins, *THIS JOURNAL*, **38**, 2658 (1916).

¹⁰ Noyes and Falk, *ibid.*, **32**, 1011 (1910).

does not suffice to account for the extremely varied behavior of solutions in non-aqueous solvents. Indeed, to one familiar with the properties of solutions in such solvents, it is at once evident that the theory will meet with great difficulties, for, according to Ghosh's Equation, the ionization in a given solvent at a given temperature is independent of the nature of the electrolyte, while the experimental data indicate that different electrolytes of the same type, even at low concentrations, exhibit a varying degree of ionization depending upon the nature of the electrolyte, as well as upon that of the solvent.

Below are considered solutions of typical salts in a few non-aqueous solvents. The number of examples might be greatly multiplied, but those which are presented suffice to bring out clearly the inadequacy of Ghosh's theory. The solutions chosen are those for which experimental data of a relatively high degree of precision are available down to comparatively low concentrations. In Fig. 1 is shown the curve for solutions of tetra-ethyl-ammonium iodide in epichlorohydrin.¹¹ The experimental curve is manifestly similar to that of potassium chloride in water. The characteristic deviations from Ghosh's equation, however, are more accentuated. Ghosh's calculated values, assuming a ternary ionization process, are represented on the figure by circles, a straight line having been drawn through them. Had a binary ionization process been assumed, the straight line corresponding to his equation would have been inclined much less steeply than the one drawn. It is evident that the deviations between the experimental and the theoretical curves are far in excess of any possible experimental error. A somewhat better agreement between the calculated and observed values at intermediate concentrations would be obtained by drawing a straight line tangent to the experimental curve in the neighborhood of the inflection point at approximately $10^{-3} N$. This line would be inclined more steeply than that due to Ghosh and would consequently correspond to a value of β greater than 6.808×10^3 , which is that derived by Ghosh for a ternary ionization. But even in this case, at concentrations below $10^{-3} N$, the deviations between the observed and the calculated values would be far in excess of the experimental error. From the general form of the curve, also, it is evident that at higher concentrations the deviations would ultimately become marked. In the case of these solutions, however, experimental data are not available at higher concentrations. The value of β corresponding most nearly with the experimental curve is 9.38×10^3 .

In Fig. 2 are plotted the results for solutions of potassium iodide in liquid ammonia according to the measurements of Franklin¹² and for tetra-propyl-ammonium iodide in ethylene chloride according to measure-

¹¹ Walden, *Z. physik. Chem.*, **54**, 212 (1905).

¹² Franklin, *ibid.*, **69**, 290 (1909).

ments of Walden.¹³ Considering first solutions of potassium iodide in liquid ammonia, the discrepancy between Ghosh's theory and the experimental values is obvious. Down to concentrations as low as 0.001 *N*, the curve is distinctly convex toward the axis of concentrations. At somewhat higher concentration this convexity is extremely marked. This type of curve is characteristic of solutions in solvents of relatively low dielectric constant; that is, in the neighborhood of 20. In such solvents, at concentrations above 0.01 *N*, the equivalent conductance, in general, changes only very little with increasing concentrations; and, indeed, in certain cases increases with increasing concentration. At very

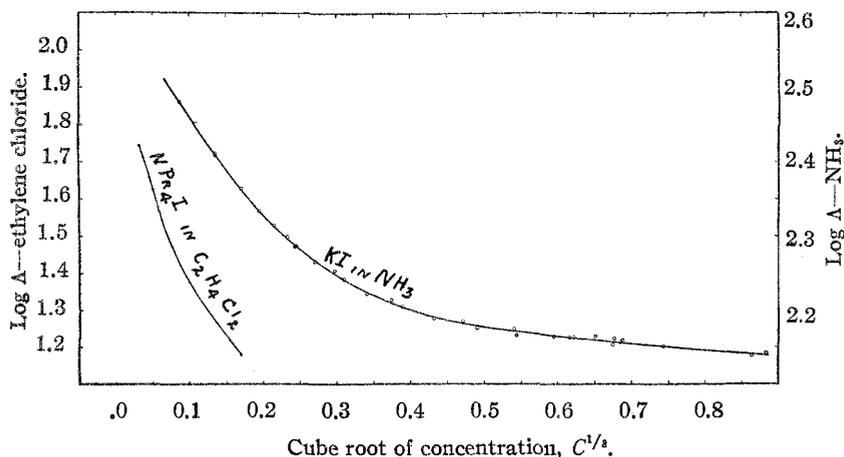


Fig. 2.—Plot of Ghosh's equation for KI in NH_3 and NPr_4I in $\text{C}_2\text{H}_4\text{Cl}_2$.

low concentrations conductance measurements are not available in the case of potassium iodide in ammonia, but from the known similarity in the behavior of solutions of different electrolytes in ammonia at low concentration it is clear that, at concentrations slightly below 0.001 *N*, the experimental curve would be concave toward the axis of concentrations. This is clearly brought out in the case of potassium nitrate in ammonia, which is shown in Fig. 3.

