THE CONDUCTANCE OF AQUEOUS SOLUTIONS OF ELECTROLYTES AND THE INTERIONIC ATTRACTION THEORY

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This paper is a summary of the results of a series of researches carried out at the Rockefeller Institute on the properties of aqueous solutions of electrolytes. The experimental work has consisted mainly in the determination, with the greatest accuracy now attainable, of conductances and transference numbers of such solutions. As will be seen, the interpretation of the results has been made with the indispensable aid of the interionic attraction theory of Debye, Hückel, and Onsager.

As is well-known, Debye and Hückel have demonstrated that an ion in a solution is surrounded by an oppositely charged "ion atmosphere" which for an undisturbed electrolyte is spherically symmetrical around the ion. This ion atmosphere is the net result of the Coulomb forces between the charged ions and the thermal vibrations. The electrostatic attractions and repulsions acting alone would result in a lattice arrangement of the ions, whereas the thermal vibrations tend to break up any regularity in the spatial distribution. By a combination of the Boltzmann and Poisson equations, Debye and Hückel have shown that as a result of these two effects the potential, ψ, around a selected ion is, neglecting higher terms,

$$\psi = \frac{\epsilon e^{-\kappa(a-r)}}{Dr\,(1-\kappa a)} \tag{1}$$

in which ϵ is the charge on the ion, a may be regarded as the distance of closest approach of the ions, r is the distance from the center of the ion, D is the dielectric constant, and

$$\kappa = \sqrt{\frac{8\pi n\epsilon^2}{DkT}} \qquad (2)$$

In the latter formula n is the number of ions per cubic centimeter, k is the Boltzmann constant, and T the absolute temperature. This theory has been successful in accounting for the thermodynamic properties of many solutions of electrolytes, at least at moderate concentrations. It is our purpose, however, to discuss experimental tests of the extension of the theory to account for the phenomena observed when a potential gradient is superposed upon those naturally present in the solution of the electrolyte. From the theoretical point of view this added condition results in much complication, and, strictly speaking, the equations which have been derived are only applicable to solutions which are near to infinite dilution.

The primary effect of the superposition of an external potential in, for instance, the measurement of the electrolytic conductance, is to cause a drift of the ions toward the electrodes. This drift, however, brings about at least two retarding effects. One of these is caused by the movement of an ion from the center of its ion atmosphere due to the impressed potential gradient. The atmosphere will adjust itself to such a shift, but not quite instantaneously. A portion of the atmosphere will thus be behind its normal position and will exert an unsymmetrical force on the ion, tending to reduce its rate of motion. This is known as the "time of relaxation effect." The ions are further slowed down by the "electrophoretic effect." This second effect is due to a counter-current of solvent. The magnitude of this retarding effect on the motion of the ions can be obtained by first computing from equation 1 the apparent charge located in the ionic atmosphere in concentric shells (of thickness dr) around an ion and then, by applying Stokes' law to each shell, obtaining the integrated effect of the ion atmosphere on the solvent.

As the result of these considerations Onsager (1) has obtained the following equation for the mobility or equivalent conductance of an ion

$$\lambda = \lambda^0 - \left[\frac{(0.9838)(10^6)}{(DT)^{3/2}} w\lambda^0 + \frac{28.95Z}{(DT)^{1/2}\eta}\right]\sqrt{(Z_1 + Z_2)C} \qquad (3)$$

λ^0 is the mobility at infinite dilution,
D is the dielectric constant of the solvent,
T is the absolute temperature,
η is the viscosity of the solvent,
Z is the charge carried by the ion (absolute value),
C is the equivalent concentration,
Z_1 and Z_2 are the charges carried by the anions and cations, and λ_1^0 and λ_2^0 are the mobilities at infinite dilution of anions and cations.

$$w = Z_1Z_2 \frac{2q}{1 + \sqrt{q}};\ q = \frac{Z_1Z_2\,(\lambda_1^0 + \lambda_2^0)}{(Z_1 + Z_2)\ (Z_2\lambda_1^0 + Z_1\lambda_2^0)} \qquad (4)$$

The first term in the brackets in equation 3 takes account of the time of relaxation effect, and the second term of the electrophoretic effect, both of which decrease the mobility of the ions. For the equivalent conductance, λ, of an ion constituent in a solution of a uni-univalent electrolyte the expression

$$\lambda = \lambda_0 - \left[\frac{5.78 \times 10^5}{(DT)^{3/2}} \lambda_0 + \frac{29.5}{(DT)^{1/2}\eta}\right]\sqrt{2C} \qquad (5)$$

in which λ_0 is the equivalent conductance at zero concentration, is thus obtained. This can be put in the simpler form

$$\lambda = \lambda_0 - (\alpha\lambda_0 + \beta)\ \sqrt{C} \qquad (6)$$

For the equivalent conductance of a uni-univalent electrolyte, Λ, the relation is

$$\Lambda = \Lambda_0 - (\alpha\Lambda_0 + 2\beta)\ \sqrt{C} \qquad (7)$$

in which Λ_0 is the limiting equivalent conductance.

