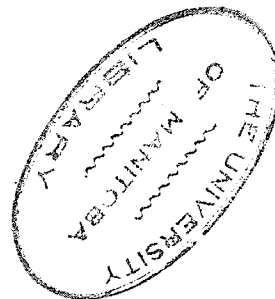


THE LIMITING CONDUCTANCES OF THE CHLORIDE, NITRATE
AND BROMIDE OF AMMONIUM AT 35°C.

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ABSTRACT

The limiting equivalent conductances of ammonium chloride, ammonium bromide and ammonium nitrate as well as the limiting equivalent ionic conductances of the ammonium and nitrate ions were determined at 35°C. with a probable error of 0.05%. The values found were $\Lambda_{\infty} \text{NH}_4\text{Cl} = 180.97$ mhos, $\Lambda_{\infty} \text{NH}_4\text{Br} = 182.73$ mhos, $\Lambda_{\infty} \text{NH}_4\text{NO}_3 = 174.21$ mhos, $\lambda_{\infty} \text{NH}_4^+ = 88.73$ mhos, and $\lambda_{\infty} \text{NO}_3^- = 85.48$ mhos. These values were obtained by the application of the Shedlovsky method of extrapolation to equivalent conductance data which were corrected for the hydrolytic effect of the ammonium ion.

Observed equivalent conductances of aqueous solutions of ammonium nitrate in the concentration range from 0.0002N. to 10N. at 35°C. have been compared with those calculated by means of the Wishaw-Stokes and Falkenhagen-Leist equations. The Wishaw-Stokes equation was found to give better experimental agreement than the Falkenhagen-Leist equation.

To My Wife

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"Although this may seem a paradox, all exact science is dominated by the idea of approximation. When a man tells you that he knows the exact truth about anything, you are safe inferring he is an inexact man."

Bertrand Russell

THEORETICAL INTRODUCTION

THEORETICAL INTRODUCTION

The nature of electrolytic solutions has been the subject of much experimental research and theoretical investigation. Applications of the Arrhenius theory of electrolytic dissociation to the colligative behaviour, electrical conductance, and ionic equilibria of weak electrolytes have shown that the theory, as proposed by Arrhenius,¹ is essentially satisfactory for these. However, in attempting to apply this theory to strong electrolytes, so many anomalies and inconsistencies have been encountered that serious questioning arose early as to the validity of some of Arrhenius' postulates with respect to the nature of strong electrolytes. For instance, the degree of dissociation, α , determined from freezing point depression, differed by as much as three to five per cent, a discrepancy considerably outside the experimental error, from those determined from conductance measurements according^{ing} to the relation

$$\frac{\Lambda_c}{\Lambda_0} = \alpha \quad (1)$$

where Λ_c is the equivalent conductance at a concentration C , and Λ_0 that at infinite dilution.

Moreover, the Ostwald Dilution Law,

$$\frac{\Lambda_c^2 C}{\Lambda_0(\Lambda_0 - \Lambda_c)} = K \quad (2)$$

where K is the dissociation constant, which is a special case of the law of mass action, fails completely when applied to strong electrolytes even though it is obeyed by weak electrolytes.

The failure of the Arrhenius theory in its application to strong electrolytes indicated the necessity for a new theoretical approach to this problem. The entirely empirical relationship of Kohlrausch,³ the well known square root law,

$$\Lambda = \Lambda_0 - A\sqrt{c} \quad (3)$$

where A is an empirical constant, describes the behaviour of very dilute solutions of strong electrolytes. Any equation deduced from theoretical considerations must therefore simplify to the Kohlrausch form in the very dilute region. The theory of Debye and Hückel⁴ resulted in an equation in which Λ varied linearly with \sqrt{c} . The assumptions of this theory are somewhat different from those of Arrhenius. Strong electrolytes are considered to be completely dissociated. Moreover, the decrease in equivalent conductance with an increase in concentration, which Arrhenius attributed to a decrease in the number of ions, is attributed to a decrease in the velocity of the ions, which results from the attractive forces between the ions themselves, and between the ions and the solvent molecules.

