

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF BROWN UNIVERSITY]

## Properties of Electrolytic Solutions. II. The Evaluations of $\Lambda_0$ and of $K$ for Incompletely Dissociated Electrolytes

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### I. Introduction

Assuming complete dissociation, the conductance of strong electrolytes in water (at low concentrations) as a function of concentration is well accounted for by the interionic attraction theory. Evidence is accumulating, however, which indicates that for all electrolytes in solvents of lower dielectric constant, as for weaker electrolytes in water, dissociation is incomplete at accessible concentrations. It has been proposed that a mass action effect be combined with the interionic effect<sup>1</sup> in order to account for the observed conductance values. This suggestion was first made by Davies<sup>2</sup> for various weak electrolytes in water and shortly afterward by Sherrill and Noyes<sup>3</sup> and by MacInnes.<sup>4</sup>

Later Onsager<sup>5</sup> derived an approximate conductance equation which took into account the mass action effect as well as interionic forces, and calculated several examples. An extrapolation method based on this equation has been applied by Davies<sup>6</sup> to non-aqueous solutions. Using a combination of the two effects, Martin<sup>7</sup> has computed conductance values for various salts in benzonitrile. The results obtained by the various writers indicate that a mass action effect must be taken into account, but the methods employed in evaluating the limiting conductance and the dissociation constant have been only approximate and it is difficult to determine how closely the experimental results may be accounted for by the assumptions made.

Perhaps the chief source of inconsistency lies in the value assumed for  $\Lambda_0$ , the limiting conductance of the electrolyte. In aqueous solutions, the value of  $\Lambda_0$  for weak electrolytes may usually be evaluated from data relating to strong salts of the corresponding acid or base. In the case of solutions in solvents of lower dielectric constant, however, it is necessary to evaluate the limiting conductance for a given electrolyte from conductance data relating to that electrolyte alone. At present, only empirical extrapolation formulas have been employed for determining  $\Lambda_0$  from conductance data which do not show the theoretical slope on a square root plot. For an exact comparison of theory and experiment, however, any

(1) We are using the expression "interionic effect" in the sense of the theory of Debye and Hückel. although, of course, mass action likewise depends on an interaction of ions due to their charges, and depends upon the electrical properties of the medium.

(2) Davies, *J. Phys. Chem.*, **29**, 977 (1925).

(3) Sherrill and Noyes, *THIS JOURNAL*, **48**, 1861 (1926).

(4) MacInnes, *ibid.*, **48**, 2068 (1926).

(5) Onsager, *Physik. Z.*, **28**, 277 (1927).

(6) Davies, "Conductivity of Solutions," John Wiley and Sons, Inc., New York, 1930, Chapt. VII.

(7) Martin, *J. Chem. Soc.*, 3270 (1928).

empirical extrapolation function may be expected to lead to an error in the value of  $\Lambda_0$ . This, in turn, may induce a relatively large error in the value found for the dissociation constant  $K$ , since the error in  $(1-\gamma)$  will be large if  $\gamma$ , the fraction dissociated, is large, and the limiting form of the calculated curve may deviate greatly from the true curve. The difficulty may be overcome by solving the equations connecting conductance and concentration, which involve  $\Lambda_0$  and the dissociation constant  $K$ . While these equations are not readily solved explicitly, they may be solved by successive approximation or by graphical means. Below is described a convenient method of solution and this method is applied to a variety of binary electrolytes in solvents of dielectric constant varying from 10.4 to 79. The calculated values are in agreement with the experimental values up to ion concentrations of approximately  $2 \times 10^{-3} N$ .

## II. The Conductance Function

We consider a solution of a binary electrolyte AB and assume the usual equilibrium



between ions and "undissociated molecules" of solute. It will not be necessary to consider the physical picture underlying (1); we shall accept the equation as implying that on the average a certain fraction of the total solute does not contribute to the transport of electricity through the solution during the conduction process. If the stoichiometric concentration is  $c$ , and the average fraction of solute free to carry the current is  $\gamma$ , then the various concentrations are

$$\begin{aligned} [A^+] &= [B'] = c\gamma \\ [AB] &= c(1 - \gamma) \end{aligned}$$

where

$$\frac{1}{2} ([A^+] + [B']) + [AB] = c$$

We assume as a first approximation that the thermodynamic properties and migration velocities of the ions depend on the total concentration of free ions  $2c\gamma$  in the manner described by the equations of the interionic attraction theory. The changes in the properties of the solvent and in the distribution of ions in the "ionic atmospheres" which are caused by the presence of undissociated (non-conducting) ion pairs will be neglected. We shall also neglect higher terms<sup>8</sup> in the calculation of interionic effects. Finally, we assume that the undissociated molecules are present as a dilute solution in the classical sense. These assumptions appear to be justified at lower concentrations, even in solvents of quite low dielectric constant.<sup>9</sup>

(8) Incidentally, we might mention that, since we limit our discussion to binary one-one salts the odd terms in the power series expansion used in computing interionic effects vanish, and that the valence factor  $(z_1 z_2)^n$  in the terms of this series always is unity.