In the following we will discuss: (1) the application of this equation to the data obtained in the measurement of the conductances of aqueous solutions of very dilute strong electrolytes;

(2) an empirical extension of the equation which extends its usefulness to moderate concentrations of most strong electrolytes; (3) precise transference data in the light of Onsager's equation; (4) the application of the extended equation to the conductances of individual ion constituents; and finally (5) the interpretation of conductance data on weak electrolytes from the point of view of the interionic attraction theory.

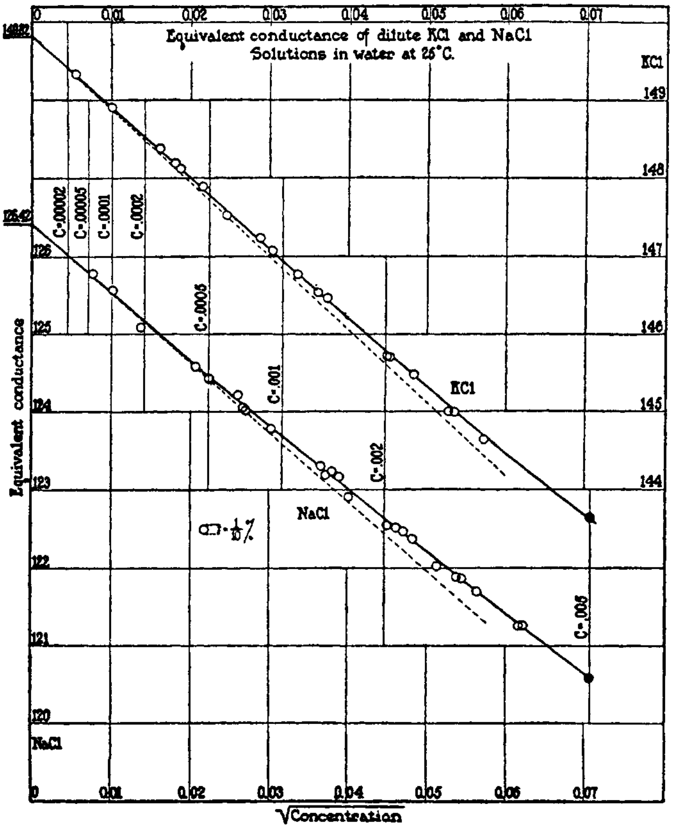

FIG. 1. EQUIVALENT CONDUCTANCE OF DILUTE POTASSIUM CHLORIDE AND SODIUM CHLORIDE SOLUTIONS IN WATER AT 25°C.

1. VERY DILUTE SOLUTIONS OF STRONG ELECTROLYTES

In Onsager's derivation of equation 7 it is assumed that the ion concentration is very low. A test of its validity as a limiting expression must be sought in measurements on very dilute solutions. One of us (T. S.) has made a study, the details of which are given elsewhere (2), with the result that determinations of the conductances of salt solutions as dilute as 0.00003 *N* have been measured with an accuracy of about 0.02 per cent. For an account of the many experimental difficulties that had to be overcome in attaining this accuracy we will refer to the original paper (2). Here we will only concern ourselves with the results. Some of these, for typical electrolytes, are plotted in figures 1 and 2. In the first of these the measured equivalent conductances of dilute sodium and potassium chloride solutions are plotted against the square root of the concentration. Many years ago Kohlrausch found empirically that a straight line would result from such a plot. It is, however, the distinguishing feature of Onsager's theory that it predicts the slope of the line. This computed slope is $(\alpha\Lambda_0 + 2\beta)$ of equation 7 and is shown on the plots by the dotted line. It will be observed that up to about 0.001 *N* this theoretical slope and a line through the experimental points agree within the very small

