

perature. A greater rate of dehydration than this would involve a decrease of the osmotic pressure with rise of temperature.

Woods, however, believes that this stage is not reached in the cases he studied and attributes the apparent decrease in his calculated values to a too rapid variation of the ratio of  $\Pi_0/\Pi_\pi$  with temperature. This conclusion seems unjustified. The loss by dehydration must reach such a magnitude at concentrations of 6 *M* and over that the increase in solvent due thereto more than balances the increase of kinetic pressure due to rise in temperatures.

### Summary.

1. In this article the authors describe a modification of the method used by Frazer and Myrick for measuring the osmotic pressure. The principle feature of the new apparatus is the use of the water interferometer in determining the magnitude of the pressures developed.

2. The apparatus affords a decided improvement over the method of Frazer and Myrick, being somewhat quicker in action and more dependable. Pressures up to 273 atmospheres have been measured, while the pressure chambers have been calibrated up to 330 atmospheres.

3. Measurements over the entire range of solubility are given for 30° and 55.7°.

4. Attention is called to the results of Woods as calculated for vapour-pressure measurements, and it is shown that his results, showing a decrease in osmotic pressure with rise in temperature with concentrated solutions, are relatively correct although his actual values for the osmotic pressure seem to be high as compared with these direct measurements.

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[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF CLARK UNIVERSITY, No. 1, 7.]

## THE EQUILIBRIUM IN MIXTURES OF BINARY ELECTROLYTES.

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### 1. Introduction.

The determination of the equilibrium in a mixture of electrolytes is a problem of considerable practical importance since many of the reactions with which we have to deal are carried out in mixtures of this kind. If the law of mass action is applicable to the resulting equilibrium, then the problem is in general soluble, provided intermediate ions are not formed. In all likelihood this condition is fulfilled in mixtures of binary electrolytes, but, as Harkins<sup>1</sup> has pointed out, when higher types of salts are present, intermediate ions are probably formed. The following discussion will therefore be limited to mixtures of binary electrolytes.

<sup>1</sup> Harkins, *THIS JOURNAL*, 33, 1807 (1911); 38, 2679 (1916).

In mixtures of strong electrolytes the problem of determining the concentration of the various molecular species present is complicated owing to the fact that the law of mass action in its simple form does not hold. We therefore have no means for calculating the equilibrium in these mixtures save such as are purely empirical in character. In the past the determination of the equilibrium in mixtures of strong electrolytes has been founded upon the isohydric principle of Arrhenius.<sup>2</sup> This principle has a theoretical foundation so long as the electrolytes involved in the reaction obey the simple law of mass action, but in the case of strong electrolytes this relation is purely an empirical one.

Presumably, in a mixture of strong electrolytes where the mass-action law does not hold, the various molecular species present will obey laws similar to those obeyed by the same molecular species in solutions containing a single electrolyte. The form of the function assumed as governing the equilibrium in a mixture should therefore agree with that of the salts alone in aqueous solution. Assuming that the ionization is measured by the ratio  $\Lambda/\Lambda_0$ , the form of the function in the case of pure electrolytes is known, although the equation remains uncertain. Nevertheless, various empirical functions which have been proposed account for the experimental values in the case of binary electrolytes with considerable precision over large ranges of concentration. As we shall see presently, the isohydric principle, when formulated mathematically, reduced to the proper form in the case of a solution of a single binary electrolyte. It is interesting to determine what other functions may be assumed to hold in mixtures which will reduce to the same form in the case of a solution of a single electrolyte.

## 2. The Isohydric Principle.

The isohydric principle is based upon the observation that if two electrolytes, having an ion in common, are mixed, then the ionization of the two electrolytes in the mixture will be the same as that in the original solutions before mixing, if the concentrations of the common ion in these solutions before mixing are equal. This result is a consequence of the law of mass action. Let  $M_1^+$  and  $X^-$  be the concentration of the ions in two solutions, where  $X^-$  is that of the common ion. If the concentrations of the common ion in the two solutions are the same before mixing, then obviously we have

$$M_1^+ = M_2^+ = X^- \quad (1)$$

The total salt concentrations of the two solutions  $C_1$  and  $C_2$  will in general be different. Let  $V_1$  liters of the first solution be mixed with  $V_2$  liters of the second solution. If the conditions of Equation 1 are fulfilled, and if no displacement takes place in the equilibrium on mixing, then we should