The curve for tetra-propyl-ammonium iodide in ethylene chloride is much steeper than that of potassium iodide in ammonia. At the higher concentrations the curve is again convex toward the axis of concentrations, while at the lowest concentrations the curve is slightly concave toward this axis. The best straight line which could be drawn through the points of this curve would lie tangent to the curve in the neighborhood of the inflection point, passing through a point at about 0.001 *N*. This yields for β the value 20.78×10^3 . It is clear, however, that the equation of Ghosh can reproduce the experimental results within the limits of error

¹³ Walden, *Z. physik. Chem.*, 78, 276 (1911).

only over an extremely small concentration interval in the neighborhood of the point through which the theoretical curve is arbitrarily made to pass.

According to Ghosh's theory, the ionization of electrolytes in a given solvent has the same value for all electrolytes of the same type under given conditions of temperature, pressure and concentration. It is known that the conductance curves of different binary electrolytes in liquid ammonia exhibit a great variety of form, even at comparatively low concentrations. For example, many of these curves intersect one another. This is not in harmony with Ghosh's theory in its present form. In Fig. 3 are shown the curves for potassium nitrate and silver iodide in liquid ammonia at its boiling point, the experimental values being due to Frank-

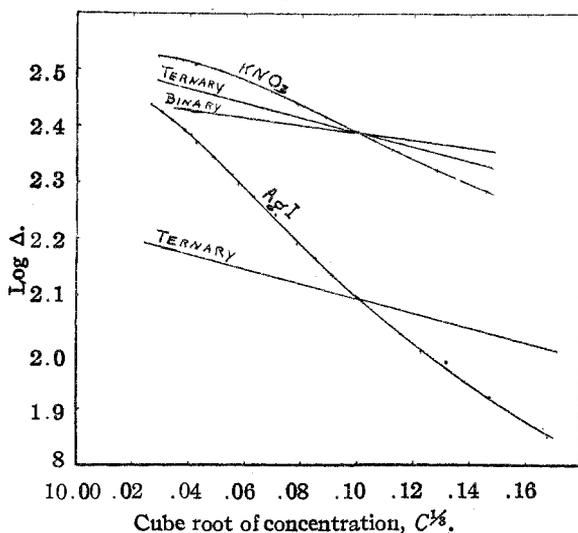


Fig. 3.—Plot of Ghosh's equation for solutions in NH_3 .

lin and Kraus.¹⁴ Considering first the curve for potassium nitrate, it is seen that at concentrations a little below 0.001 N the curve is distinctly concave toward the axis of concentrations, while above this point the curve is convex toward this axis, having an inflection point in the neighborhood of 0.001 N . Intersecting the curve for potassium nitrate are drawn two straight lines representing Ghosh's Equation for a binary and a ternary assumed ionization process. These curves correspond to the values $\beta = 3.620 \times 10^8$ and 6.808×10^8 respectively. A straight line drawn through the experimental curve, passing through the maximum number of points in the neighborhood of the inflection point, corresponds to a value $\beta = 12.63 \times 10^8$. The curve for silver iodide shown on the same figure exhibits a smaller curvature than does that of potassium nitrate, both at low and high concentrations. If a straight line is drawn in such

¹⁴ Franklin and Kraus, *Am. Chem. J.*, 23, 277 (1900).

manner as to pass through the maximum number of experimental points, it is necessary to assume a value of $\beta = 25.44 \times 10^3$, in place of 6.808×10^3 . A straight line corresponding to a ternary ionization is shown on the figure.

In order to account for the varied inclination of the curves for different electrolytes in ammonia solutions, according to Ghosh's theory, it would be necessary to assume a large variety of ionization processes, or of the relative distribution of the charges in the medium. The values following from a ternary ionization do not account for any of the results obtained with solutions in liquid ammonia. Here, in contrast to aqueous solutions, the individual characteristics of the electrolyte come clearly into view. According to Ghosh's theory, we should expect the conductance curves to fall into a few distinct classes. This, however, is not the case. It follows, therefore, that the agreement which Ghosh believes to have existed in the case of non-aqueous solutions is not substantiated, and that, in fact, assuming binary and ternary ionization processes, his theory does not account for the experimental results in such solutions even approximately.