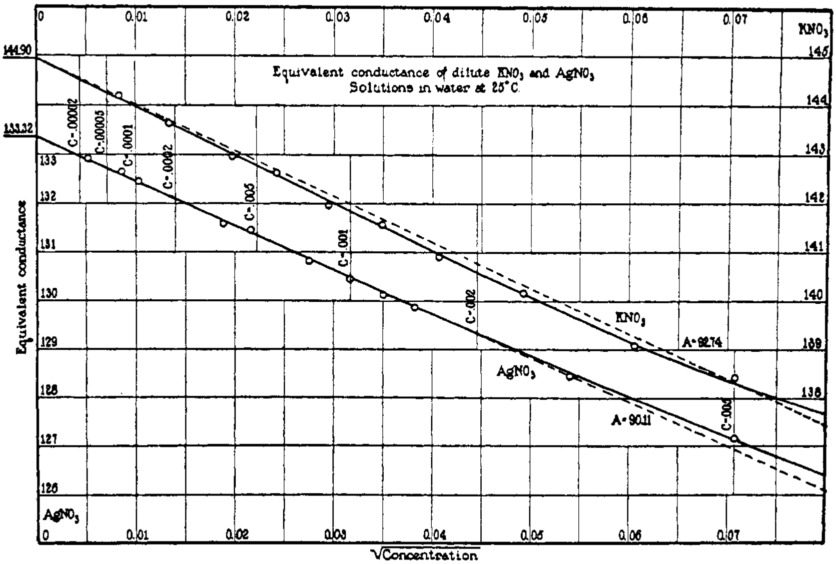

FIG. 2. EQUIVALENT CONDUCTANCE OF DILUTE POTASSIUM NITRATE AND SILVER NITRATE SOLUTIONS IN WATER AT 25°C.

experimental error. There is, however, a real deviation upward of the experimental curve which apparently begins in the most dilute solutions. This deviation is typical of that shown by most binary electrolytes and is, by the way, in the reverse direction to that which would be expected from incomplete dissociation. The behavior shown in figure 2 is much less frequently observed. It will be seen that the data for silver nitrate show no deviation whatever from the straight line predicted from Onsager's theory up to a concentration of 0.002 N and that the curve for the measurements on potassium nitrate lies below the limiting slope in the region of very dilute solutions but crosses it at about 0.005 N. It is, however, clear from these data and from others already published which are equally striking that the Onsager equation is the limiting expression to which an equation representing the measured conductances must reduce for very low concentrations.

2. MODERATE CONCENTRATIONS OF STRONG ELECTROLYTES

It is evident therefore that the equation describing the equivalent conductance of strong electrolytes at higher concentrations than those considered in the previous section will be one that reduces to the Onsager equation in the limit. According to a recent paper by Onsager and Fuoss (3) the extension of the equation which would follow if the approximations involved in the limiting expression were not made would probably involve a term of the form $BC \log C + DC$ (in which B and D are constants) The mathematical difficulties of such an extension are, however, considerable. Onsager has made use of an extension of the form:

$$\Lambda = \Lambda_0 - (\alpha\Lambda_0 + 2\beta)\sqrt{C} + KC \tag{8}$$

in which K is an empirical constant. This procedure increases the usefulness of the equation only to concentrations of about 0.01 N. One of the authors (T. S.) has, however, suggested an extension of the equation which reproduces the experimental results, almost within the experimental error up to nearly 0.1 N (4). This equation has the form:

$$\Lambda_0 = \frac{\Lambda + 2\beta\sqrt{C}}{1 - \alpha\sqrt{C}} - BC \tag{9}$$

in which α and β have the same values as in equation 7 and B is an empirical constant. If the term BC is zero, this is identical with Onsager's expression (equation 7). The constant B can be readily obtained by plotting values of

$$\Lambda'_0 = (\Lambda + 2\beta\sqrt{C})/(1 - \alpha\sqrt{C})$$

against the concentration C. The result in the normal case is a straight line with a slope equal to B and an intercept equal to Λ_0. Some typical examples of such plots from the work of this laboratory are shown in figure 3. It is an interesting fact, and one that may prove to have theoretical importance, that for such normal cases the value of B is always within 15 per cent of the theoretical coefficient of $\sqrt{C}$, i.e., $(\alpha\ \Lambda_0 + 2\ \beta)$. A certain number of electrolytes, two of which (silver nitrate and potassium nitrate) have been considered in the previous section, give curves rather than straight lines when their equivalent conductances are treated in the manner just described. These substances are abnormal in at least one other respect, as we will see in the next section.

