length to diameter equal to 4.8 which has been found to be a convenient size for adiabatic demagnetization experiments in this Laboratory.

The susceptibility of gadolinium oxide was determined by the induction in coils surrounding an ellipsoidal sample. These results were then used to interpret similar observations on a cylindrical sample.

The magnetic susceptibility of gadolinium oxide has been given for various temperatures in the range 1.5–88°K.

The investigation was carried out at low temperatures so that a paramagnetic substance of relatively large and field independent susceptibility could be used. Ferromagnetic materials are unsuited for this purpose because of a variable permeability and hysteresis.

An equation has been developed so that susceptibility may be deduced from induction measurements with coils located at various positions with respect to ellipsoidal samples.

Extrapolation of the Conductivities of Strong Electrolytes of Various Valence Types

BY BENTON BROOKS OWEN

The equivalent conductivities of strong uni-univalent electrolytes in water follow the Onsager[1] equation

$$\Lambda = \Lambda_0 - (\alpha\Lambda_0 + \beta)\sqrt{c} \qquad (1)$$

so closely at high dilutions that it is possible to obtain a satisfactory extrapolation against $\sqrt{c}$ without actually calculating the limiting slope predicted by theory. For higher valence types the region of concordance with the equation is shifted to such extreme dilutions that this simple procedure is no longer practicable. Even for such a favorable example as barium chloride, for which accurate data are available at high dilutions, the theoretical limiting slope cannot safely be ignored. The conductance of this salt has been extrapolated by five different empirical equations, which approach linearity with $\sqrt{c}$ at the limit, and the value of Λ_0 was found[2] to be influenced strongly by the extrapolation function employed.

The simplest use of the limiting slope is to plot Λ against $\sqrt{c}$ and cause the extension of a smooth curve through the lowest experimental points to merge with the limiting slope before intercepting the axis of zero concentration. A more sensitive procedure[3] is based on the fact that a plot of

$$\Lambda_0' = \frac{\Lambda + \beta\sqrt{c}}{1 - \alpha\sqrt{c}} \qquad (2)$$

against c is linear, or only moderately curved, for dilute solutions of simple strong electrolytes. Plots of this nature have been used widely in the estimation or Λ_0 for uni-univalent and uni-bi-

valent electrolytes, but are not well suited to the extrapolation of data for higher valence types, or incompletely dissociated electrolytes. Figure 1 shows that a fairly accurate value of Λ_0 might be derived for lanthanum chloride by producing the experimental curve horizontally[4] but for potassium ferrocyanide and zinc sulfate it is clear that Λ_0' varies too rapidly with c to permit precise extrapolation. For convenience in comparing the
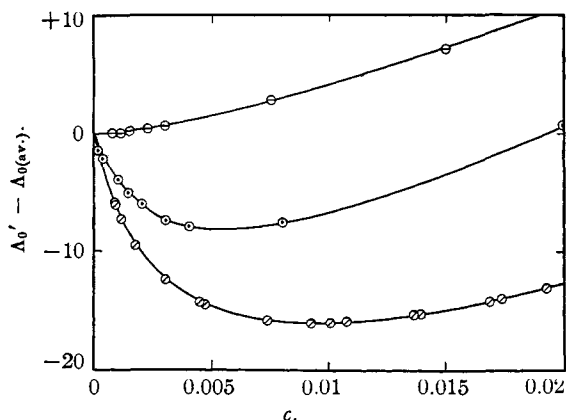

Fig. 1.—Variation of Λ_0' with C in dilute solutions at 25°. For convenience in plotting, $\Lambda_{0(av.)}$ of Table I has been subtracted from Λ_0': ⊖, LaCl₃; ⊙, K₄Fe(CN)₆; ⊘, ZnSO₄.

results for salts of different valence types in this and subsequent figures, Λ *represents the equivalent conductance, and c is expressed in equivalents per liter.* These units have been taken into account in evaluating the constants and empirical parameters appearing in the conductance equations and Table I. The most satisfactory methods of

(1) L. Onsager, *Physik. Z.*, **27**, 388 (1926); **28**, 277 (1927).

(2) Jones and Dole, THIS JOURNAL, **52**, 2247 (1930).

(3) Shedlovsky, *ibid.*, **54**, 1405 (1932).