(9) By "lower concentrations," we mean up to 0.003-0.004  $N$  in liquid ammonia, for example. The only way to test the validity of the assumptions is to apply them to a practical case and see whether calculated results based on the assumptions agree with the observed experimental facts.

The equilibrium function describing reaction (1) is then given by

$$\frac{[A^+] f_{A^+} [B] f_{B^-}}{[AB] f_{AB}} = K$$

where the activity coefficients are represented by  $f$ . Our assumption that the neutral molecules are present in dilute solution is equivalent to setting  $f_{AB} = 1$ . We shall employ Debye's first approximation to calculate these coefficients for the ions, using, in accordance with our assumptions,  $2c\gamma$  for the total ion concentration. Then

$$-\log_{10} f = \beta \sqrt{c\gamma} / (1 + \delta \sqrt{c\gamma}) \quad (2)$$

where

$$\beta = 0.4343 \frac{e^2}{2DkT} \left( \frac{8\pi N e^2}{1000 DkT} \right)^{1/2} \quad (2a)$$

and

$$\delta = \left( \frac{8\pi N e^2}{1000 DkT} \right)^{1/2} a \quad (2b)$$

Here,<sup>10</sup>  $e$  = the electronic charge =  $4.770 \times 10^{-10}$  e. s. u.,  $N$  = Avogadro's number =  $6.06 \times 10^{23}$ ,  $k$  = Boltzmann's constant =  $1.371 \times 10^{-16}$  erg/1°,  $D$  is the dielectric constant of the solvent,  $T$  is the absolute temperature, and  $a$  is the ionic radius.<sup>11</sup>

If we substitute our symbols for the concentrations, and assume  $f_{A^+} = f_{B^-}$  the equilibrium equation becomes

$$c\gamma^{2/2} / (1 - \gamma) = K \quad (3)$$

For convenience in later manipulation, we shall introduce a variable  $x$  defined by

$$x = (1 - \gamma) / \gamma^2 = c\gamma^2 / K \quad (4)$$

For a solution containing  $c\gamma/1000$  equivalents per cc. of anions and cations with mobilities  $v_{B^-}$  and  $v_{A^+}$ , respectively, the specific conductance  $\kappa$  is given by

$$1000\kappa = Fc\gamma(v_{A^+} + v_{B^-}) \quad (5)$$

where  $F = 96,494$  international coulombs per equivalent.<sup>12</sup> The equivalent conductance is defined as

$$\Lambda = 1000 \kappa / c \quad (6)$$

According to the interionic attraction theory, the mobilities vary linearly with the square root of the ion concentration; if we use Debye's equation to represent this change, we have, in view of (5) and (6)

$$\Lambda = \gamma(\Lambda_0 - \alpha \sqrt{c\gamma}) \quad (7)$$

where  $\Lambda_0$  is the limiting value of the equivalent conductance, and  $\alpha$  has the value computed by Onsager

$$\alpha = \frac{8.18 \times 10^5}{(DT)^{3/2}} \Lambda_0 + \frac{82}{\eta(DT)^{1/2}} \quad (8)$$

(10) Birge, *Phys. Rev. Supplement*, **1**, 1 (1929).

(11) The value of  $a$  may be estimated from the limiting conductance by means of Stokes' law with sufficient accuracy to be used in a correction term.

(12) Ref. 10, p. 36.

Here  $\eta$  is the viscosity of the solvent and the other symbols have their usual meanings.

We now have a system of equations (2), (3) and (7) which implicitly describe the conductance curve

$$\Lambda = \Lambda(c)$$

Explicit solution in this form is difficult, due to the mixed form (transcendental, quadratic and cubic) of the system, but by means of the variable  $x$ , it is possible to transform the equations in such a way that calculation will be convenient. The explicit solution may be carried out in principle as follows: we regard  $c$  and  $\Lambda$  as known quantities from experiment, and may solve (7) in the form  $\Lambda_0 = \Lambda_0(\gamma)$ . From (2) and (3), we eliminate  $f$  and obtain  $\gamma = \gamma(K, a)$ , which, in view of the approximate relation between  $\Lambda_0$  and  $a$  contained in Stokes' law, and the relative unimportance of the  $\delta$ -correction term, may be written  $\gamma = \gamma(K)$ . From these two equations, we eliminate  $\gamma$  and obtain a relation between  $\Lambda_0$  and  $K$ ,  $F(K, \Lambda_0) = 0$ . We have as many equations (7) as we have experimental points  $\Lambda = \Lambda(c)$ . Corresponding to any two pairs of values of  $c$  and  $\Lambda$ , the equations  $F_1(K, \Lambda_0) = 0$  and  $F_2(K, \Lambda_0) = 0$  may be solved for  $K$  and  $\Lambda_0$ .