6. The Temperature Effect.

Ghosh believes that his theory accounts for the effect of temperature on the ionization of electrolytes. In order to determine the correctness of this conclusion the conductance of solutions of potassium iodide in sulfur dioxide at -33° and at $+10^\circ$ have been examined, the results of Franklin¹⁵ being employed for this purpose. The curves for these solutions are shown in Fig. 4. It will be observed that even at concentrations as low as $0.001 N$ the curves are markedly convex toward the axis of concentrations. As the concentration increases, the convexity of the curves increases markedly and, at the higher temperature, the curve exhibits a minimum, corresponding to the minimum in the conductance-concentration curve of these solutions. It is well known that this phenomenon is a general one which reappears in the case of all solutions in solvents having a dielectric constant lower than approximately 16. The lower the dielectric constant, the lower is, in general, the concentration at which the minimum point occurs; and, in solvents of very low dielectric constant, this minimum point lies as low as $0.01 N$ or lower. It is clear that, in the case of solutions of this type, Ghosh's theory does not apply even approximately.

The two straight lines, drawn through the points on the curve corresponding to a concentration of $0.001 N$, represent Ghosh's equation for a ternary ionization process. The values of the constant β have been calculated from the dielectric constant of the solvent at the temperatures

¹⁵ Franklin, *J. phys. Chem.*, 15, 675 (1911).

in question. The values of the dielectric constant were determined by extrapolation from the measurements of Eversheim.¹⁶ These were found to be 15.1 at $+10^\circ$ and 19.0 at -33° . It is evident that, according to Ghosh's theory, the temperature can have only a small influence upon the ionization of an electrolyte in sulfur dioxide, since the value of β/DT at $+10^\circ$ is 1.592; and at -33° , 1.492. The two conductance curves, therefore, should be very nearly parallel, according to Ghosh. As indicated in the figure, however, this is not the case; moreover, the in-

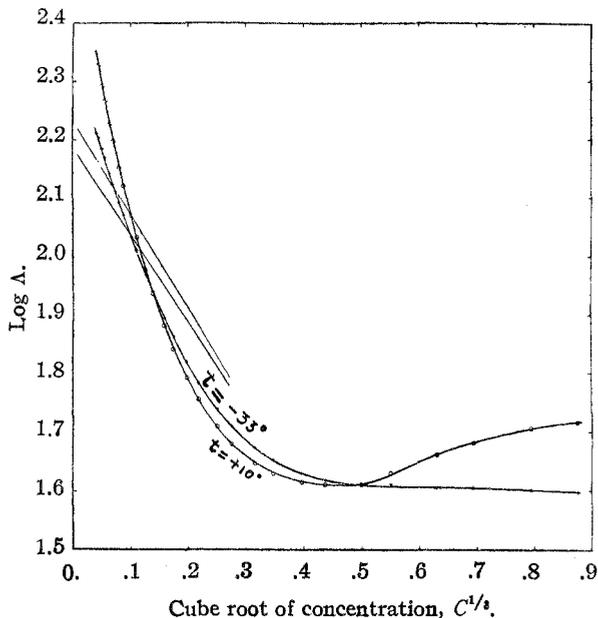


Fig. 4.—Plot of Ghosh's equation for KI in SO_2 at -33° and $+10^\circ$.

clination of the two curves in the neighborhood of $0.001 N$ differs much more than corresponds to the change in the value of β/DT . If straight lines are passed through the points in the neighborhood of $0.001 N$, they yield the values $\beta = 13.63 \times 10^8$ at -33° and 19.44×10^8 at $+10^\circ$, while, according to Ghosh, the value of β should be constant and equal to 6.808×10^8 . Assuming that Ghosh's theory yields a rough approximation to the actual facts, it is obviously necessary to assume that β is not a constant independent of the temperature but, on the contrary, one whose value depends on the temperature. This has an important bearing on the interpretation of Ghosh's theory.

