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CONDUCTANCES, TRANSFERENCE NUMBERS, AND ACTIVITY COEFFICIENTS OF SOME RARE EARTH CHLORIDES IN AQUEOUS SOLUTION

by

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I. INTRODUCTION

Modern theories of electrolytic solutions are based upon the model and mathematical treatment first brought to completion by Debye and Hückel (1). Certain simplifying assumptions in both the model and the mathematics employed limit the fit of the data to solutions of relatively low concentrations while adequately describing the deviations of measured properties of these dilute electrolytic solutions from ideal behavior.

At higher concentrations, deviations from the theory are observed. These deviations are smaller for the activity coefficients, a thermodynamic property, than for such non-equilibrium processes as conductance and transference. In the latter properties, deviations begin to occur at greater dilutions.

Since the development of the original theory, many attempts have been made to devise a theory which will be valid over a larger concentration range. In the main, this development has depended upon an extension of the original theory of Debye and Hückel; this is quite natural since this theory fits the experimental data so well in dilute solutions that its fundamental postulates must be sound.

Attempts have been made to extend the validity of the theory of activity coefficients, by the application of more rigorous mathematics to the physical model previously set up. This approach may be limited by an inconsistency in the fundamental mathematical expressions, as has been pointed out by several investigators (2,3). Another approach used in extending the theory to higher concentrations is the correction of the original model to include such things as the variation in dielectric constant of the solvent with concentration, ion pair formation etc. This approach may be limited by the simultaneous breakdown of several assumptions of the original model. The success of these extensions has to date been largely confined to the indication of the functional dependence necessary to fit the data and allows one or more additional constants to be adjusted for the best fit of the data.

Deviations from the theory occur at lower concentrations for polyvalent electrolytes than for univalent ones. For this reason it is desirable to obtain data for higher valence ions so that the direction of breakdown of the theory can be indicated and a correlation can be made with both concentration and ionic charge.

The main deterrent to the study of high valence electrolytes has been the unavailability of suitable salts for study. In order to make interpretation of the experimental data possible, it is necessary that the electrolytes exhibit only a slight hydrolysis. For this reason, compounds of

Al III, Sn IV and most other common polyvalent cations are unsuitable for these studies.

Compounds of the rare earth elements show a slight hydrolysis which becomes more pronounced for the heavy rare earth elements, but this hydrolysis either does not affect the electrolytic properties measured, or a correction for the hydrolysis can be made, based upon measurements of the pH values of the solutions. Another thing which makes the interpretation of the data simpler is the small complexing tendency exhibited with such strong acid anions as chloride, bromide and perchlorate.

Until recently, little work was done on rare earth solutions because of the unavailability of the salts. Before the development of separation methods based upon ion-exchange chromatography (4,5,6,7), the rare earth elements were separated mainly by tedious fractionation methods requiring thousands of operations, and the resulting salts had a reasonable purity for only a few of the commoner rare earth elements. With the development of separation methods based upon ion-exchange chromatography, however, even the less abundant rare earths became available in multi-gram amounts, which possessed a high degree of purity.

The rare earth elements provide an ideal testing ground for the theories of chemistry and physics not only because of the trivalent state but also because they exhibit a gradual decrease in radius throughout the series. This "Lanthanide

Contraction" is due to increasing nuclear charge which exerts an increasing pull upon the electrons resulting in a smaller radius. By studying the changes in properties which occur through the series, these properties may be correlated with the change in radius, with most of the other properties remaining constant. It is true that this progression may be modified by other factors such as a change in hydration number, but the general trend will be determined by the decreasing radius.

In addition to the change in radius of the ions which occurs in the rare earth series, several other properties may give an insight into the short range forces which operate between atoms and ions. The incomplete 4-f shell present in the rare earths gives rise to sharp lines in the absorption spectra, and a paramagnetism of the ions. Both of these phenomena are influenced by the surrounding fields, but since the 4-f electrons are surrounded by completed 5s and 5p shells as well as the valence electrons, this influence is of a secondary nature. By a study of the change of these properties or such others as Raman spectra with surrounding crystalline fields, one may be able to determine the nature of the short range forces which operate in the solid state and in solution.

The purpose of this thesis is to extend the knowledge of 3-1 electrolytes by an extension of measurements on rare earth chlorides, and to determine the effect of the hydrolysis exhibited by these elements on the electrochemical properties of the aqueous solutions. From a study of the data obtained, the concentration range in which the theories are correct can be determined, and an indication of the factors which cause the breakdown of the theories can be made. The transference numbers, conductances and activity coefficients were chosen for this study because these properties have well defined theoretical limiting laws and it would be very desirable to be able to extend these laws to a higher concentration range. A proposed extension of the mathematics of Onsager's theory of conductance is made in this thesis, which purports to explain the transference number behavior of unsymmetrical electrolytes. The results also agree with conductance measurements to higher concentrations than is true with the simpler mathematical treatment.