(4) Jones and Bickford, *ibid.*, **56**, 606 (1934).

extrapolating such data have been based upon the assumption that the minima observed in Fig. 1 are due to ion association, and that the solutes may be treated as weak electrolytes. Davies,[5] Fuoss[6] and Shedlovsky[7] have proposed convenient functions for use in this connection, and these have been shown to lead to essentially the same value of Λ_0 for bi-bivalent electrolytes such as zinc or copper sulfates.[8] All three methods introduce the thermodynamic expression for the ionization constant of the solute, and therefore require the estimation of activity coefficients by direct experiment, or by the Debye–Hückel equation in some form.[9-11] For complex valence types trustworthy values of the activity coefficients cannot be calculated from theory alone, and their experimental determination is laborious and often very difficult. Because of minor differences in the range over which the Onsager equation is assumed to be valid, these three methods do not lead to concordant values of the ionization constant, K. Even in the favorable case of zinc sulfate, for which accurate activity coefficients are available, the values of K obtained[8] were 0.0049, 0.0054 and 0.0044 to 0.0047 by the methods of Shedlovsky,[7] Fuoss[6] and Davies,[5] respectively. These differences would be increased by the uncertainties in extrapolating highly curved plots if the limiting law, without extended terms, has been used in estimating activity coefficients. In view of such variations, the numerical value of K loses much of its physical significance, and Λ_0 itself cannot be very satisfactorily determined for salts of high valence types unless the activity coefficients are known accurately. From purely practical considerations, it therefore seems justifiable to ignore the value of K for the time being and avoid the use of activity coefficients if a method, based on conductance data alone, can be found that will yield values of Λ_0 in good agreement with the procedures discussed above.

Such a method can be developed very simply from the relation obtained by Onsager and Fuoss,[12] viz.

$$\Lambda = \Lambda_0 - (\alpha\Lambda_0 + \beta)\sqrt{c} + Ac \log c + Bc \quad (3)$$

The $c \log c$ and c terms are predicted by theory to

account for deviations of strong electrolytes from the limiting slope in dilute solutions, but the theoretical values of A and B never have been calculated completely. Fuoss[13] has deduced the contribution of the time of relaxation toward these constants, but the contribution of the electrophoretic effect is unknown. It will serve our purpose to regard A and B as purely empirical parameters to be determined by experiment.

Outline of the Method

Among the many procedures by which the three constants of equation (3) can be evaluated, the method herewith described is believed to be most advantageous because much of the arithmetic may be done with the aid of a 20″ (51-cm.) slide rule. If equation (3) is written in the form

$$(\Lambda + (\alpha\Lambda_0 + \beta)\sqrt{c} - \Lambda_0)/c = A \log c + B \quad (4)$$

it is clear that when the correct value of Λ_0 is used, a plot of the left-hand member of this equation against $\log c$ must be a straight line of slope A and intercept B. The selection of the correct value of Λ_0 can be done very readily by trial, because the value used in calculating the term $\alpha\Lambda_0$ is not a very important factor in determining the shape of the plot. A preliminary value of Λ_0 (and α) is therefore obtained from a rough extrapolation of Λ against $\sqrt{c}$, and used to calculate values of $\Lambda + (\alpha\Lambda_0 + \beta)\sqrt{c}$, which remain unaltered during the selection, by trial, of a value of Λ_0 roughly satisfying the graphical requirements of equation (4). This latter value is then used to calculate more accurate values of $\Lambda + (\alpha\Lambda_0 + \beta)\sqrt{c}$ and the process repeated until a self-consistent value of Λ_0 is found which will express the data by equation (4) up $c \simeq 0.01$ normal within the probable experimental error. The upper limit to the apparent validity of this equation is shifted to greater dilutions as the evidence of ion association is more pronounced. For zinc sulfate, or for hydrochloric acid in 70% dioxane, equation (4) begins to fail when $c \simeq 0.005$ normal. Figure 2 illustrates the final plots for potassium chloride,[14] barium chloride[15] and lanthanum chloride[4] in water at 25°. The scattering of the experimental points at extreme dilution is due to magnification of the experimental errors by division by c. The effect of a constant error of 0.01 in Λ is represented by the radii of

(5) Davies, Trans. Faraday Soc., 23, 351 (1927).

(6) Fuoss, This Journal, 57, 448 (1935).

(7) Shedlovsky, J. Franklin Inst., 225, 739 (1938).

(8) Owen and Gurry, This Journal, 60, 3074 (1938).

(9) Debye and Hückel, Physik. Z., 24, 185 (1923).

(10) Gronwall, La Mer and Sandved, ibid., 29, 358 (1928).

(11) La Mer, Gronwall and Greiff, J. Phys. Chem., 35, 2245 (1931).

(12) Onsager and Fuoss, J. Phys. Chem., 36, 2689 (1932).

(13) Fuoss, Physik. Z., 35, 59 (1934).

(14) Shedlovsky, Brown and MacInnes, Trans. Electrochem. Soc., 66, 165 (1934).