Before considering the general case, however, it is of interest to mention two limiting cases. If  $K$  is large,  $\gamma$  approaches very near to unity and (7) reduces first to Onsager's equation

$$\Lambda = \Lambda_0 - \alpha \sqrt{c} - \Lambda_0 c / K \quad (9)$$

and, for  $K$  still larger, to the limiting law for complete dissociation

$$\Lambda = \Lambda_0 - \alpha \sqrt{c} \quad (10)$$

It should also be noted that, *in any case*, the limiting slope on a  $\Lambda - \sqrt{c}$  plot is  $\alpha$ . If, on the other hand,  $K$  is very small,  $(1 - \gamma)$  may be replaced by unity in (3), and  $\alpha \sqrt{c\gamma}$  becomes negligible compared to  $\Lambda_0$ , so that

$$\gamma \approx \Lambda / \Lambda_0 \quad (11)$$

and the equilibrium equation becomes

$$c\Lambda^2 = K\Lambda_0^2 \quad (12)$$

We should expect, therefore, that  $\log \Lambda$  plotted against  $\log c$  would be a straight line with slope

$$\frac{d \log \Lambda}{d \log c} = -\frac{1}{2} \quad (13)$$

when  $K$  is small. Also, if the limiting conductance is known, approximate values of  $K$  may be computed by (12).

In the general case, both the change of ion concentration and of ion mobility with concentration must be considered. If we rewrite equations (7) and (2) in terms of  $x$ , we obtain

$$\frac{\Lambda}{\Lambda_0} = \gamma - \frac{\alpha \sqrt{K}}{\Lambda_0} \frac{x^{1/2} \gamma^{3/2}}{f} \quad (14)$$

and

$$-f \log f = \beta \sqrt{K} \sqrt{x\gamma} / (1 + \delta \sqrt{c\gamma}) \quad (15)$$

By solving (4), we obtain

$$\sqrt{x} = \sqrt{1 - \gamma/\gamma} \quad (16)$$

$$\gamma = (\sqrt{1 + 4x} - 1)/2x \quad (17)$$

For small values of  $x$ , the power series

$$\gamma(x) = 1 - x + 2x^2 - 5x^3 + 14x^4 - 42x^5 + \dots \quad (18)$$

may be used to calculate  $\gamma$  from  $x$ .

The values of the limiting conductance  $\Lambda_0$  and of the dissociation constant  $K$  are determined from conductance data as follows. An approximate<sup>13</sup> value  $\gamma'$  of  $\gamma$  is obtained simply by replacing  $\gamma$  in the interionic attraction term of (7) by  $\Lambda/\Lambda_0$

$$\gamma' = \frac{\Lambda/\Lambda_0}{1 - \alpha\Lambda_0^{-1/2}\sqrt{c}\Lambda} \quad (19)$$

The value of  $\Lambda_0$  used here is obtained by any convenient method, such as a free-hand extrapolation of the experimental  $\Lambda-\sqrt{c}$  curve; the final result is independent of the value of  $\Lambda_0$  initially assumed. The approximation is repeated according to the scheme

$$\gamma'' = \frac{\Lambda/\Lambda_0}{1 - \alpha\Lambda_0^{-1}\sqrt{c}\gamma'}, \text{ etc.}$$

which converges to a constant value. Having determined  $\gamma$ ,  $\sqrt{x}$  is computed from (16) and  $f$  from (2). The  $\sqrt{x}$  is plotted against  $f\sqrt{c}$ . (The square root plot generally gives the more convenient scale.) According to (4), this plot should be a straight line with slope  $\sqrt{K}$ , passing through the origin. If the value of  $\Lambda_0$  used in (19) is greater than the actual value of  $\Lambda_0$ , the  $f\sqrt{c}-\sqrt{x}$  curve will have a positive intercept on the  $\sqrt{x}$  axis. If this is the case, the computation is repeated for several smaller values of  $\Lambda_0$ , until a small negative intercept is obtained; the  $\Lambda_0$  values used are then plotted against the corresponding  $\sqrt{x}$  intercepts and a value is interpolated which gives a zero intercept. The value of  $\sqrt{K}$  is determined by plotting the slopes of the  $f\sqrt{c}-\sqrt{x}$  lines against the intercepts and interpolating as above. Since the  $f\sqrt{c}-\sqrt{x}$  curve is very nearly linear (except in the extremely dilute region) even when the value of  $\Lambda_0$  chosen is not the true value, it is sufficient to carry out the above calculation at only two concentrations which are taken in the range of concentration where the experimental error is small. This will give a value of  $\Lambda_0$  which is as accurate as the two data; the computation may then be repeated with this value of  $\Lambda_0$ , using all of the experimental data, and weighting the points according to their accuracy if desired. If the  $\sqrt{x}$  intercept thus determined is not quite zero, the values of  $\Lambda_0$  and  $K$  may be corrected by means of the average slope of the interpolation plots. In our calculations we used at least five conductance determinations and, in this case, the interpolated

(13) Equation (7) is cubic in  $\gamma^{1/2}$  and may be solved by the usual algebraic methods or by the use of tables. In general, however, the convergent approximation method as here outlined is more rapidly handled.

values of  $\Lambda_0$  and  $K$  needed no correction to bring them into agreement with the remaining data.