II. GENERAL THEORY

A. Introduction

The general theory of ionic solutions is fundamentally the same for all of the properties measured in this thesis, and as a result the basic assumptions and theoretical developments essential to an understanding of the experimental data will be discussed before division of the thesis into a discussion of the separate properties.

Strong electrolytes in aqueous solutions exist as charged ions. It is the treatment of such ions as charged spheres in a medium of uniform and known dielectric constant which has resulted in the striking successes of the modern theory of ionic solutions. It is assumed that only coulombic forces operate between ions. With this assumption and the application of the fundamental concepts of statistical mechanics, hydrodynamics and electrostatics, a quantitative theory has been developed which allows the prediction of observed macroscopic properties of the solution when the assumptions used in the model and mathematics are valid.

B. Thermodynamic Background

The first and second laws of thermodynamics can be expressed by the following perfectly general differential equation:

$$dE = T\,dS - P\,dV + \sum_{i=1}^{k} \left(\frac{\partial E}{\partial n_i}\right)_{S,V,n_j,x_i} dn_i + \sum_{i=1}^{k} \left(\frac{\partial E}{\partial x_i}\right)_{S,V,n_i,x_j} dx_i \,, \qquad (1)$$

in which

E	is the energy of the system as defined by the first law of thermodynamics.
S	is the entropy of the system as defined by the second law of thermodynamics.
T,P,V	are the absolute temperature, pressure, and volume of the system.
n_i	is the number of moles of a given component, i, present in the system, which has a total of k components.
x_i	refers to any other variable upon which the energy of the system may depend, such as magnetic, or electrical field strength.

The quantities represented by the term, $(\partial E/\partial n_i)_{S,V,n_j,x_i}$ are called the chemical potentials of the system and are given the symbol μ_i.

It is desirable to express the laws of thermodynamics in terms of several other functions which are especially suited for the handling of certain problems. These functions are defined as follows:

$$\begin{aligned} &\text{Enthalpy} = H = E + PV \\ &\text{Work Function} = A = E - TS \\ &\text{Free energy} = F = H - TS \end{aligned} \qquad (2)$$

The chemical potential, μ_i, is a very important quantity for the chemist. It is a measure of the "escaping tendency" of the component i. At constant temperature and pressure, the chemical potential of any component in a system is the same in all the phases of the system at equilibrium.

G. N. Lewis (8) introduced the concepts of fugacity and activity which are more convenient quantities to use than the chemical potentials. The fugacity, ξ_i, is defined by,

$$d\mu_i = RT\ d\ \ln \xi_i ; \qquad \frac{\xi_i}{p_i} \longrightarrow 1 \text{ as } P \longrightarrow 0 \ , \qquad (3)$$

where p_i is the partial pressure (or vapor pressure) of the ith component and P is the total pressure. The activity, a_i, is a more convenient quantity for use in solutions, and is defined by

$$a_i = \frac{\xi_i}{\xi_i^o} \quad , \qquad (4)$$

in which ξ_i is the fugacity of component i in the solution and ξ_i^o is its fugacity in an arbitrary standard state. It is to be emphasized that the fugacity of a substance is a definite quantity at a given temperature, pressure, and composition, while the value of the activity depends upon the standard state chosen. An alternative definition of activity is

$$\mu_i = \mu_i^o + RT \ln a_i \quad , \tag{5}$$

where $\underline{\mu_i^o}$ is the chemical potential of component $\underline{i}$ in the standard state.

It must be pointed out that in solutions of an electrolyte, electrical neutrality imposes the condition that the individual ionic constituents cannot be varied independently. When we speak of the electrolyte in solution we must consider the salt as a component of the solution even though the constituents may consist of the solvent and the separate ions. Thermodynamics does not permit the evaluation of free energies, activities, etc. of the separate ions in a solution even though it is the properties of these ions which affect the measured value. Because the properties of the ions affect the thermodynamic quantities however, it is advantageous to express a number of thermodynamic developments in terms of ionic activities, with the understanding that only a certain type of mean activity can be determined experimentally.