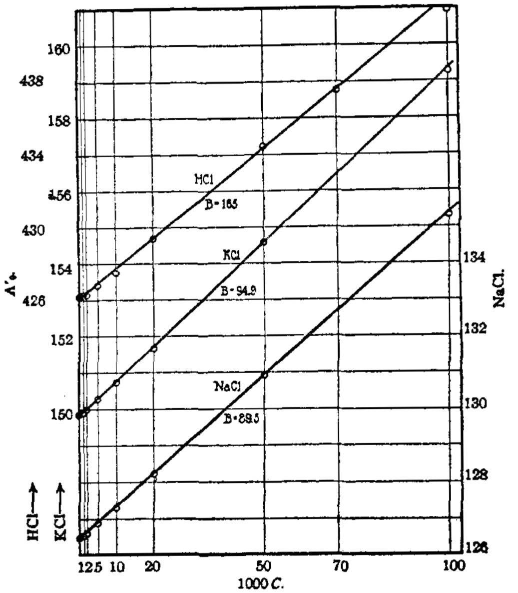

FIG. 3. THE VARIATION OF Λ'_0 WITH THE CONCENTRATION

In summary then we have shown that up to about 0.001 N the equivalent conductances follow Onsager's equation within the experimental error. Above that concentration the data for most electrolytes can be expressed to about 0.07 N with an equation involving only one empirical constant in addition to the limiting conductance, Λ_0.

3. THE INTERPRETATION OF TRANSFERENCE DATA

One of the activities of this laboratory, over a number of years, has been the determination, by means of the moving boundary method, of transference numbers of electrolytes. Recently the accuracy of these determinations has reached very nearly that of the best conductance measurements, or about 0.02 per cent. An extended account of the method has recently appeared in This Journal (5). Until recently transference measurements which were scattered and of doubtful accuracy have had but little influence in connection with theories of solutions of electrolytes. We feel the results of our measurements must be incorporated into any theory which may be formulated in the future. It was one of the weaknesses of the Arrhenius theory that it postulated no changes of the transference number with concentration. Correspondingly, it is a strength of the present theories that they call for such variations, and that they are in the direction and of magnitudes actually observed. Since the transference number T is equal to the ion mobility λ divided by the equivalent conductance Λ, a limiting expression for the change of the transference number with the concentration may be obtained simply by dividing equation 6 by equation 7 (see Dole (6)). On this basis it is readily shown (7) that the Onsager theory requires that the curve obtained by plotting the transference number of the positive ion, T_+, against the square root of the concentration should go into the axis of zero concentration with the slope

$$\left(\frac{dT_+}{d\sqrt{C}}\right)_{C=0} = \frac{T_+^0 - 1}{2\Lambda_0}\beta \tag{10}$$

In this equation T_+^0 and Λ_0 are the limiting cation transference number and equivalent conductance of the salt respectively, and

β is the constant of the Onsager equation occurring in equation 7. Thus the limiting value of the change of the cation transference number with the change of $\sqrt{c}$ is seen to be proportional to the variation of the number from 0.5 and to be inversely proportional to Λ_0. A test of the validity of equation 10 as a limiting expression is given in figure 4, in which points representing the