<sup>2</sup> Arrhenius, *Z. physik. Chem.*, 5, 1 (1890); compare also 2, 284 (1888).

have for the concentration of the ions  $M_1^+$  in mixture the value  $\frac{M_1^+ V_1}{V_1 + V_2}$

for that of the common ion  $\frac{M_1^+ V_1 + M_2^+ V_2}{V_1 + V_2}$ , and for that of the un-

ionized fraction of the first salt  $M_1 X_1 \left( \frac{V_1}{V_1 + V_2} \right)$ .

If the law of mass action holds, we have,

$$\frac{M_1^+ V_1}{V_1 + V_2} \times \frac{M_1^+ V_1 + M_2^+ V_2}{V_1 + V_2} = K_1. \quad (2)$$

$$M_1 X_1 \frac{V_1}{V_1 + V_2}$$

Equation 1 being fulfilled, it is obvious that we have

$$\frac{M_1^+ V_1 + M_1^+ V_2}{V_1 + V_2} = M_1^+;$$

and Equation 2 reduces to

$$\frac{M_1^+ + X_1^-}{M_1 X_1} = K_1.$$

In other words, if the conditions expressed in Equation 1 is fulfilled by the original solutions before mixing, then no displacement takes place in the equilibrium when these solutions are mixed in any proportions what ever.

In the case of mixtures of weak acids and bases where the law of mass action holds, this consequence of the law of mass action has been substantiated. Since the conductance of solutions of acids is due chiefly to the hydrogen ion, it follows that the conductance of a mixture of two acids will be the same as that of the acids before mixing, provided the original solutions have the same specific conductance. In this it is assumed that the conductance of the anion in the two acids is the same. If this condition is not fulfilled, it is obvious that the conductance of the mixture will vary as a linear function of the composition of the two solutions which have the same concentration of the hydrogen ion.

It has been found, however, that even in the case of solutions which do not conform to the law of mass action, that is, solutions of strong electrolytes, a similar condition holds. If, for example, solutions of ammonium chloride and potassium chloride are mixed, the specific conductance of the mixture will be (approximately) independent of the proportions of the original solutions taken, provided that these solutions have the same specific conductance. Apparently, then, the isohydric principle holds even though the law of mass action is not obeyed. This principle has, therefore, been employed for the purpose of calculating the equilibrium in mixtures of strong electrolytes.

The law of equilibrium for a given electrolyte in a mixture must obviously reduce in the limit to that of solutions of electrolytes in the pure solvent. It has been shown that for strong electrolytes the following equation<sup>3</sup> holds approximately,

$$P_i/C_u = D(\Sigma C_i)^m + K, \quad (3)$$

where  $P_i$  is the value of the ion product,  $C_u$  is the concentration of the unionized fraction,  $\Sigma C_i$  is the concentration of all the positive or negative ions in the solution, and  $D$ ,  $m$  and  $K$  are constants. It is evident that this equation conforms to the isohydric principle. Indeed, any equation of the form

$$P_i/C_u = F(\Sigma C_i) \quad (4)$$

conforms to the isohydric principle. Here  $F(\Sigma C_i)$  is any explicit function of the total ion concentration of the mixture. For, on mixing two solutions whose ion concentrations are  $C_i'$  and  $C_i''$ , the equilibrium will be unaffected by the relative volumes of the solutions mixed, provided that  $C_i' = C_i''$ . Equation 4, therefore, is the analytical expression for the equilibrium in the mixture according to the isohydric principle. In the limit, as the second component in the mixture disappears, the equation reduces to that of the first salt alone. Obviously the same equation may be applied to mixtures of electrolytes without a common ion.