Figure 1 illustrates the application of the method to Kraus and Parker's<sup>14</sup> data for iodic acid in water. Curve I (scales above and left) covers the entire concentration range (0.0003–0.2  $N$ ) and corresponds to  $\Lambda_0 = 391.19$ ; the three lower Curves II, III and IV (scales below and right), show the dilute region (0.0003–0.002  $N$ ) on a ten-fold magnified scale and correspond to  $\Lambda_0 = 390.8$ , 391.19 and 391.60, respectively. The points in the most dilute region are extremely sensitive to experimental

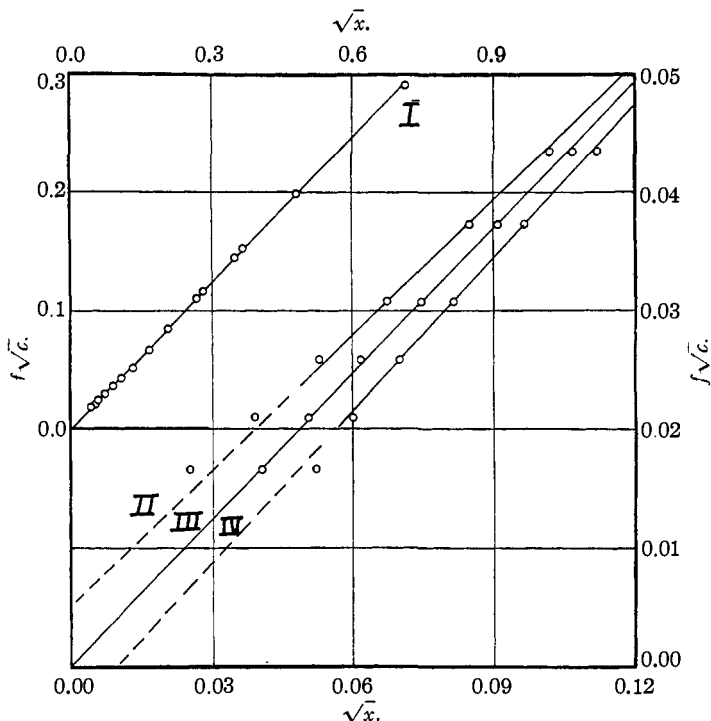


Fig. 1.— $f\sqrt{c}-\sqrt{x}$  plots for iodic acid in water.

error, because  $\gamma$  is greater than 0.99; nevertheless, it is obvious that  $\Lambda_0 = 391.60$  is too great and  $\Lambda_0 = 390.8$  is too small, because the average straight lines corresponding to these values definitely do not go through the origin, while the line for  $\Lambda_0 = 391.19$  does satisfy this condition. Similar results have been obtained for about twenty-five electrolytes in various solvents.

The approximate linearity of the  $f\sqrt{c}-\sqrt{x}$  plots, when the value of  $\Lambda_0$  used above is near to the true value, is readily accounted for. The mass action equation (3) may be written

(14) Kraus and Parker, *THIS JOURNAL*, **44**, 2429 (1922).

$$f^2 c \cdot \frac{\Lambda^2 (1 - \alpha \Lambda_0^{-1} \sqrt{c\gamma})^2}{1 - \Lambda (1 - \alpha \Lambda_0^{-1} \sqrt{c\gamma}) / \Lambda_0} = K \Lambda_0^2$$

Now  $f\sqrt{c}$  depends on the chosen value of  $\Lambda_0$  through  $\gamma$  in the expression for  $\log f$  and hence is not very sensitive to changes in  $\Lambda_0$ . On the other hand,  $\gamma$ , and hence  $\sqrt{x}$ , depends directly on  $\Lambda/\Lambda_0$ , so that the main effect of changing  $\Lambda_0$  is to change the values of  $\sqrt{x}$ . But, if  $\Lambda_0$  is near to the true value, the left-hand side of the above function does not change much with  $c$ , so that  $K\Lambda_0^2$  remains constant except for differences of higher order. For  $K\Lambda_0^2$  constant,  $f\sqrt{c}$  is linear against the square root of the reciprocal of the second factor on the left, which is the  $\sqrt{x}$  value computed for the chosen value of  $\Lambda_0$ . The "true" value of  $\Lambda_0$ , however, is the value approached by  $\Lambda$  (observed) as  $c$  approaches zero, and this value obviously corresponds to the condition that  $x = 0$  when  $c = 0$ .

If  $\Lambda_0$  and  $K$  are known, the conductance curve may be computed as follows. A sufficiently dense set of values of  $\sqrt{x}$  ranging from zero to  $\sqrt{c_m/K}$  are listed, where  $c_m$  is the maximum concentration to be considered, and the corresponding values of  $\gamma$ ,  $x^{1/2}$ ,  $\gamma^{3/2}$  and  $\sqrt{x\gamma}$  are read<sup>15</sup> from the graph (Fig. 2, Curves I, II and III). From a plot of  $-f \log f$  against  $f$  (Curve IV, Fig. 2), approximate values  $f'$  of  $f$  are determined according to the equation

$$-f' \log f' = \beta \sqrt{K} \sqrt{x\gamma}$$

With these values for  $f$ , approximate concentrations are computed from

$$\sqrt{c'} = \sqrt{K} \sqrt{x}/f'$$

and are used to determine the correction term in (15); then a second approximation  $f''$  for  $f$  is obtained from

$$-f'' \log f'' = \beta \sqrt{K} \sqrt{x\gamma} / (1 + \delta \sqrt{c'\gamma})$$

This approximation scheme converges rapidly; when  $f$  becomes constant,  $\sqrt{c}$  is given by (4). Then  $\Lambda$  is calculated according to (14) and a smooth curve is finally drawn through the computed  $(\Lambda, \sqrt{c})$  points.