In order to obtain expressions for the "hypothetical" individual ionic activities, it is convenient to consider the following dissociation scheme:

$$M_{\nu_+}A_{\nu_-} \rightleftharpoons \nu_+ M^{Z_+} + \nu_- A^{Z_-} \quad . \tag{6}$$

The activity of the salt may be written

$$a = (a_+^{\nu_+})\cdot(a_-^{\nu_-}) = a_{\pm}^{\nu} ; \qquad \nu = \nu_+ + \nu_- \quad , \tag{7}$$

where a_+ and a_- are the conventional individual ionic activities, and $a_{\pm}$ is called the mean ionic activity.

The activity of a substance is dependent upon the standard state chosen. It has been found experimentally that the activity of a solute approaches proportionality to the mole fraction when the solutions become very dilute. Utilizing this fact, the standard state is chosen so that the activity becomes equal to the mole fraction in very dilute solutions, and an "ideal solution" is defined as a solution for which the mole fraction is equal to the activity for all concentrations. The deviation from ideality is measured by the activity coefficient, f_i, defined by

$$f_i = \frac{a_{N_i}}{N_i} \quad . \tag{8}$$

The mean mole fraction and mean activity coefficients are defined by

$$f_{\pm} = \frac{a_{N_{\pm}}}{N_{\pm}} ; \qquad N_{\pm} = (N_+^{\nu_+}\, N_-^{\nu_-})^{1/\nu} \quad . \tag{9}$$

$f_{\pm}$ is usually called the rational activity coefficient.

In many cases it is preferable to employ activities related to molalities or molarities, and define the corresponding activity coefficients by,

$$\gamma_{\pm} = \frac{a_{m_{\pm}}}{m_{\pm}} \; ; \qquad m_{\pm} = (m_{+}^{\nu_{+}} m_{-}^{\nu_{-}})^{1/\nu} = m(\nu_{+}^{\nu_{+}} \nu_{-}^{\nu_{-}})^{1/\nu} \, ,$$

$$y_{\pm} = \frac{a_{C_{\pm}}}{C_{\pm}} \; ; \qquad C_{\pm} = (C_{+}^{\nu_{+}} C_{-}^{\nu_{-}})^{1/\nu} = C(\nu_{+}^{\nu_{+}} \nu_{-}^{\nu_{-}})^{1/\nu} \, . \tag{10}$$

The activities are written as $a_{N_{\pm}}$, $a_{m_{\pm}}$, and $a_{C_{\pm}}$, to emphasize the fact that these are all different, because they employ different standard states. The standard states are chosen so that

$$f_{\pm} \longrightarrow 1 \quad \text{as} \quad N_{\pm} \longrightarrow 0 \, ,$$

$$\gamma_{\pm} \longrightarrow 1 \quad \text{as} \quad m_{\pm} \longrightarrow 0 \, , \tag{11}$$

$$y_{\pm} \longrightarrow 1 \quad \text{as} \quad C_{\pm} \longrightarrow 0 \, .$$

At all times these values must be consistent with the idea of a single chemical potential, regardless of the standard state chosen, so that

$$\bar{\mu} = \overline{\mu_N^o} + \nu RT \ln(f_{\pm} N_{\pm}) = \overline{\mu_m^o} + \nu RT \ln(\gamma_{\pm} m_{\pm}) =$$

$$= \overline{\mu_C^o} + \nu RT \ln(y_{\pm} C_{\pm}) \; . \tag{12}$$

Utilizing the standard state definition, that at high dilutions

$$f_{\pm} = \gamma_{\pm} = y_{\pm} = 1 \quad ,$$

one can find the value of $\overline{\mu^o}$ as defined for the various concentration variables by introducing the limiting values of $C_{\pm}/m_{\pm}$, and $N_{\pm}/m_{\pm}$. One then obtains the relations

$$\overline{\mu_N^o} = \overline{\mu_m^o} + \nu RT \ln\left(\frac{1000}{M_1}\right) = \overline{\mu_C^o} + \nu RT \ln\left(\frac{1000\ d_o}{M_1}\right) \quad . \tag{13}$$

Combining equations (12) and (13), one arrives at the relationship between the activity coefficients,

$$\begin{aligned} \ln(f_{\pm}) &= \ln(\gamma_{\pm}) + \ln(1 + \nu m M_1/1000) \\ \ln(f_{\pm}) &= \ln(y_{\pm}) + \ln\left[\frac{d}{d_o} + C\,\frac{\nu M_1 - M_2}{1000\ d_o}\right] \\ \ln(\gamma_{\pm}) &= \ln(y_{\pm}) + \ln\left[\frac{d}{d_o} - C\,\frac{M_2}{1000\ d_o}\right] \quad , \end{aligned} \tag{14}$$

in which M_1 and M_2 are the molecular weights of the solvent and solute, respectively, and d, d_o are the densities of the solution and solvent.