### 3. An Alternative Principle Which May Be Assumed to Govern the Equilibrium in Mixtures of Electrolytes.

Equation 4 is not the only function which fulfils the condition that it reduces to the form of Equation 3 in the case of a single electrolyte. We may assume for the mixture the function,

$$P_i/C_u = F(P_i), \quad (5)$$

where  $P_i$  is the ion product. In the limit the concentrations of the positive and negative ions become equal for a solution of a single electrolyte and consequently the equation reduces to the form of Equation 3. Equations 4 and 5, therefore, both fulfil the condition that they reduce to the proper form in the special case that only a single electrolyte is present in solution. In order to determine which of these equations is more nearly applicable to a mixture, it is obviously necessary to measure some independent property of these mixtures; such as the conductance, for example. Assuming that the conductance of the ions in the mixture is the same as that of the same ions dissolved alone in water, it is possible to calculate the specific conductance of the mixture if the form of the conduction functions for the pure electrolytes is known and if a function is assumed to hold for the mixture. If the assumed function is correct, then the calculated specific conductance of the mixture should correspond

<sup>3</sup> Kraus and Bray, *THIS JOURNAL*, **35**, 1315 (1913); Kraus, *ibid.*, **42**, 1 (1920).

to the measured specific conductance within the limits of experimental error. If the calculated values do not so correspond, it indicates that the function so assumed for the mixture is not applicable.

#### 4. Test of Functions 4 and 5 in the Case of Mixtures of Sodium Chloride and Hydrochloric Acid.

Bray and Hunt<sup>4</sup> have measured the specific conductance of mixtures of sodium chloride and hydrochloric acid in water at 25°. They have likewise calculated the specific conductance of the mixtures assuming the isohydric principle; that is, assuming Equation 4. The results are given in the following table, where the concentrations of sodium chloride and

TABLE I.

MEASURED SPECIFIC CONDUCTANCE OF MIXTURES OF SODIUM CHLORIDE AND HYDROCHLORIC ACID COMPARED WITH VALUES CALCULATED ACCORDING TO EQUATIONS 4 AND 5.

No.	Concentration (approx.) Millimols.		Measured.	Specific Conductance <i>L</i> .			
	NaCl.	HCl.		Calc. Eq. 4.	Diff. %.	Calc. Eq. 5.	Diff. %.
1	100	100	47.25	48.21	-2.1	47.09	+0.3
2	100	50	29.14	29.62	-1.6	28.82	+1.1
3	100	20	18.06	18.31	-1.4	17.84	+1.2
4	100	10	14.36	14.50	-1.0	14.18	+1.2
5	100	5	12.52	12.59	-0.6	12.39	+1.1
6	100	2	11.41	11.45	-0.3	11.35	+0.5
Mean.					-1.15		+0.85
7	20	50	21.75	21.89	-0.7	21.65	+0.4
8	20	20	10.157	10.27	-1.1	10.13	+0.3
9	20	10	6.253	6.307	-0.9	6.221	+0.5
10	20	4	3.889	3.919	-0.8	3.870	+0.3
11	20	2	3.101	3.118	-0.6	3.094	+0.2
12	20	1	2.709	2.721	-0.4	2.702	+0.3
Mean.					-0.75		+0.33
13	5	12.5	5.651	5.678	-0.5	5.646	+0.1
14	5	5	2.632	2.650	-0.7	2.634	-0.1
15	5	2	1.621	1.630	-0.6	1.619	+0.1
16	5	1	1.011	1.016	-0.5	1.010	+0.1
Mean.					-0.57		+0.05

hydrochloric acid are given in the second and third columns respectively, the measured specific conductance in the fourth column, and in the fifth column the specific conductance calculated according to Equation 4. Finally, in the sixth column are given the percentage deviations between the measured and the calculated values. In the same table, in Column

<sup>4</sup> Bray and Hunt, *THIS JOURNAL*, 33, 781 (1911).

7, are given the values of the specific conductance calculated according to Equation 5, and in the last column the percentage deviations between the calculated and the observed values.

Comparing the measured values with those calculated on the basis of Equation 4, it is seen that the deviations from the isohydric principle are consistently larger than any conceivable experimental error. With mixtures containing 0.1 *N* solutions of sodium chloride, the mean error is  $-1.15\%$ ; for 0.02 *N* solutions of sodium chloride, the mean deviation is  $-0.75\%$ ; and for 0.005 *N* solutions of sodium chloride, the mean deviation is  $-0.57\%$ . The values of the specific conductance calculated according to Equation 4 are throughout greater than the observed values. At the lower concentrations the agreement between the observed and calculated values is measurably better than at the higher concentrations, but, in all cases, the discrepancies are far in excess of any conceivable experimental error. It is true that at the high concentrations the results may be affected owing to the influence of viscosity, but this certainly cannot be the case at the lowest concentrations.