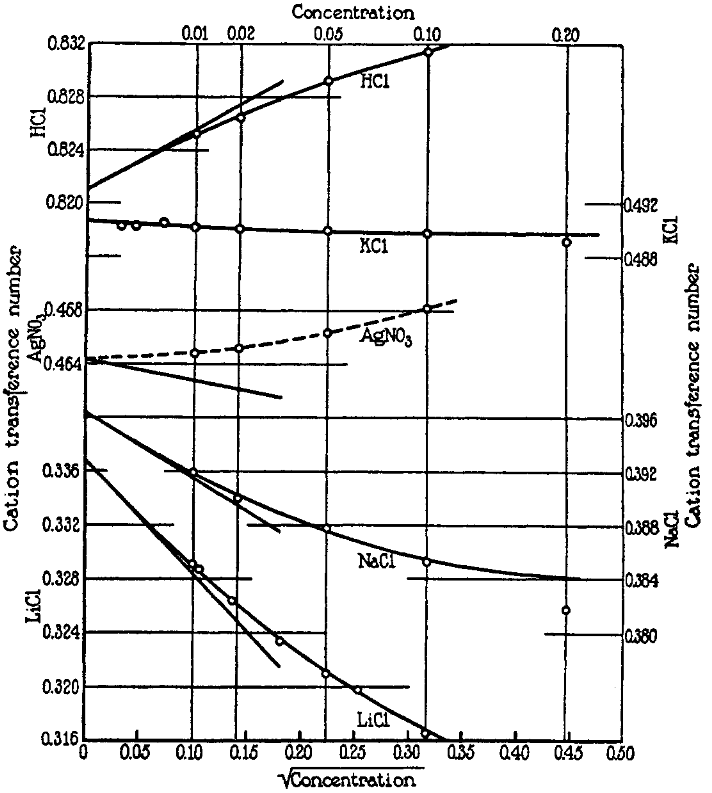

FIG. 4. TRANSFERENCE NUMBERS AS FUNCTIONS OF THE CONCENTRATION

actual transference measurements are plotted against the square root of the concentration. From the ordinate representing the limiting value of each transference number (which can be accurately computed by a method we will presently discuss), a straight line is drawn with a slope computed from equation 10. It will be observed that smooth curves passed through the observed points merge into these straight lines as the concentration decreases. In the case of potassium chloride the observed and computed lines are identical. Other examples of the same kind could be cited from the data we have at hand. A marked exception to the rule is also shown on the plot. This is the data on silver nitrate, in which the observed variation of the transference number with the concentration and the computed limiting variation have opposite signs. A somewhat similar behavior has also been observed in the case of potassium nitrate. The exceptional behavior of the conductances of these two substances has already been commented upon. It would appear, therefore, that except for the data on several substances suspected to be abnormal, the transference number measurements provide excellent support to the interionic attraction theory of strong electrolytes.

4. THE CONDUCTANCES OF INDIVIDUAL ION CONSTITUENTS

The validity of Kohlrausch's law of independent ion mobilities

By multiplying the equivalent conductance, Λ, of a salt at a given concentration by the value of the transference number, T, measured at the same concentration, a value of the equivalent conductance of the corresponding ion constituent may be obtained. These data may be conveniently considered in the light of Shedlovsky's extension of the Onsager equation. For a single ion constituent this equation is:

$$\lambda_0 = \frac{\lambda + \beta\sqrt{C}}{1 - \alpha\sqrt{C}} - bC \tag{11}$$

in which λ ($= T\Lambda$) is the equivalent conductance of an ion constituent and λ_0 is its value at infinite dilution. The other terms have the same significance as in equation 6. Here again we can study the data by observing the trend of values of

$$\lambda'_0 = \frac{\lambda + \beta\sqrt{C}}{1 - \alpha\sqrt{C}}$$

with the concentration C. Figure 5 is a plot of this kind representing the results for the potassium ion constituent from four different salts. Although we expect to discuss these results and others of the same type in detail in a later publication, several facts are evident from a casual inspection of the plot. In the first place the data for a given salt are seen to fall on a smooth curve which is nearly a straight line. All the curves converge to a single point on the axis of zero concentration. This is obviously the limiting value λ_0 of the conductance of the ion constituent in question. Furthermore, although the curves for the potassium ion from different sources diverge at moderate concentrations their values agree, probably within the experimental error up to about 0.01 normal. This means that Kohlrausch's law of independent ion mobilities is valid to that concentration. An exception is the λ'_0 value of potassium ion from potassium nitrate, which here again shows its abnormality. This test of the law of independent ion mobilities is essential for our work on weak electrolytes to be considered in the following section.