As a consequence of electrical attractions between ions

of opposite charge, each ion on the average is surrounded by an ionic atmosphere of opposite charge. In the absence of an external electrical field, the ionic atmosphere exhibits spherical symmetry, but when a current is passed through the solution so that ions of, say, positive sign move to the left, each positive ion must build up its atmosphere to the left, whereas the charge density to the right will die out. If the formation and destruction of the ionic atmosphere were to take place instantaneously, the moving ion would experience no net force of attraction. However, there is in effect a time of relaxation during which the atmosphere is building up to the left and decaying to the right. There will consequently be an excess of negative ions to the right of the moving positive ion which will tend to retard its motion. This influence on the velocity of the ions is known as the "relaxation effect." In addition to the relaxation effect, another factor will cause a decrease in the velocity of the ions; i.e., the tendency of the applied field to move the ions comprising the ionic atmosphere, as well as the solvent molecules attached to these ions, in a direction opposite to that of the central ion. This additional retardation is known as the "electrophoretic effect."

On the basis of these arguments, Debye and Hückel were able to derive an expression which was later improved by Onsager,⁵ who took into account the Brownian movement of the

ions. This expression related the equivalent conductance at a particular concentration to that at infinite dilution, thus:

$$\Lambda = \Lambda_0 - \left(\frac{e\kappa}{300} \cdot \frac{Z_+ + Z_-}{6\pi\eta} F + \frac{e^2\kappa}{6DkT} \Lambda_0 \omega \right) \quad (4)$$

where e is the electronic charge, κ the effective radius of the ionic atmosphere, given by:

$$\kappa = \sqrt{\frac{4\pi e^2 \sum n_i z_i^2}{DkT}} \quad (4a)$$

Z_+ and Z_- are the numerical valences of the positive and negative ions respectively, η the viscosity of the solvent, D its dielectric constant, k the Boltzmann constant, F the value of the faraday, and T the absolute temperature. The factor ω is defined by

$$\omega = \frac{29Z_+Z_-}{1 + \sqrt{q}} \quad (5)$$

where

$$q = \frac{Z_+Z_- (\lambda_+ + \lambda_-)}{(Z_+ + Z_-)(Z_+\lambda_- + Z_-\lambda_+)} \quad (6)$$

λ_+ and λ_- being the equivalent conductances of the individual ions.

Upon inserting the values of the various constants, equation (4) becomes

$$\Lambda = \Lambda_0 \left[\frac{29.15(Z_+ + Z_-)}{(DT)^{1/2} \eta} + \frac{9.90 \times 10^5}{(DT)^{3/2}} \Lambda_0 \omega \right] \sqrt{c(Z_+ + Z_-)} \quad (7)$$

which, for uni-univalent electrolytes, reduced to

$$\Lambda = \Lambda_0 - [\alpha + \beta \Lambda_0] \sqrt{c} \quad (8)$$

$$\alpha = \frac{82.4}{(DT)^{1/2} \eta} \quad (9)$$

$$\beta = \frac{8.20 \times 10^5}{(DT)^{3/2} \eta} \quad (10)$$

At constant temperature, and for a particular solvent, α and β are constant. Equation (8) therefore becomes identical in form with the square root law of Kohlrausch, i.e.:

$$\Lambda = \Lambda_0 - A\sqrt{c} \quad (11)$$

where

$$A = (\alpha + \beta \Lambda_0) \quad (12)$$

The Debye-Hückel-Onsager equation has been found valid for the dilute region, up to a concentration of approximately 0.002 N. Above this concentration, the equation becomes quite inadequate, e.g., the equivalent conductances of silver nitrate as calculated from equation (8) become negative beyond a concentration of 3N.

It is appropriate to indicate at this point the simplifications or assumptions introduced by Debye, Hückel, and Onsager, which render the theory untenable in concentrated solutions. Among them are:

1. The dielectric constant of the solution is not essentially different from that of the solvent. Hückel⁶ attributed part of the failure of the theory for concentrated solutions to the fact that the dielectric constant is a function of the concentration:

$$D = D_0 - 2 \bar{\delta} c \quad (13)$$

where $\bar{\delta} = \frac{\delta^- + \delta^+}{2}$, δ^+ and δ^- being the contributions of the anion and the cation to the depression of the dielectric constant.