(15) Shedlovsky and Brown, This Journal, 56, 1066 (1934).

the circles on the plot. This sensitivity of the dilute ends of the plots to small changes in $\Lambda - \Lambda_0$ can be used to great advantage in the rapid selection of the final value of Λ_0.
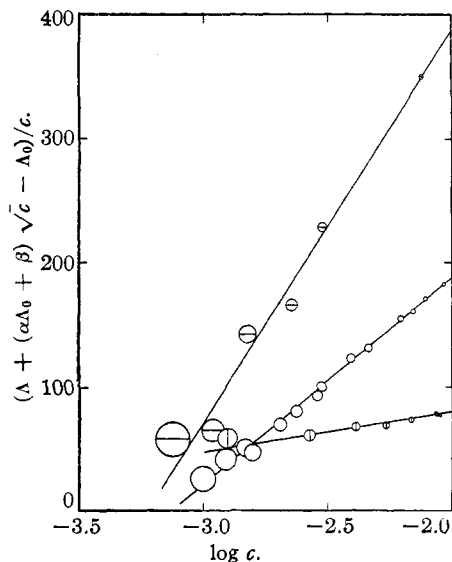

Fig. 2.—Graphical evaluation of the parameters A and B of equation (3): $\oplus$, KCl; $\bigcirc$, BaCl$_2$; $\ominus$, LaCl$_3$. The radii of the circles correspond to an experimental error of 0.01 in Λ.

Discussion of the Results

The ability of equation (3) to express the experimental data satisfactorily can be demonstrated by noting the constancy of Λ_0 calculated for various values of Λ and c. The necessary values of A and B and the (weighted) average values of Λ_0 calculated therefrom are recorded in the first three columns of Table I. The results for potas-

TABLE I[16]

Electrolyte	A	B	$\Lambda_{0(av.)}$	Λ_0	1000 K
KCl	31.8	144	149.87	149.86	...
BaCl$_2$	175	540	140.00	139.98	...
LaCl$_3$	320	1030	145.8	145.8	...
K$_4$Fe(CN)$_6$	3345	6170	185.0	184.0	5.5
ZnSO$_4$	5736	10627	132.92	132.8	4.9
HCl (70% dioxane)	4800	9800	93.1	93.1	7.7

sium ferrocyanide are based on the data of Jones and Jelen[17] and Swift.[18] The data for zinc sulfate[8] and for hydrochloric acid in 70% dioxane[19] were obtained in this Laboratory.

(16) In evaluating A and B by equation (3) c was expressed in equivalents per liter. In evaluating K the concentrations were expressed in the usual manner as moles per liter. Unsmoothed experimental data were used to avoid the influence of other extrapolation functions. All results are consistent with the primary standards of Jones and Bradshaw [THIS JOURNAL, **55**, 1780 (1933)].

(17) Jones and Jelen, ibid., **58**, 2561 (1936).

(18) Swift, ibid., **60**, 728 (1938).

(19) Owen and Waters, ibid., **60**, 2371 (1938).

The difference between individual calculated values of Λ_0 and their average value, $\Lambda_{0(av.)}$, is plotted in Fig. 3. $\Lambda_{0(av.)}$ was "weighted" slightly by minimizing the effects of several experimental points at the highest dilutions. Since the diameters of the circles in Fig. 3 represent an uncertainty of 0.06 conductance unit, it can be seen that equation (3) fits the data for potassium chloride, barium chloride, lanthanum chloride and zinc sulfate within about ± 0.03 unit. For the other two salts the deviations are as much as five to ten times as great, but are apparently without consistent trends. For the most part,
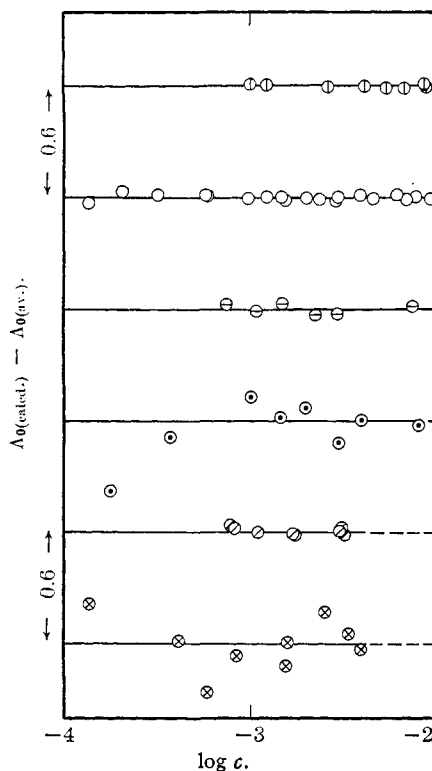