C. History of Ionic Interaction Theories

The modern theory of electrolytic solution behavior is based upon the assumption that the solutions contain charged particles, called ions, in exact electrical balance. This idea was first put forward by Arrhenius (9) in 1887 in a classical work on electrolytic dissociation. Arrhenius assumed that the changes with concentration of such properties as equivalent conductance were due to incomplete dissociation. Indeed, he proposed that the degree of dissociation $\underline{\alpha}$ was given by the ratio

$$\alpha = \frac{\Lambda}{\Lambda_0} \quad . \tag{15}$$

The assumption was also made that the mobility of an ion was independent of concentration.

After the turn of the century, certain aspects of the Arrhenius theory began to fall into disfavor. A fund of data tended to substantiate the concept of complete dissociation, and the variation of the transference number with concentration refuted the idea of constant mobilities for the ions, and led to the modern concept that there is little association in solutions of strong electrolytes. The great success of the Debye-Hückel theory of strong electrolytes substantiates this premise.

The effect of coulomb forces upon the ions in solution was first recognized by J. J. van Laar (10), who pointed out that coulomb forces between the ions must produce an effect on the conductance, osmotic pressure, and other properties. Sutherland (11) in 1907 made an attempt to calculate the magnitude of this effect, and although his calculations were only approximate, they showed that the coulomb forces between ions could produce the observed decrease in conductance with concentration. Milner (12) in 1912 developed a mathematical theory based on statistical methods and graphical solutions which was correct, but too cumbersome for practical use. He was able to show, however, that at low concentrations, the deviations from ideal behavior should be proportional to the square root of the concentration.

Debye and Hückel (1) developed a method for the integration of Milner's equations which resulted in a great simplification of the method and led to very successful interpretations of such diverse data as conductances, activity coefficients, transference numbers, and various partial molar quantities. Since the original work of Debye and Hückel, many extensions of the theory have been proposed, but the modern theory is still essentially the same as developed by these first investigators.

D. Present Status of the Ionic Interaction Theory

In the development of their theory, Debye and Hückel made several assumptions about the nature of the electrolytic solution:

(1) Strong electrolytes in solution exist as ions in complete electrical balance and with no undissociated salt present;

(2) If the ions were not charged, the solutions would show ideal behavior;

(3) An electrolytic solution may be thought of as a dilute solution of point charges, or charged spheres with definite radii, in a medium of uniform dielectric constant with the same dielectric constant as the bulk solvent.

These assumptions permit the application of the Poisson equation of electrostatics, which is

$$\nabla^2\psi = -\frac{4\pi\rho}{D} \quad , \tag{16}$$

in which

ψ is the electrostatic potential at the point;

ρ is the charge density at the point;

D is the dielectric constant of the solvent.

The charge density, ρ, is a function of position and depends upon the distribution of ions in the solution. On the average, a positive ion will be surrounded by more negative ions than positive ions as a result of coulomb forces. This will result in the formation of a negatively charged "atmosphere" around a positive ion, and a positively charged "atmosphere" around a negative ion. In a given volume element near an ion, other ions of both the same and the opposite charge will wander in and out, and on a time average there will be a characteristic concentration of each ion in the element, which will depend upon both the charge on the ion coming into the element of volume and that on the central ion as well as the distance of the volume element from the central ion. Using this concept, we can express the average concentration of ions in the volume element by n_{ji}, which is the average concentration of i ions in the presence of the j ion, the latter being the central ion under consideration. Then the charge density at any distance r from the central ion will be given by

$$\rho = \sum_{i=1}^{s} n_{ji} e_i \quad , \tag{17}$$

in which e_i is the charge on the *ith* ion, and s is the total number of kinds of ions in the solution. The Poisson equation then becomes

$$\nabla^2 \psi_j^o = - \frac{4\pi}{D} \sum_{i=1}^{s} n_{ji} e_i \quad , \tag{18}$$

in which ψ_j^o is the potential near the j ion. The superscript refers to the unperturbed electrolyte.

From a consideration of the thermal motion of the ions it is assumed that the concentration of an ion in the neighborhood of another ion is determined by the Maxwell-Boltzmann distribution law in the form

$$n_{ji} = n_i \, e^{-U_{ji}/kT} \quad , \tag{19}$$

where U_{ji} is the potential energy of the i ion in the vicinity of the j ion and k is the Boltzman constant. The potential energy is given by the product of the electrostatic potential at the point and the charge on the ion,

$$U_{ji} \cong \psi_j^o e_i \quad . \tag{20}$$

This is an assumption of the theory which limits the applicability of the final result, and makes fruitless any attempt to evaluate exactly the resulting differential equation. The reason for this is that we assume that the presence of the _i_ ion does not affect the distribution of the atmosphere of the _j_ ion. This is not serious at low concentrations, but is more serious for ions of high charge than for low charge types.