Drude and Nernst⁷ showed thermodynamically that the electric field around an ion exerts a pressure on the solvent, thereby increasing its density. Since, in general, the dielectric constant of a liquid increases with an increase in density, as had been shown by Flachenberg,⁸ it follows that the dielectric constant in the immediate vicinity of an ion will be greater than that of the solution as a whole. For concentrated solutions, a correction should therefore be applied to the Debye-Hückel-Onsager equation which takes this into account.

2. The interionic potential energy is small compared

to the thermal energy of the ions. Debye and Hückel assumed that the distribution of the ions in the ionic atmosphere surrounding any given ion is governed by the Boltzmann distribution law. According to this law, since the potential energy of say the i -ion is $Z_i e \psi_j$, the average local concentration of the i -ions at some particular point is given by

$$n_i' = n_i \exp\left(-\frac{z_i e \psi_j}{kT}\right) \quad (14)$$

where Z_i and n_i are the valence and the bulk concentration of the i -ions respectively, and ψ_j is the electrical potential due to a central j -ion chosen as the origin of the coordinate system in terms of which the positions of all the i -ions may be described. The other symbols have their usual meaning. Since each i -ion carries a charge of $Z_i e$, the net charge density at the point in question, summing over all ionic species, is

$$\rho_j = \sum_i n_i z_i e \exp\left(-\frac{z_i e \psi_j}{kT}\right) \quad (15)$$

According to equation (15), the Boltzmann distribution law leads to an exponential relation between the charge density ρ and the potential ψ . However, a well established theorem of electrostatics, known as the linear superposition of fields, requires a linear relationship between ρ the charge density and ψ the potential.

To overcome this dilemma, Debye and Hückel expanded equation (14) in a power series, and neglecting all terms after the second one, on the grounds that the electrical energy $Z_i e \psi_j$ of the ions is negligible in comparison to their thermal energy as given by kT , obtained an expression for the charge density which is in harmony with the superposition principle, i.e.,

$$\rho_j = - \sum_i \frac{n_i Z_i^2 e^2 \psi_j}{kT} \quad (16)$$

In dilute solutions, one may well assume that $kT \gg Z_i e \psi_j$, since at low concentrations the ions are relatively far apart; however, in concentrated solutions, due to the increased proximity of the ions, this is no longer true.

3. It was assumed that the size of the ions could be neglected in comparison with the distance between them. This assumption may be valid in dilute solutions, but is not allowable in concentrated solutions, again because of the increased proximity of the ions.

Various empirical extensions of the Onsager equation have been proposed in order to render it applicable in higher concentration regions. Chief among them are: the Shedlovsky⁹ equation, the semi-theoretical one of Fuoss and Onsager,¹⁰ and the power series equation.

Shedlovsky observed that Λ_0 , calculated from conductance data at appreciable concentrations, using the

Onsager equation, was not constant, but rather is varied linearly with the concentration. He therefore proposed the following relation as an extension for the Onsager limiting law:

$$\Lambda_0' = \Lambda_0 + Bc \quad (17)$$

where

$$\Lambda_0' = \frac{\Lambda + \alpha\sqrt{c}}{1 - \beta\sqrt{c}} \quad (18)$$

and B is an empirical constant, usually of the same order of magnitude as $(\alpha + \beta\Lambda_0)$, determined by the method of least squares. The constants α and β have their usual Onsager limiting law values.

Shedlovsky showed that equation (17) represented reasonably well the data for a number of 1:1 electrolytes, notably the alkali halides, up to about 0.1 N, but that it failed for the alkali nitrates and iodates. For the latter salts, the curve of Λ_0' vs. C exhibits a shallow upturn in the lower concentration region. For the alkali earth chlorides, Shedlovsky and Brown¹¹ modified equation (17) and used

$$\Lambda_0 = \frac{\Lambda + \alpha\sqrt{c}}{1 - \beta\sqrt{c}} - Bc - Dc \log c + Ec^2 \quad (19)$$

where B, D, and E are empirical constants and the logarithmic term is consistent with the theoretical considerations of

Onsager and Fuoss.