7. The Variation of the Constant β .

According to the theory of Ghosh, the ionization curves for different

¹⁶ Eversheim, *Ann. Physik*, [4] **8**, 539 (1902).

electrolytes in a given solvent at a given temperature should fall into a small number of types, depending upon the number of charges associated with an ion and upon their relative distribution in the solvent medium. Since, according to this theory, the conductance curves should consist of a system of parallel straight lines for a given value of β , assuming the temperature to remain constant, it follows that, in the plots, the conductance curves should approximate a series of parallel straight lines. An examination of the curves for different electrolytes in liquid ammonia solution shows that this is not the case. Furthermore, it follows from the conductance curves of solutions of potassium iodide in sulfur dioxide at different temperatures that β is not a constant for a given electrolyte, but is a function of the temperature. Since, therefore, for a given electrolyte, there is a continuous shift in the value of β , with temperature change, it is necessary to assume a continuous displacement in the ionization process and in the nature of the assumed fixed spatial relations of the ions in the medium. But it is also clear that, for a given electrolyte at a given temperature in a given solvent, the curve is not linear, as required by Ghosh's theory. It follows, therefore, that β is a function both of temperature and of concentration.

The conductance of aqueous solutions of potassium chloride has been measured with a high degree of precision to concentrations as low as $2 \times 10^{-5} N$. The commonly assumed value of 130.0 for the limiting conductance of potassium chloride solutions can scarcely be in error by more than a few tenths of a unit. Assuming, therefore, this value of Λ_0 , we may calculate the value of β for these solutions at different concentrations. The change in the value of β will, of course, be affected by the value chosen for Λ_0 , but it is to be borne in mind that a variation must necessarily result in the calculated value of β at different concentrations, quite irrespective of the value chosen for Λ_0 . In general, it may be assumed that β will not both increase and decrease with change of concentration at low concentrations. This sets an upper limit to any possible value of Λ_0 . Whatever value may be chosen for Λ_0 , however, a change in the value of β is a necessary consequence of the experimental facts. In the following table are given the values for β , for potassium chloride in water at 18° at different concentrations.

TABLE IV.
VALUES OF β AT DIFFERENT CONCENTRATIONS OF POTASSIUM CHLORIDE IN WATER
AT 18°.

Assuming $\Lambda_0 = 130.0$.

V .	5×10^4 .	2×10^4 .	10^4 .	5×10^3 .	2×10^3 .	10^3 .
$\beta \times 10^{-3}$	1.578	1.678	1.700	1.757	1.954	2.201
V .	5×10^2	2×10^2	10^2	50	20	10
$\beta \times 10^{-3}$	2.384	2.526	2.874	3.049	3.260	3.833

It will be observed from this table that, as the concentration increases, the value of β increases markedly up to a concentration of 0.1 *N*. It is obvious, also, that in the case of non-aqueous solvents the variation of β , with increasing concentration, is much greater than it is in the case of aqueous solutions of potassium chloride. Furthermore, in solvents of low dielectric constant, the value of β at high concentration must ultimately decrease as the concentration increases, as may be seen from an inspection of the curve for potassium iodide in sulfur dioxide at $+10^\circ$, as shown in Fig. 4.

In the following table are given the calculated values of the constant β for solutions of typical salts in a number of different solvents, derived from the best straight line that may be drawn through the experimental points at low concentrations.

TABLE V.
VALUES OF β FOR SOLUTIONS OF SALTS IN DIFFERENT SOLVENTS.

Solvent	H ₂ O	epichlorohydrin	NH ₃	NH ₃	NH ₃	SO ₂ (-33°)	SO ₂ (+10°)	C ₂ H ₄ Cl
Electrolyte	KCl	NEt ₄ I	KNO ₃	AgI	KI	KI	KI	NPr ₄ I
$\beta \times 10^{-3}$	3.620	9.390	12.63	25.44	7.867	13.63	19.44	20.78

From an inspection of this table it is clear that β is in no sense a constant for solutions of different electrolytes in a given solvent, or for solutions of a given electrolyte in different solvents, or for a given solvent at different temperatures.

Those assumptions in Ghosh's theory which lead to the result that β is a constant are in contradiction with the experimental facts, and must, therefore, be modified or discarded. The actual determination of the value of β , according to Ghosh, depends on an evaluation of the potential of the field due to the ions. In order to evaluate this potential, he finds it necessary to ascribe to the ions not only certain definite charges, but also certain definite fixed positions in the medium. Since, now, β varies as a function of temperature and concentration, as well as of the nature of the solvent medium and the dissolved electrolyte, it follows that, in order to account for the variation in β , it is necessary to discard the assumption that the ions occupy a fixed position in the medium, independent of temperature and concentration. If this assumption is dropped, it obviously becomes impossible to calculate the potential due to the field of the ions in the medium, unless some other hypothesis is made with regard to the distribution of the charges. If the charges do not occupy a fixed position but a variable position dependent upon both temperature and concentration, it appears that we must necessarily revert to a kinetic interpretation of the state of the ions in the solution. The distribution of the ions, therefore, must be determined according to a kinetic hypothesis, taking into account the influence of the charges upon the distribution of the particles in the medium and their motion relative to one another.