We now have the equation

$$\nabla^2 \psi_j^o = -\frac{4\pi}{D} \sum_{i=1}^{s} \left[n_i e_i \, e^{-(e_i \psi_j^o/kT)} \right] \quad , \tag{21}$$

and if we assume that $\underline{e_i \psi_j^o}$ is small compared to _kT_ we may expand the exponential and drop terms higher than first order in $\underline{\psi_j^o}$.

$$\nabla^2 \psi_j^o = -\frac{4\pi}{D} \sum_{i=1}^{s} \left[n_i e_i (1 - \psi_j^o e_i/kT) \right] \quad , \tag{22}$$

and electrical neutrality requires that

$$\sum_{i=1}^{s} n_i e_i = 0 \quad ,$$

so that

$$\nabla^2 \psi_j^o = + \frac{4\pi}{DkT} \sum_{i=1}^{s} \left[n_i e_i^2 \psi_j^o \right] = \kappa^2 \psi_j^o \quad , \tag{23}$$

where

$$\underline{\kappa^2} = \frac{4\pi\epsilon^2}{DkT} \sum_{i=1}^{s} n_i Z_i^2 \quad ; \tag{24}$$

$\underline{\epsilon}$ is the electronic charge;

$\underline{Z_i}$ is the number of charges on the $\underline{i}$ ion.

Now if we assume spherical symmetry for the potential and convert this equation to spherical coordinates, it becomes

$$\frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial \psi_j^o}{\partial r} \right) = \kappa^2 \psi_j^o \quad , \tag{25}$$

which has the general solution

$$\psi_j^o (r) = \frac{Ae^{-\kappa r}}{r} + \frac{A' e^{\kappa r}}{r} \quad , \tag{26}$$

and since

$\psi_j(r) \longrightarrow 0$ as $r \rightarrow \infty$, this makes $A' = 0$, so that

$$\psi_j^o(r) = \frac{Ae^{-\kappa r}}{r} \quad . \tag{27}$$

Continuity of the electric field demands that at $\underline{r = a}$, the distance of closest approach, the field of the ion plus its atmosphere, $\underline{\partial \psi_j^o / \partial r}$, must be equal to the field of the ion alone, $\underline{-Z_j\epsilon/Dr^2}$. This condition may be written

$$\left(\frac{\partial \psi_j^o}{\partial r}\right)_{r=a} = -\frac{Ae^{-\kappa a}}{a^2}(1+\kappa a) = -\frac{Z_j\epsilon}{Da^2} ,$$

so that

$$A = \frac{Z_j \epsilon e^{\kappa a}}{D(1+\kappa a)} .$$

Equation (27) then becomes

$$\psi_j^o(r) = \left[\frac{Z_j \epsilon e^{\kappa a}}{D(1+\kappa a)}\right] \frac{e^{-\kappa r}}{r} . \qquad (28)$$

By considering the difference in the energy necessary to charge the isolated ion, and the energy required to charge the ion in a potential field given by $\underline{\psi_j^o(r)}$, Debye and Hückel obtained, for the electrical contribution to the free energy of an ion,

$$\Delta\overline{\mu_j}\,(\mathrm{el}) = -\frac{(Z_j\epsilon)^2\kappa}{2D(1+\kappa a)} , \qquad (29)$$

which gives for the activity coefficient,

$$\ln f_j = -\frac{(Z_j\epsilon)^2\kappa}{2DkT(1+\kappa a)} . \qquad (30)$$

Combination of the individual ionic activity coefficients given by (30), gives, for an electrolyte dissociating into

s types of ions,

$$\log f_{\pm} = - \frac{S_f\sqrt{\Gamma}}{1 + A\sqrt{\Gamma}} \; ; \quad \Gamma = \sum_{i=1} c_i z_i^2 \; , \tag{31}$$

in which Γ is called the ional strength, and s_f is given by

$$S_f = \frac{2.303}{\nu} \left[\sum_{i=1}^{s} \nu_j z_j^2 \right] \epsilon^3 \left(\frac{N\pi}{1000(DkT)^3} \right)^{1/2} \; , \tag{32}$$

where the dissociation of one molecule of electrolyte produces a total number of ions, ν, of which ν_j are of the jth kind. Also

$$A = \frac{\overset{o}{a} \cdot 10^8}{\sqrt{\Gamma}} = \frac{35.57\,\overset{o}{a}}{(DT)^{1/2}} \; ,$$

in which $\overset{o}{a}$ is the distance of closest approach expressed in Angstrom units.