Subsequently, Gordon¹² showed that when equation (19) instead of equation (17) was used to represent the conductance data for AgNO_3 and the alkali nitrates and iodates, the so-called anomalies for these salts were simply due to the fact that for them the coefficient D was relatively large.

When the DClogC term is small in comparison to the other terms, so that it may be neglected, equation (19) reduces to a simple power series in C, i.e.:

$$\Lambda = \Lambda_0 - A^1 c^{1/2} + B^1 c - C^1 c^{3/2} + D^1 c^2 - E^1 c^3 \quad (20)$$

The special advantage of a power series lies in the fact that the empirical constants, A^1 , B^1 , C^1 , D^1 and E^1 may be readily evaluated by a least square method.

Apart from empirical extensions of the Onsager limiting law, which are very useful in that they serve as a guide for extrapolations and provide one with a means of representing experimental data, no real theoretical advance was witnessed in the twenty-five years following the advent of the Debye-Hückel-Onsager treatment. In 1952, however, Falkenhagen, Leist, and Kelbg¹³ published an important theoretical extension and modification of the Debye-Hückel-Onsager theory. The extension consisted in taking into account the finite size of the ions; the modification assumes a slightly different distribution function for the ions from

the usual Boltzmann one, viz., that of Eigen and Wicke.¹⁴

This change amounts to writing for the local concentration of ions n_i' the expression

$$n_i' = n_i \left[\left(1 - \frac{n_i}{N_i}\right) \exp\left(\frac{z_i e \psi}{kT}\right) + \frac{n_i}{N_i} \right]^{-1} \quad (21)$$

where N_i (the "besetzungszahl") is the reciprocal of the effective volume of the ion, and the other symbols have their usual significance. Since, however, there was at the time an uncertainty in the formulation of a boundary condition in the Eigen-Wicke distribution function as applied to solutions of strong electrolytes, two other workers, Robinson and Stokes,¹⁵ used the more common Boltzmann distribution law in conjunction with the extension of Falkenhagen, Leist, and Kelbg, and were able to derive the following relationship between Λ and Λ_0 :

$$\Lambda = \left(\Lambda_0 - \frac{B_2 \sqrt{c}}{1 + B_2 \sqrt{c}} \right) \left(1 - \frac{B_1 \sqrt{c}}{1 + B_2 \sqrt{c}} \times F \right) \quad (22)$$

where

$$B_1 = \frac{8.20 \times 10^5}{(DT)^{3/2}} \quad (23)$$

$$B_2 = \frac{82.5}{\eta (DT)^{1/2}} \quad (24)$$

$$B_2 \sqrt{c} = \frac{50.29 a \sqrt{c}}{(DT)^{1/2}} \quad (25)$$

$$F = \frac{(0.2929 \kappa a - 1)}{0.2929 \kappa a} \quad (26)$$

Except for \hat{a} , which represents the distance of closest approach of the ions, the symbols have their usual significance.

In 1954, Falkenhagen and Leist¹⁶ announced that they were able to clarify the uncertainty in the boundary condition of the Eigen-Wicke distribution function and published the following equation:

$$\Lambda = \Lambda_0 - \frac{e^2}{3DKT} \cdot \frac{\kappa \Lambda_0}{1 + \kappa a} \cdot \frac{q}{(1 + \sqrt{q})(1 + \kappa a \sqrt{q})} - \frac{ne^2 1000 \kappa}{3\pi C q (1 + \kappa a) 10^{11}} \quad (27)$$

where the symbols have their usual meaning and $q = \frac{1}{2}$ for 1:1 electrolytes.

Both equations, i.e., equation (22) and (27), represent conductance data with a fair degree of accuracy up to a concentration of 1N.^{15,16} In order to be able to represent conductance data beyond the above-mentioned limit, both groups of investigators were forced to multiply the right-hand sides of their equations by the relative fluidity, i.e., by $\frac{\eta_0}{\eta}$.

In the modified form, both equations show truly remarkable agreement with experiment up to a concentration of about 5N,^{16,17,18} and in a few isolated cases up to 10N.¹⁶