8. Theoretical Considerations.

Ghosh assumes that all ions having a kinetic energy above a certain critical value are effective in transmitting the current through a solution. In determining the fraction of the ions having a velocity above a given value, he assumes Maxwell's law for the distribution of velocities.¹⁷ The application of Maxwell's law of the distribution of velocities to a system of charged particles, and particularly to a system of charged particles, subject to restriction as regards their positions relative to one another, appears a doubtful procedure, since, at best, Maxwell's law of distribution cannot be expected to hold save in the case of systems free from constraints.

It is a weakness of Ghosh's theory that it is not able to render an account of those properties of electrolytes which depend on the nature of the electrolyte itself. This defect is inherent in the fundamental assumption that electrolytes are completely ionized and that the work involved in the ionization process is purely electrical in nature. That the work done against the electrical forces is a large factor in the ionization process is not to be doubted, but we have no certainty that electrical forces are the only ones involved. At any rate, it is very difficult to account for the properties of different electrolytes on the basis of this assumption. It would seem that the different ionization values for different electrolytes could be accounted for satisfactorily only by assuming forces other than of purely an electrical nature to exist between the various constituents present in the solution, or, rather, that the forces involved do not all obey the inverse-square law. The properties of electrolytic solutions appear to be much too varied in their nature to admit of being accounted for by hypotheses as simple as those underlying Ghosh's theory. While Ghosh has pointed out a method of attacking the problem of electrolytic solutions, it is necessary to modify his postulates as to the distribution of the charges in the medium and as to the determination of the number of carriers which are effective in transporting the current. The problem to be solved is to determine, by means of kinetic considerations, the equilibrium in a system of charged particles and electrical doublets.

In treating osmotic phenomena, Ghosh applies Clausius' Virial Theorem. This theorem leads to results of the first order of approximation only, in the case of ordinary gases, as has been pointed out by Jeans.¹⁸ Its application to a system of charged particles subject to constraints is certainly open to question. At any rate, Ghosh's equation for i is not in harmony with experiment.

In calculating the potential due to the field in a solution of a binary

¹⁷ Ghosh, Ref. 5, p. 450. Compare Chapman and George, *Phil. Mag.*, **41**, 799 (1921).

¹⁸ Jeans, "Dynamical Theory of Gases," 2 Ed., p. 147.

electrolyte, Ghosh assumes the work necessary to separate a pair of univalent ions to be E^2/Dr , the medium between the particles being assumed to act normally. In determining, now, the work required to carry one mol of a binary electrolyte from its condition at a given concentration to a condition in which the particles are separated to such distances that the force between them may be neglected. Ghosh evaluates r on the assumption that positive and negative particles are distributed in a fixed manner throughout the solution, forming a cubical space lattice. From this he derives the expression

$$r = \left(\frac{V}{2N} \right)^{1/3};$$

and substituting this in the expression for the work above, and multiplying by N , the number of pairs of positive and negative particles, he evaluates the potential due to the assumed distribution of the charges in the medium. It appears, however, that in this procedure Ghosh has taken account of the work due to the separation of the N pairs of positive and negative particles in the solution, leaving out of account the forces acting between a given charge and all other charges. It is true that Ghosh assumes that the electrolyte forms doublets, but this assumption is inconsistent with the assumptions made in evaluating r , the distance between the charges.

Summary.

1. The equation of Ghosh expressing the conductance of electrolytic solutions as a function of the concentration is compared with the experimental values in aqueous and non-aqueous solutions.
2. Plotting values of $\log \Lambda$ against those of the cube root of the concentration, the experimental points lie upon a curve concave toward the axis of concentrations at low concentrations and convex toward this axis at high concentrations. If Ghosh's equation were applicable, the points should lie upon a straight line. The deviation of the points from a linear relation is consistent throughout, and cannot be accounted for by errors in the original observations. In its present form Ghosh's theory does not satisfactorily account for the properties of electrolytic solutions.
3. The postulates and assumptions underlying Ghosh's theory are briefly discussed, and some inconsistencies are pointed out.

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