If it is desired to compute values of  $\Lambda$  for particular values of  $c$ , rather than to draw the conductance curve, a somewhat different procedure is followed. As a zeroth approximation,  $\gamma$  is set equal to unity in (2), and the corresponding value  $(f^0)^2$  of  $f^2$  is determined by

$$-\log (f^0)^2 = 2\beta \sqrt{c} / (1 + \delta \sqrt{c})$$

The corresponding value  $x^0$  of  $x$  is computed from the given concentration by means of (4), and then a first approximation  $\gamma'$  for  $\gamma$  is obtained by substituting  $x^0$  in (17) (or in (18) if  $x^0$  is small). Then  $(f')^2$  is computed from

$$-\log (f')^2 = 2\beta \sqrt{c\gamma'} / (1 + \delta \sqrt{c\gamma'})$$

and the process repeated until  $\gamma$  converges to a constant value. Then, with  $\gamma$  and  $f$  determined,  $\Lambda$  is computed according to (7).

(15) For calculations requiring a higher accuracy than is permitted by a graph, a table of the values of  $\sqrt{x}$ ,  $\gamma$ ,  $\sqrt{x\gamma}$  and  $x^{1/2} \gamma^{3/2}$  for round values of  $x$  is very convenient.

The general nature of the conductance function is evident from (14), where the conductance ratio  $\Lambda/\Lambda_0$  is given as the difference between two terms,  $\Lambda$  and  $(\alpha \sqrt{K}/\Lambda_0) (x^{1/2} \gamma^{3/2}/f)$ . The first represents the effect of mass action and the second the effect of interionic forces, corrected for incomplete dissociation. When the dissociation constant  $K$  is large,  $\gamma$  remains near unity and varies approximately as the *first power* of  $x$ , while the interionic attraction term has a large numerical coefficient and varies as the *square root* of  $x$ . Consequently, the variation of  $\Lambda/\Lambda_0$  with  $c$  is governed primarily by the latter term. On the other hand, when  $K$  is small, even small concentrations soon correspond to large values of  $x$  where  $\gamma$  is decreasing rapidly (Curve I, Fig. 2). The interionic attraction term

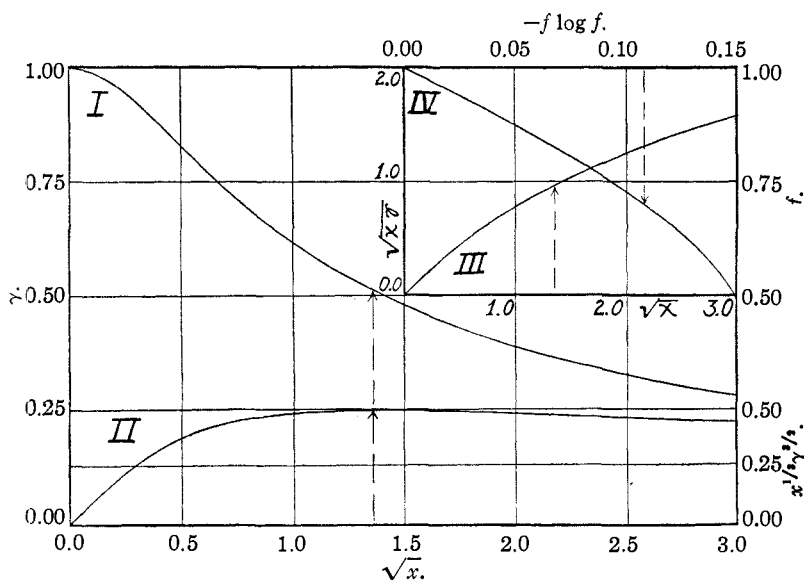


Fig. 2.—Functions involved in calculation of conductance.

now has a small numerical coefficient and becomes merely a correction term to  $\gamma$  in determining  $\Lambda/\Lambda_0$ , since  $x^{1/2} \gamma^{3/2}$  reaches a maximum at  $x = 2$  (Curve II, Fig. 1). The decrease of  $f$  with increasing concentration increases the term in question, but the increase is retarded by the proportionality of  $f \log f$  with  $\sqrt{x\gamma}$ . The various relations are illustrated by Fig. 2; if, for simplicity, we neglect the change of  $f$  with  $c$ , the conductance curve is simply the resultant of Curves I and II, where Curve I has the ordinate scale given in the figure and the scale for the Curve II is multiplied by  $(\alpha \sqrt{K}/\Lambda_0)$ . As might be expected, the conductance curves for weak electrolytes (*cf.* Fig. 3) markedly resemble the  $\gamma$ -curve of Fig. 2.