Fig. 3.—Deviation: $\oplus$, KCl; $\bigcirc$, BaCl$_2$; $\ominus$, LaCl$_3$; $\odot$, K$_4$Fe(CN)$_6$; $\oslash$, ZnSO$_4$; $\otimes$, HCl in 70% dioxane. Diameters of circles is 0.06 conductance unit, acid distance between successive plots is 0.60 unit.

these larger deviations seem to result from the fact that the data for potassium ferrocyanide were combined from two different sources, and the data for hydrochloric acid involve measurements in two independent preparations of the 70% dioxane solutions used as solvent. It therefore seems permissible to conclude that equation (3) can express satisfactorily the experimental data for all valence type electrolytes at high dilutions

so long as $K \geqslant 5 \times 10^{-3}$. It may be remarked parenthetically that this conclusion requires that the curves shown in Fig. 1 must approach the axis of ordinates with infinite slope, for as c approaches zero

$$\frac{d\Lambda_0'}{dc} = \frac{\Lambda_0' - \Lambda_0}{c} = \frac{A \log c - B}{1 - \alpha\sqrt{c}} = -\infty \quad (5)$$

The values of $\Lambda_{0(av.)}$ determined by equation (3) are in excellent agreement with those originally derived *from the same data* by other methods. The latter are recorded as Λ_0 in the next to the last column of Table I. Λ_0 for potassium chloride[14] and barium chloride[15] were determined analytically by the use of an equation which is more complicated than equation (3), but reduces to it in the limit. Λ_0 for lanthanum chloride[4] was estimated from a plot of Λ_0' against c. Recent independent measurements of Shedlovsky are reported[20] to lead to a slightly higher value, $\Lambda_0 = 145.9$. Λ_0 and K for potassium ferrocyanide are taken from the calculations of Davies[21] based on the data of Jones and Jelen[17] alone. Because of the use of the Debye–Hückel limiting law in the estimation of the activity coefficients used in Davies' calculations, the discordance of one unit in Λ_0 does not seem excessive. The values of K and Λ_0 for hydrochloric acid in 70% dioxane[19] and zinc sulfate in water[8] were determined by the methods of Fuoss[6] and Shedlovsky,[7] respectively.

Although the suitability of equation (3) as a practical extrapolation function for all valence types seems demonstrated by Fig. 3 and Table I,

(20) Longsworth and MacInnes, THIS JOURNAL, **60**, 3070 (1938).
(21) Davies, *ibid.*, **59**, 1760 (1937).

its limitations should not be overlooked. In the first place its use is confined to concentrations below 0.01 normal for the strongest electrolytes, and for electrolytes whose apparent ionization constants are as low as 5×10^{-3} it is unreliable above 0.005 normal. In the second place the relatively large values of A observed for the last three electrolytes in the table, and the fact that the effect of the $Ac \log c$ term, as here employed, is to duplicate that of the introduction of K in better known methods, lead one to suspect that the numerical values of A and B "observed" for these electrolytes are without definite physical significance. This situation would be greatly clarified by a theoretical computation of the constant A, for if this is known it would be a simple matter to use equation (3) *and* the concept of ion association, a combination that should yield precise values of both Λ_0 and K, and give the numerical value of the latter quantity more definite physical significance than it now enjoys.

Summary

The equation of Onsager and Fuoss is shown to be in formal agreement with the conductivity data for 1–1, 2–1, 3–1, 4–1, and 2–2 valence type strong electrolytes over a limited range in concentrations. It is pointed out that this equation therefore offers a practical means of extrapolating the data for higher valence type strong electrolytes for which accurate activity coefficient data are not available. A simple graphical technique is outlined in some detail.

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Infrared Bands and Association of Some Hydroxylic Compounds

BY H. W. THOMPSON[1]

The phenomenon of association and the existence of "hydrogen bonds" has been studied in many recent measurements of infrared spectra. The present paper summarizes data relating to a series of molecules which, although in physical properties such as solubility and volatility are not entirely suited to this type of investigation, nevertheless appeared worth examination. These substances were β-hydroxypropionitrile (ethylene cyanhydrin), γ-hydroxybutyronitrile, β-mercap-

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toethanol (β-hydroxyethyl mercaptan), ethanolamine (β-hydroxyethylamine), and acetone cyanhydrin, and the investigation centered primarily on a study of the position and nature of the O–H absorption in the region of the third harmonic 8000–10,000 Å. Work with other similar substances suggested that several phenomena might be noticed. Thus the presence of the O–H group might in itself lead to association such as is found in the alcohols[2]; second, some of the molecules might be

(2) Badger and Bauer, *J. Chem. Phys.*, **5**, 859 (1937); Fox and Martin, *Proc. Roy. Soc.* (London), **162**, 419 (1937).