The development of this equation, (31), gave a theoretical basis for the concept of ionic strength, which had been derived empirically by G. N. Lewis (94). This equation has been tested a number of times, and represents the data very well up to concentrations of about 0.1 normal. Generally, the value of $\overset{o}{a}$ is determined by using the data to fit the theory, with $\overset{o}{a}$ being an adjustable constant. For the rare earth chlorides, $\overset{o}{a}$ is about equal to the sum of the ionic radii of the two ions plus the diameter of one water molecule, and it is reasonable to assume that the negative ion cannot easily displace a water molecule of hydration from around the rare earth ion.

At concentrations above which this theory is no longer valid, it is quite possible that complexing may be beginning with anions such as chloride which will add complications to any attempt to extend the range of validity of the theory. Many of the assumptions of the theory hold only for dilute solutions, and as a result it is quite possible that several of these assumptions may become invalid at nearly the same concentration, which will also make it difficult to find the path of extension. It has been pointed out (2,3) that it is illogical to attempt evaluation of higher terms of the Poisson-Boltzmann equation because of a failure of the statistics. Probably the most profitable approach to attempt to follow in looking for extensions of the theory is the study of short range forces in solutions by the study of optical phenomena.

It is well known that electrolytic solutions will conduct current under the influence of an electrical field and that within reasonable limits, the system obeys Ohm's Law. The measurement of the resistance of such solutions has long been used as a tool for the study of solutions. The specific resistance, $\rho = RA/d$, can be determined, where R is the measured resistance, A is the area of each electrode, and d is the distance between the electrodes. From this, one determines the specific conductance of the solution, $L = 1/\rho$.

The equivalent conductance Λ is defined by $\Lambda = 1000\ L/c$ where c is the concentration in equivalents per liter. The equivalent conductance is made up of contributions from each ion so that

$$\Lambda = \sum_{j=1}^{s} \lambda_j \quad . \tag{33}$$

The quantity λ_j is related to the mobility of the ion, u_j, by the relationship

$$\lambda_j = 96{,}500\ u_j \quad . \tag{34}$$

The mobility of an ion, u_j, is its velocity under a potential gradient of one volt per centimeter.

An isolated ion will have a definite mobility u_j^o in the absence of all other ions, which is characteristic of the ion at constant temperature, pressure, and solvent, and is dependent upon the ionic size and its tendency to carry solvent molecules through the solution. The theoretical treatments of conductance have so far allowed this mobility at infinite dilution to be an empirical constant. To obtain this mobility, the constant, λ_j^o, the ionic equivalent conductance at infinite dilution, is determined from experimental data.

It is observed experimentally that the mobility of an ion is a function of concentration, and it is the work of Onsager (13) which has accounted for the quantitative treatment of this phenomenon on a theoretical basis. Onsager observed that the "ionic atmosphere" could affect the motion of the central ion in two ways.

(1) The atmosphere must form ahead of the ion, and die away behind during its motion through the solution. This requires a finite time and results in an asymmetrical atmosphere, or dipole with the central ion, which is opposed to the external applied field, and results in a partial cancellation of the field, and hence, a slowing down of the ion. This is called the "time of relaxation" effect. The mathematical treatment of this effect is given by Onsager (13).

(2) The atmosphere has a charge opposite in sign to that of the central ion and so tends to move in the opposite direction under the influence of the field. This motion imparts energy to the solvent molecules through which the central ion is moving and the net velocity of the central ion is less than would be expected if the solvent molecules were stationary. This is called the electrophoretic effect.

Since this thesis proposes an extension of the mathematics of the electrophoretic effect, it will be desirable to discuss this in more detail. The treatment used by Onsager (13) follows.

In an electric field, the force acting on a charge e_i is $X e_i$, where X is the potential gradient. If n_i is the average concentration of i ions in the solution, the average external force per unit volume is

$$X \sum_{i=1}^{s} n_i e_i \quad ,$$

and these forces are transferred to the solvent molecules under a force k_o per molecule such that the total force is zero. That is,

$$X \sum_{i=1}^{s} n_i e_i + n_o k_o = 0 \quad . \tag{35}$$

Now if we consider instead of an average quantity, an element of volume $d\tau$ near the i ion, the average concentration of i ions is n_{ji}, and the net force on the element of volume $d\tau$ is given by

$$X \sum_{i=1}^{s} \left[n_{ji} e_i + n_o k_o \right] d\tau = \left[X \sum_{i=1}^{s} n_{ji} e_i - X \sum_{i=1}^{s} n_i e_i \right] d\tau \quad .$$