The inflection point in the  $\gamma$ - $\sqrt{x}$  curve (I, Fig. 2) lies at

$$\sqrt{x} = \sqrt{\sqrt{3}/8} = 0.4653$$



and the corresponding concentration

$$c_{inf} = 0.2165 K/f_{inf}^2 \quad (20)$$

is proportional to the dissociation constant. A rough estimate of the concentration at which the inflection point appears may be obtained by setting  $f$  equal to unity. For example, if  $K$  is  $5 \times 10^{-4}$ , the inflection point in the  $\gamma-\sqrt{x}$  curve appears in the neighborhood of  $10^{-4} N$ , and one should not expect a  $\Lambda-\sqrt{c}$  plot to have a slope equal to the limiting value at concentrations greater than  $10^{-4} N$ . It is only at much lower concentrations that

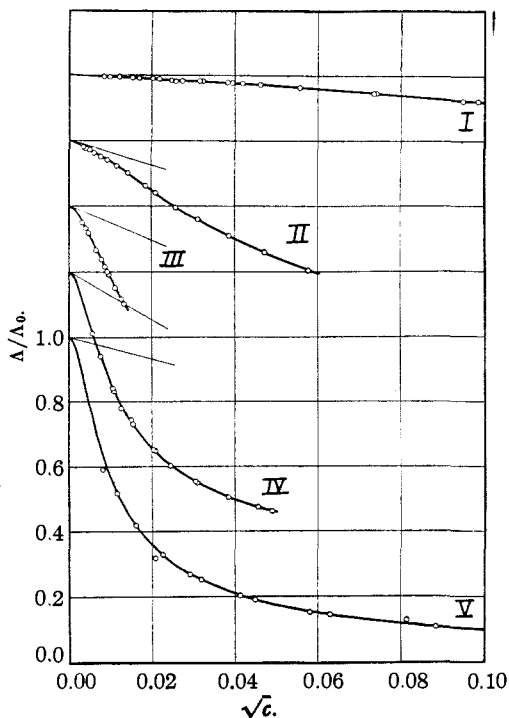


Fig. 3.—Comparison of calculated and observed conductance values: I, iodic acid in water; II, sodium bromate in ammonia; III, sodium iodide in amyl alcohol; IV, tetraisoamylammonium nitrate in ethylene dichloride; V, potassium amide in ammonia.

The interionic term becomes the controlling term, rather than a correction term to  $\Lambda/\Lambda_0$ . Incidentally, the presence of the inflection point accounts for the fact that many conductance curves are apparently linear in  $\sqrt{c}$  over a certain range of concentration, but with a slope considerably greater than  $\alpha$ .

### III. Comparison with Experiments

The method of computation presented above has been applied to a number of sets of conductance data, chosen to cover a fairly wide range of the specific constants involved. The results for several examples are shown in Fig. 3, where the conductance ratio  $\Lambda/\Lambda_0$  is plotted against the square root of total concentration. (Each curve begins on the left at  $(\sqrt{c} = 0, \Lambda/\Lambda_0 = 1)$ ; in order to avoid confusion due to crossing

curves, the different curves are displaced vertically. The ordinate unit is 0.2.) The circles indicate the various observed points. The curves are drawn according to equations (2), (3) and (7), where the constants have the values given in Table I, and the limiting tangents are drawn in accordance with (8).

A comparison of calculated and observed values for iodic acid in water is given in Table II. The specific conductance of the water used in Series

TABLE I  
 CONSTANTS FOR CONDUCTANCE CURVES

| No. | Solvent                                       | Solute   | $t, ^\circ\text{C.}$ | $D$        | $\eta$  | $\alpha$ |
|-----|---|--|----------------------|------------|---------|----------|
| I   | H <sub>2</sub> O                              | HIO <sub>3</sub>   | 25                   | 78.57      | 0.00895 | 148.75   |
| II  | NH <sub>3</sub>                               | NaBrO <sub>3</sub>   | -33.5                | 22.0       | .00256  | 1052     |
| III | C <sub>2</sub> H <sub>5</sub> OH              | NaI  | 25                   | 16.0       | .038    | 59.19    |
| IV  | C <sub>2</sub> H <sub>4</sub> Cl <sub>2</sub> | (C <sub>2</sub> H <sub>5</sub> ) <sub>4</sub> NNO <sub>3</sub> | 25                   | 10.4       | .00785  | 500      |
| V   | NH <sub>3</sub>                               | KNH <sub>2</sub>   | -33.5                | 22.0       | .00256  | 1191     |
|     |   | $\delta$   | $\beta$              | $\Delta_0$ | $K$     |          |
| I   |   | 0.0153   | 0.5044               | 391.19     | 0.1686  |          |
| II  |   | 1.54   | 4.742                | 286.2      | .00253  |          |
| III |   | 2.80   | 5.517                | 11.246     | .00295  |          |
| IV  |   | 2.86   | 10.52                | 65.8       | .00115  |          |
| V   |   | 1.26   | 4.742                | 351.3      | .000070 |          |

6 and 7 was about five times that used in Series 4 and 5; it will be noted that the agreement between calculated and observed conductances is much better for the former two than for the latter two series. Excepting the most dilute points in each of Series 6 and 7, the deviations are within the experimental error of several hundredths of 1% up to about 0.02  $N$ ;