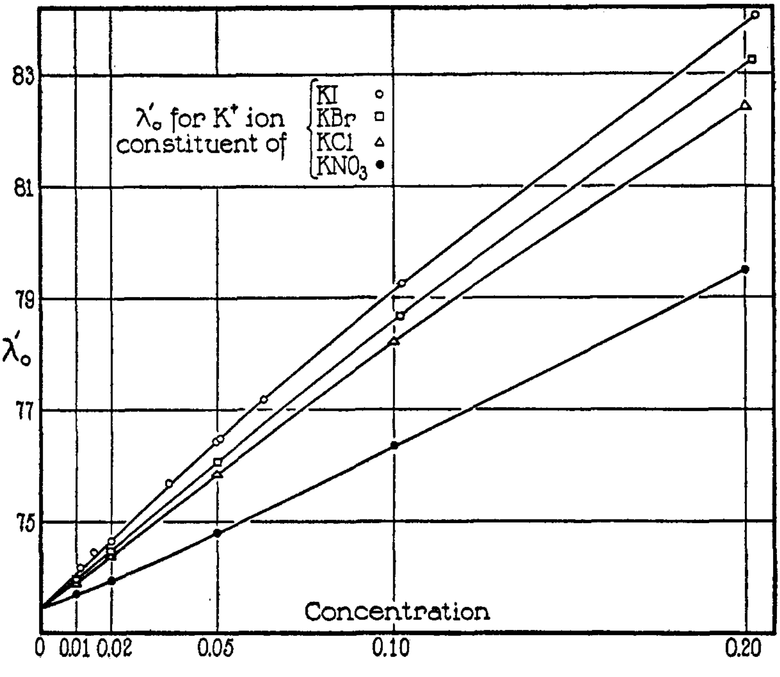

FIG. 5. THE VARIATION OF λ'_0 WITH THE CONCENTRATION

From data such as those plotted in figure 5 it has been possible to prepare table 1, which gives values of the limiting conductances, λ_0, of some common ion constituents. The figures in this table, which are based entirely on the work of this laboratory (8), are not dependent, as were earlier tables, on a single transference number, but, in the case of the chloride and potassium ions, are consistent with four series of transference and conductance measurements. The limiting values of transference numbers used in the previous section may obviously be obtained from the data in this table. Thus the limiting transference number of the lithium ion in lithium nitrate may be found by dividing the λ_0 value for lithium by the sum of the values for the lithium and nitrate ions.

TABLE 1

Limiting ion conductances at 25°C.

CATIONS		ANIONS	
K^+	73.50	Cl^-	76.32
Na^+	50.10	NO_3^-	71.42
H^+	349.72	CH_3COO^-	40.87
Ag^+	61.90		
Li^+	38.68		

The ionization of solutions of weak electrolytes

According to the "classical" dissociation theory, weak electrolytes were found to follow the law of mass action (known in this case as the "Ostwald dilution law") in their ionization, whereas strong electrolytes were found to depart markedly from that relation. This was the familiar "anomaly of the strong electrolyte." The many ingenious attempts that were made to overcome this difficulty were not successful as long as Arrhenius' assumption concerning the computation of the degree of dissociation was uncritically accepted. According to this assumption the degree of dissociation is equal to the conductance ratio, Λ_c/Λ_0, in which Λ_c is the equivalent conductance at the concentration c and Λ_0 is the equivalent conductance at infinite dilution. It can readily be shown that degrees of dissociation can be obtained in this way only if the ion mobilities do not change with the concentration. In an earlier section we have, however, given evidence that the change of conductance of most strong electrolytes with concentration can be accounted for on the assumption that they are completely dissociated and that interionic attractions which increase with the ion concentration produce decreases in the mobilities of the ions. Arrhenius' assumption cannot, therefore, be true even for weak electrolytes, since the ion concentrations change, although slowly, with the total concentration. It was this relatively slight change of the ion concentration with the concentration of weak electrolytes which was partly responsible for the apparent validity of Ostwald's dilution law. From recent studies (9, 10, 11) it will be shown that the ionization of weak electrolytes follows the law of mass action if (a) in computing degrees of ionization allowance is made for the changes of ion mobilities with ion concentration, (b) certain strong electrolytes can be assumed to be completely dissociated, and (c) the activities of the ions follow the Debye-Hückel relations, at least in dilute solution.

For the ionization of a weak acid, $HAc = H^+ + Ac^-$, the law of mass action is correctly stated in the form:

$$K = \frac{(H^+)\,(Ac^-)}{(HAc)} = \frac{C\alpha^2\gamma_i^2}{(1-\alpha)\gamma_u} \tag{12}$$

in which K is the thermodynamic ionization constant, the parentheses represent activities of the components enclosed, α is the degree of dissociation, and γ_i and γ_u are the mean activity coefficient of the ions and the activity coefficient of the undissociated portion, respectively. Since the undissociated portion is uncharged it can be assumed in dilute solution to be a normal electrolyte with an activity coefficient of unity, and equation 12 can be put in the form

$$K = K'\gamma_i^2 \tag{13}$$

in which K' is equal to $C\,\alpha^2/(1 - \alpha)$. However, as the ion concentration $C\,\alpha$ must change with concentration and with it the ion mobilities, we cannot accept the ratio Λ_c/Λ_0 as a measure of the degree of dissociation α. A correct degree of dissociation can be obtained from the ratio of the measured equivalent conductance to the equivalent conductance *of the completely dissociated electrolyte at the same ion concentration.* If the latter quantity is represented by Λ_e the correct degree of dissociation α is:

$$\alpha = \Lambda_c/\Lambda_e \tag{14}$$

Since it has been shown in the previous section that Kohlrausch's law of independent ion mobilities holds accurately, up to say 0.005 N, equivalent conductances are additive at a given, low, ion concentration, so that values of Λ_e of the acid HAc can be computed from the following relation

$$\Lambda_{e\mathrm{HAc}} = \Lambda_{\mathrm{HCl}} - \Lambda_{\mathrm{NaCl}} + \Lambda_{\mathrm{NaAc}} \tag{15}$$