The values of the specific conductance as calculated according to Equation 5 exhibit, throughout, a better agreement with the measured values than those calculated according to the isohydric principle, particularly at the lower concentrations. In mixtures containing 0.10 *N* sodium chloride the mean deviation of  $+0.85\%$  is unquestionably far in excess of the experimental error. However, in mixtures containing 0.02 *N* sodium chloride the mean deviation has fallen to  $+0.33\%$ , which is not greatly in excess of the experimental error. Finally, in mixtures containing 0.005 *N* sodium chloride, the mean deviation has fallen to  $0.05\%$ , which is well within the limits of experimental error. At the higher concentrations, the values of the specific conductance, calculated according to Equation 5, are throughout somewhat less than the measured values. At the lowest concentration, namely, 0.005 *N* sodium chloride, the differences are both positive and negative.

In calculating the specific conductance of the mixtures according to Equation 5, the values assumed for  $\lambda_0$  were 127.0 and 424.0 for sodium chloride and hydrochloric acid, respectively. Bray and Hunt state that the calculated value of the specific conductance is not materially affected by the value assumed for  $\lambda_0$ . So, also, in calculating the specific conductance according to Equation 5, the values assumed for  $\lambda_0$  have only a secondary effect upon the resulting value of the specific conductance. For example, assuming for hydrochloric acid and sodium chloride the  $\lambda_0$  values 422 and 125.4 respectively, the calculated specific conductance according to Equation 5 is 3.097 for point 11. The divergence resulting from change in the values of  $\Lambda_0$  naturally varies somewhat with the concentration.

The results given above cannot be said to establish the correctness of the principle expressed by Equation 5, in the case of mixtures of strong electrolytes. Nevertheless, it appears that this principle yields results which are more nearly in agreement with experiment than are those based on the isohydric principle, which is commonly employed for this purpose. The isohydric principle leads to erroneous results even at very low concentrations, whereas the alternative principle leads to results in agreement with the experimental values at low concentrations. It is, of course, possible that in the case of mixtures other than those of sodium chloride and hydrochloric acid a similar agreement may not be found. However, electrolytes of a given type in aqueous solutions exhibit such similarity in their behavior that it is probable that similar results will be found in other mixtures.

The isohydric principle has been extensively employed for calculating the concentrations of the various molecular constituents present in mixtures. Since this principle does not hold, it is obvious that the concentrations of the various constituents so found are subject to considerable error. These errors may not greatly affect the concentrations found for certain of the molecular species, but, in the case of others, the errors may be very great. In those cases where the effect of electrolytes upon the solubility of other electrolytes has been studied, the conclusion has been reached that the concentration of the un-ionized fraction of the salt present as solid phase is greatly diminished by the addition of a second electrolyte. Since the isohydric principle, which underlies these calculations, is not correct, it seems not improbable that the great change found in the concentration of the un-ionized fraction is a consequence of applying to the mixture a principle which in fact does not hold. If we make the assumption that the un-ionized fraction of a salt, which is present as solid phase, remains constant on the addition of a second electrolyte, then it follows, from Equation 5, that the ion product likewise remains constant. This result is, on the whole, in agreement with observations on the solubility of binary electrolytes in the presence of other electrolytes with a common ion. In another paper the solubility relations in the case of binary electrolytes will be discussed more in detail.

### Summary.

1. It is shown that the isohydric principle, when applied to mixtures of electrolytes, leads to a functional relation of the form  $(C_i)^2/C_u = F(\Sigma C_i)$ .
2. As the concentration of the second electrolyte diminishes, the function  $P_i/C_u = F(P_i)$  reduces, in the limit, to the same form as the function resulting from the isohydric principle.
3. The values of the specific conductance of mixtures of sodium chlo-

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.

BY CHARLES A. KRAUS.

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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 articles<sup>1</sup> 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.<sup>2</sup> 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

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

<sup>2</sup> 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.