 TABLE II  
 CONDUCTANCE OF IODIC ACID IN WATER

| Series 4        |                  |                    |              |        |
|-----------------|------------------|--------------------|--------------|--------|
| $c \times 10^3$ | $\Lambda$ (obs.) | $\Lambda$ (calcd.) | $\Delta, \%$ | $K$    |
| 0.068517        | 389.02           | 389.80             | -0.19        | ...    |
| .144572         | 388.94           | 389.08             | -.03         | ...    |
| .233308         | 388.31           | 388.40             | -.02         | ...    |
| .399158         | 387.46           | 387.35             | +.03         | 0.1938 |
| .648686         | 386.12           | 386.01             | +.03         | .1823  |
| .986010         | 384.54           | 384.45             | +.02         | .1764  |
| 1.49429         | 382.36           | 382.39             | -.01         | .1675  |
| 2.11108         | 380.06           | 380.16             | -.02         | .1646  |
| Series 5        |                  |                    |              |        |
| 0.096291        | 389.02           | 389.52             | -0.13        | ...    |
| .168284         | 388.62           | 388.88             | -.07         | ...    |
| .286320         | 388.04           | 388.04             | .00          | 0.1666 |
| .465172         | 387.00           | 386.99             | .00          | .1729  |
| .710642         | 385.76           | 385.71             | +.01         | .1747  |
| 1.02335         | 384.31           | 384.29             | .00          | .1701  |
| 1.52809         | 382.26           | 382.26             | .00          | .1685  |
| 2.10323         | 380.09           | 380.18             | -.02         | .1648  |
| Series 6        |                  |                    |              |        |
| 0.62349         | 384.97           | 386.14             | -0.29        | ...    |
| 1.73067         | 380.92           | 381.51             | -.15         | ...    |
| 3.00736         | 376.58           | 377.03             | -.11         | 0.1562 |
| 5.38453         | 370.33           | 370.65             | -.08         | .1630  |
| 9.03267         | 362.15           | 362.28             | -.03         | .1669  |
| 16.1179         | 349.42           | 349.28             | +.03         | .1698  |
| 30.5179         | 330.18           | 329.66             | +.12         | .1715  |

TABLE II (Concluded)

| $c \times 10^8$ | $\Lambda$ (obs.) | Series 7           |              |        |
|-----------------|------------------|--------------------|--------------|--------|
|                 |                  | $\Lambda$ (calcd.) | $\Delta, \%$ | $K$    |
| 1.43615         | 382.20           | 382.62             | -0.10        | 0.1473 |
| 3.04044         | 376.77           | 377.15             | - .09        | .1580  |
| 5.47988         | 370.13           | 370.40             | - .07        | .1636  |
| 9.69682         | 360.79           | 360.91             | - .03        | .1672  |
| 18.3879         | 345.88           | 345.70             | + .04        | .1698  |
| 34.9757         | 325.85           | 324.72             | + .28        | .1748  |
| 67.3634         | 298.05           | 297.50             | + .14        | .1707  |
| 193.258         | 244.36           | 245.22             | - .21        | .1658  |

beyond this concentration, the small differences increase with concentration. The maximum difference is 0.28%. The last column gives the values of  $K$ , calculated for each point.

Kraus and Parker, using the Ostwald dilution law for extrapolation, obtained  $\Lambda_0 = 389.55$  and  $K = 0.0717$ ; the present values are  $\Lambda_0 = 391.19$  and  $K = 0.1686$ . Onsager<sup>5</sup> obtained  $\Lambda_0 = 391.3$  and  $K = 0.17$ , which are in substantial agreement with our values. On the scale used, the curve for iodic acid (I, Fig. 2) shows little structure beyond the fact that it is slightly concave toward the concentration axis. Considering the high ionization of the acid, the value of  $K$  as calculated for the different points is remarkably constant; this is particularly true of Series 3 and 4. For  $c = 4 \times 10^{-4} N$ ,  $\gamma = 0.998$ , and here an error of 0.1% in  $\Lambda$  makes an error of 50% in  $(1 - \gamma)$ ;  $K$  was therefore not calculated for the points in the most dilute region. The dissociation is too nearly complete to permit of accurate measurement of the undissociated fraction.

Sodium bromate in liquid ammonia (Curve II)<sup>16</sup> is a relatively much weaker electrolyte than iodic acid in water and, as might be expected from our discussion in the preceding section, gives a steeper conductance curve, which has an inflection point near 0.0003  $N$ . Due to the lower dielectric constant and viscosity of ammonia compared to water, the slope of the limiting tangent for ammonia (Curves II and V) is greater than for water (Curve I), but on a  $\Lambda - \sqrt{c}$  plot, the observed points and the calculated curve lie below the limiting tangent even at  $10^{-5} N$ , the lowest concentration measured. Our present values for the constants of sodium bromate are  $\Lambda_0 = 286.2$  and  $K = 0.002532$ . Kraus and Bray<sup>17</sup> obtained  $\Lambda_0 = 278$  and  $K = 0.0023$ , based on the classical mass action equation. Davies<sup>8</sup> gives  $\Lambda_0 = 281$  and  $K = 0.0073$ , using Onsager's approximate equation (9) for extrapolation. With dissociation constants as small as  $10^{-3}$ , this simple parabolic equation may no longer be used (*cf.* (18)).