The use of equations 14 and 15 implies that all the electrolytes involved are substantially completely dissociated at the concentrations at which they are used. This seems to be a safe assumption, at least for dilute solutions, for salts which follow Shedlovsky's equation. Our experiments have shown that the salts of the weak acids that we have studied (acetic and chloroacetic) as well as hydrochloric acid and the alkali halides belong in this group. With values of Λ_e at a series of concentrations we can proceed to obtain degrees of dissociation α. Since the ion concentration is $\alpha\, C$ the correct value of Λ_e cannot be found until α is known. The computation can, however, be made by means of a short series of approximations, and is facilitated if Λ_e is expressed as a function of the concentration in the form of equation 9.

With these values of the degrees of dissociation at hand it is possible to compute a series of values of K'. These are, however, not constant but are found to vary with the concentration. If equations 12 and 13 are valid this is to be expected, since the activity coefficient γ_i varies with the ion concentration. As is well-known, Debye and Hückel have derived the following limiting relation

$$-\log \gamma_i = A\sqrt{C\alpha} \tag{16}$$

connecting the activity coefficient γ_i with the ion concentration $C\,\alpha$. In this expression A is a constant (with the value of 0.5065 at 25°C.) and depends upon the temperature, the dielectric constant, and universal constants. The data we have obtained on the conductances of acetic and chloroacetic acid, together with those on the strong electrolytes which are necessary to compute values of K' have made it possible to test the validity of equation

12 and thus the fundamental postulates of the interionic attraction theory. Equation 13 may be put in the form

$$\log K = \log K' + \log \gamma_i^2 \tag{17}$$

and utilizing equation 16

$$\log K = \log K' - 2A\sqrt{C} \tag{18}$$

Thus the logarithms of the K' values, computed as described above, when plotted against the square root of the ion concentration should (within the range of validity of equation 16) lie on a line with the slope $2A$ and an intercept equal to $\log K$. A plot from our data on acetic acid (figure 6) indicates that this is accurately true for the more dilute solutions investigated. In this plot the solid line e has the slope 2×0.5065 as demanded by the theory.

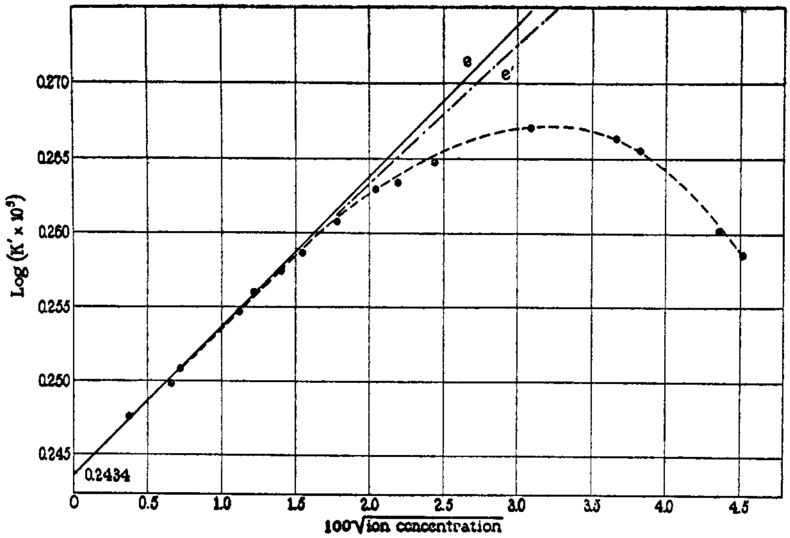

FIG. 6. THE STOICHIOMETRIC "CONSTANT" OF ACETIC ACID AS A FUNCTION OF THE CONCENTRATION

The value of the thermodynamic ionization constant K (1.753×10^{-5}) obtained as the intercept at zero concentration on this plot is particularly interesting since we have independent evidence that it is correct. Harned and Ehlers (12) have obtained, by a quite independent method, the value 1.754×10^{-5}). Their method involved the measurement of the potentials of galvanic cells without liquid junctions.