The curve for potassium amide<sup>18</sup> in liquid ammonia (V, Fig. 3) repre-

(16) Paul B. Bien, Thesis, Brown University, 1932.

(17) Kraus and Bray, THIS JOURNAL, **55**, 1337 (1913). These authors use the data of Franklin and Kraus, *Am. Chem. J.*, **23**, 277 (1900). The older data are in substantial agreement with the more recent values.

(18) Franklin, *Z. physik. Chem.*, **69**, 290 (1909).

sents a still weaker electrolyte. The shape of the curve recalls the curve for  $\gamma$  in Fig. 2 and, indeed, mass action controls the gross change of equivalent conductance for this salt. The interionic correction term, nevertheless, remains appreciable at all concentrations in the experimental range. If this correction is omitted and the simple mass action law is used for extrapolation, the resulting values are  $\Lambda_0 = 301$  and  $K = 1.20 \times 10^{-4}$ , given by Kraus and Bray. These diverge widely from our present values:  $\Lambda_0 = 351.3$  and  $K = 0.700 \times 10^{-4}$ . On the other hand, for a salt of this type, extrapolation by means of the simple square root law is impossible, since the approach to the limiting slope  $\alpha$  does not appear at accessible concentrations.

Curve IV represents the conductance of tetraisoamylammonium nitrate<sup>19</sup> in ethylene dichloride, a solvent with dielectric constant 10.4. The corrections due to interionic effects are greater in this solvent than in ammonia because of its smaller dielectric constant.

The conductance of sodium iodide<sup>20</sup> in amyl alcohol is shown by Curve III. This solvent has a very high viscosity and a fairly low dielectric constant. The curve was not computed above the range of concentration covered by the data.

The examples described above cover a wide range of the various constants involved: dielectric constant 10.4–78.6; viscosity 0.038–0.00256; equivalent conductance 11.2–391; dissociation constant 0.00007–0.17. The agreement between calculated and observed values is in all cases satisfactory; we may therefore conclude that our assumptions are justified in the range of concentration considered, namely, up to *ion* concentrations of about 0.002 *N*.

Attention is called to a group of electrolytes whose behavior is incompatible with the equations here used to describe the conductance of weak electrolytes. A large group of strong electrolytes in water (for example, hydrochloric acid, potassium hydroxide, potassium chloride, etc.) give conductance curves which approach the limiting tangent from above, while a mass action effect causes the curves to fall below the limiting tangent. Apparently, some effect is here coming into play, which either is not taken into account in our equations or has been excluded by our assumptions. This behavior, *i. e.*, observed conductance greater than that calculated from our equations, is not limited to aqueous solutions, for most of the electrolytes which we have examined show positive deviations at higher concentrations (greater than about 0.01 *N*). In solvents of lower dielectric constant, the conductance curve generally exhibits a minimum. This increase of conductance with concentration at higher concentrations may be analogous to the effect observed in water, which has a very high dielectric constant.

(19) Kraus and Fuoss, *THIS JOURNAL*, **55**, 21 (1933).

(20) Kraus and Bishop, *ibid.*, **44**, 2206 (1922).

### Summary

1. An exact method of solving the conductance equations for incompletely dissociated binary electrolytes is presented.

2. A method is described for determining the limiting equivalent conductance and the dissociation constant.

3. Five examples of application of the method are given, in which the constants of solvent and of electrolyte vary as widely as possible. Calculated and observed conductance values agree within the limit of experimental error up to ion concentrations of several thousandths normal.

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## The Reaction between Osmium Tetroxide and Hydrobromic Acid. I. Equilibrium Study

BY H. DARWIN KIRSCHMAN AND WILLIAM R. CROWELL

### Introduction

A study of the catalytic influence of ruthenium compounds on the decomposition of perchloric acid by hydrobromic acid recently made<sup>1</sup> has led to a similar investigation of the catalytic effect of osmium compounds on this reaction. This work is now under way. Since under certain conditions there is an appreciable action between the hydrobromic acid and octavalent osmium, it became necessary to study the latter effect separately.

The products of the reaction were found to be bromine (largely in the form of tribromide ion) and some form of osmium in a lower valence state. Data obtained in an examination of the reaction rate indicated that a state of equilibrium was reached. In the present paper are presented the results of a study of this equilibrium, together with possible interpretations of the results and an attempt to derive an equilibrium constant at 100°.

### Apparatus and Materials

The apparatus used was that employed in the potentiometric determination of bromine, octavalent and quadrivalent osmium.<sup>2</sup> The materials and their preparation have been described in the articles mentioned. In the present work, however, the bromine solution was 1.00 *N* in hydrobromic acid since it was found that the stability of the solution was much greater than in one-tenth normal acid as previously used, the concentration of the bromine solution in the stronger acid remaining unchanged for a period of

(1) Crowell, Yost and Carter, *THIS JOURNAL*, **51**, 786 (1929).

(2) (a) Crowell and Kirschman, *ibid.*, **51**, 175 (1929); (b) **51**, 1695 (1929); (c) Crowell, *ibid.*, **54**, 1324 (1932).