A similar plot made from computations based on the data we have obtained recently on the stronger acid, chloroacetic acid, is given in figure 7. By comparing the scales of abscissae on this and the preceding figure it will be seen that for the chloroacetic acid the experimental points lie on the line representing the limiting law to a considerably higher ion concentration, but that otherwise the shapes of the two curves are similar.

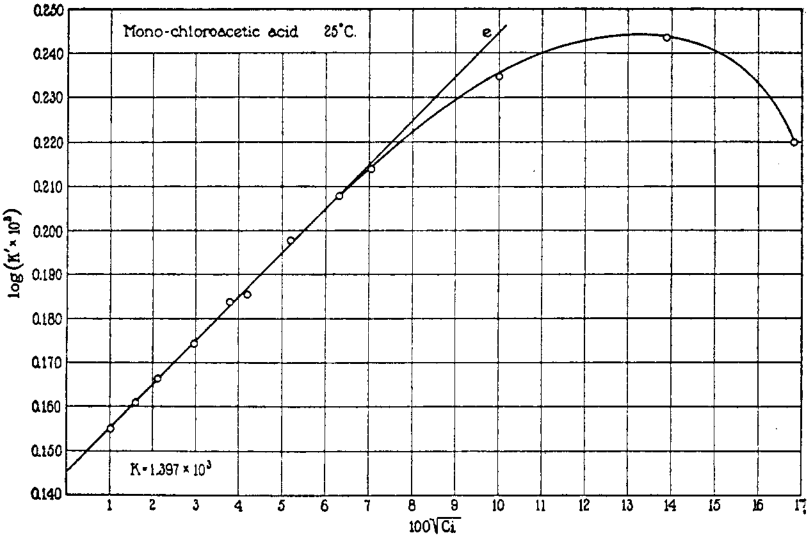

FIG. 7. THE VARIATION OF THE STOICHIOMETRIC "CONSTANT" OF CHLOROACETIC ACID WITH THE CONCENTRATION

The curves through the experimental points in figures 6 and 7 depart more abruptly from the line representing the limiting equation than would be expected from measurements on strong electrolytes. A correction for the size of the ions (assuming the reasonable value of 4 Ångström units from crystal structure data) leads only to the line *e′* in figure 6. The large deviations are undoubtedy due to a change of the properties of the solvent (a "medium effect"), arising from the fact that as the concentration is progressively increased there is an accumulation of undissociated acid in the solution. This effect will be discussed more fully in another communication.

SUMMARY

The conclusions from this study may be outlined as follows.

The conductance measurements on very dilute solutions (from 0.00003 *N* to 0.001 *N*) of strong electrolytes are in accord, within a small experimental error, with the interionic attraction theory of Debye, Hückel, and Onsager.

With an additional empirical term, Onsager's equation can be modified to express the results of conductance measurements on most strong uni-univalent electrolytes to about 0.07 *N*. The constant of this extra term may prove to have theoretical significance as interesting regularities have been observed. The data on certain salts, however, show decided deviations from this semi-empirical equation.

The results of precision measurements of transference numbers show changes with concentration that are in accord with the interionic attraction theory, except, so far as measurements have been made, in the cases in which deviations are observed from the semi-empirical equation just mentioned.

By combining conductance and transference measurements Kohlrausch's law of independent ion mobilities has been found to be strictly true in the limit, and almost within the experimental error up to 0.01 *N*. Above 0.01 *N* the conductance of a given ion constituent depends somewhat on the nature of the oppositely charged ion. The results for the separate ion constituents can, however, be expressed by means of a semi-empirical equation similar to that mentioned above.

The results of precision measurements on conductances of solutions of the weak electrolytes, acetic and chloroacetic acids, have been interpreted in the light of the interionic attraction theory. For the dilute solutions a thermodynamic ionization constant is obtained if the degrees of ionization are computed by a method which allows for changing ion mobilities, and allowance is made for variation of activity coefficients according to the Debye-

Hückel relation. At higher concentrations there is a "medium effect" which arises, in large part at least, from the accumulation of undissociated acid as the concentration is increased.

That the true value of the thermodynamic ionization constant is obtained by the method outlined above is shown by the close check of our value for acetic acid, 1.753×10^{-5}, with the value 1.754×10^{-5} recently obtained by Harned and Ehlers (12), using a quite independent method involving concentration cells without liquid junctions.

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