In spherical coordinates, the force acting on a spherical shell at a distance r from the central ion will be

$$dF = 4\pi r^2 X \left[\sum_{i=1}^{s} e_i (n_{ji} - n_i) \right] dr \quad . \tag{36}$$

This force is in the direction of the applied field and is distributed evenly over the surface so that Stokes Law is applicable. This is

$$dV = \frac{dF}{6\pi \eta r} \quad , \tag{37}$$

where η is the viscosity of the solvent, and dV is the change in velocity of the ionic atmosphere from the inside of the spherical shell to the outside due to the movement of the atmosphere. Using this expression, the velocity of the atmosphere may be determined as a function of r, and the total decrease in the velocity of the ion, ΔV_j, is obtained by integrating from the distance of closest approach, a, to infinity. This result is

$$\Delta V_j = \int_a^\infty \frac{dF}{6\pi \eta r} = \frac{2X}{3\eta} \int_a^\infty \left[r \sum_{i=1}^{s} e_i (n_{ji} - n_i) \right] dr \ . \qquad (38)$$

The value of n_{ji} as a function of r, was shown earlier (equations 19 and 20) to be

$$n_{ji} = n_i \exp\left(- \frac{e_i \psi_j^o}{kT}\right) \cong n_i \left[1 - \left(\frac{e_i \psi_j^o}{kT}\right) + 1/2 \left(\frac{e_i \psi_j^o}{kT}\right)^2 \right] , \qquad (39)$$

and

$$\psi_j^o = \frac{e_j}{D} \left[\frac{e^{\kappa a}}{(1+\kappa a)} \frac{e^{-\kappa r}}{r} \right] , \qquad (28)$$

giving for the velocity in differential form:

$$dV_j = \frac{2X}{3\eta} \sum_{i=1}^{s} \left\{ -n_i e_i^2 \left[\frac{e_j}{DkT} \frac{e^{\kappa a}}{(1+\kappa a)} \right] e^{-\kappa r} + \right.$$

$$\left. + 1/2\, n_i e_i^3 \left[\frac{e_j}{DkT} \frac{e^{\kappa a}}{(1+\kappa a)} \right]^2 \frac{e^{-2\kappa r}}{r} \right\} dr \ . \qquad (40)$$

Integrating, one obtains

$$\Delta V_j = -\frac{e_j 2X\left(\sum_{i=1}^{s} n_i e_i^2\right) e^{\kappa a}}{3\eta\, DkT\,(1+\kappa a)}\int_a^{\infty} e^{-\kappa r}\,dr \; +$$

$$+\left[\frac{Xe_j^2\left(\sum_{i=1}^{s} n_i e_i^3\right) e^{2\kappa a}}{3\eta\left[DkT\,(1+\kappa a)\right]^2}\right]\int_a^{\infty}\frac{e^{-2\kappa r}}{r}\,dr\;, \qquad (41)$$

which gives, for the electrophoretic velocity,

$$\Delta V_j = \frac{-2X\left(\sum_{i=1}^{s} n_i e_i^2\right) e_j}{3\eta\, DkT\,\kappa\,(1+\kappa a)} \; +$$

$$+\frac{X\left(\sum_{i=1}^{s} n_i e_i^3\right)}{3\eta}\left[\frac{e_j e^{\kappa a}}{DkT(1+\kappa a)}\right]^2 E_1(2\kappa a)\;, \qquad (42)$$

where

$$E_1(x) = -0.5772 - \ln(X) + X - \frac{X^2}{2.2!} + \ldots\ldots = \int_x^{\infty}\frac{e^{-t}}{t}\,dt\,. \qquad (43)$$

Considering only the first term in $\underline{\Delta V_j}$ and neglecting $\underline{\kappa a}$ compared to one, gives

$$\Delta V_j = -\frac{2Xe_j\sum_{i=1}^{s} n_i e_i^2}{3\eta\, DkT\;\kappa}\;,$$

but by equation (24),

$$\kappa^2 = \frac{4\pi}{DkT} \sum_{i=1}^{s} n_i e_i^2 \quad ;$$

making this substitution, multiplying numerator and denominator by κ gives

$$\Delta V_j = - \frac{2Xe_j \left(\sum_{i=1}^{s} n_i e_i^2 \right) \cdot \kappa}{3\eta DkT} \cdot \frac{DkT}{4\pi \sum_{i=1}^{s} n_i e_i^2} \quad ,$$

$$\Delta V_j = - \frac{Xe_j \kappa}{6\pi \eta} \quad , \qquad (44)$$

which is Onsager's original result. The correction on the mobility due to electrophoresis is obtained as follows:

$$\Delta u_j = - \frac{|\Delta v_j|}{X} \quad ,$$

with the negative sign used because this effect is always a drag on the ion. In practical units

$$\Delta u_j = - \frac{|\Delta v_j|}{300 \ X} = - \frac{|e_j| \kappa}{1800\pi\eta} \quad ;$$

also $\lambda_j = 96,500 \ u_j$, so finally

$$\Delta \lambda_j = \frac{-96,500 \kappa |e_j|}{1800 \ \pi \ \eta} \quad , \qquad (45)$$

which is the electrophoretic correction on the ionic equivalent conductance. Combining this correction with the correction due to the "time of relaxation" effect gives

$$\lambda_j = \lambda_j^o + \frac{\Delta X_j}{X}\lambda_j^o - \frac{96,500|e_j|\kappa}{1800\,\pi\eta} \quad , \tag{46}$$

where, for the case of an electrolyte dissociating into only two kinds of ions

$$\frac{\Delta X_j}{X} = \frac{e_1 e_2 \kappa}{3DkT}\left[\frac{q^*}{1+\sqrt{q^*}}\right] , \tag{47}$$

with

$$q^* = \frac{|z_1 z_2|}{(|z_1| + |z_2|)} \; \frac{\lambda_1^o + \lambda_2^o}{\left(|z_2|\lambda_1^o + |z_1|\lambda_2^o\right)} \quad . \tag{48}$$

Rewriting equation (46) for two kinds of ions;

$$\lambda_j = \lambda_j^o - S_{(\lambda)}\Gamma^{1/2} \quad , \tag{49}$$

in which, after evaluating some constants;

$$S_{(\lambda)} = \frac{1.970\text{x}10^6}{(DT)^{3/2}}\left[\frac{q^*}{1+\sqrt{q^*}}\right]|z_1 z_2|\lambda_j^o + \frac{28.98|z_j|}{\eta(DT)^{1/2}} \; . \tag{50}$$

Combining the equations for each ion gives

$$\Lambda = \lambda_1 + \lambda_2 = \Lambda_o - S_{(\Lambda)}\Gamma^{1/2} \quad , \tag{51}$$

where

$S_{(\Lambda)} =$

$$= \frac{1.970\text{x}10^6}{(DT)^{3/2}} \left[\frac{q^*}{1 + \sqrt{q^*}} \right] |Z_1 Z_2| \Lambda_o + \frac{28.98(|Z_1| + |Z_2|)}{\eta\,(DT)^{1/2}} \;. \qquad (52)$$

The transference number of an ion is defined by

$$T_j = \frac{i_j}{\sum_{i=1}^{s} i_i} \;, \qquad (53)$$

where $\underline{i_j}$ is the current carried by the <u>jth</u> ion, and $\underline{\sum_{i=1}^{s} i_i}$ is the total current carried by all the ions in the solution. Equation (53) may be written

$$T_j = \frac{u_j}{\sum_{i=1}^{s} u_i} = \frac{\lambda_j}{\sum_{i=1}^{s} \lambda_i} = \frac{\lambda_j}{\Lambda} \;. \qquad (54)$$

Transference numbers are seen to be simply related to the individual ionic conductances and as a result, the Onsager Theory developed for the conductance of an ion should also yield the correct transference number. From equation (49) one may develop, for the limiting case of low concentrations,

$$T_j = T_j^o + S_{(T)} \Gamma^{1/2} \;, \qquad (55)$$

where

$$T_j^{\circ} = \frac{\lambda_j^{\circ}}{\Lambda^{\circ}} \quad ;$$

$$S_{(T)} = \frac{28.98 \left[T_j^{\circ} \left(|Z_j| + |Z_i| \right) - |Z_j| \right]}{\eta \, (DT)^{1/2} \Lambda_{o}} \quad . \qquad (56)$$

At higher concentrations, the Onsager Theory predicts non-linearity with $\underline{\Gamma^{1/2}}$, and the transference number is most easily calculated by a calculation of the individual ionic conductances using equation (49).

The theory of conductance as outlined above agrees with the experimental measurements up to concentrations of about 0.001 normal for most salts, substantiating its theoretical correctness. In the case of transference numbers, agreement is obtained only for 1-1 electrolytes, with marked deviations for 2-1 and 3-1 electrolytes. This thesis proposes a different mathematical treatment than that used by Onsager which purports to eliminate this discrepancy in transference numbers and also results in theoretical conductance values which agree with experiment up to about 0.008 Normal. This development will be carried out in another section.

III. CONDUCTANCES

A. Introduction

The theory of the conductance of an ionic solution was discussed earlier in this thesis and the required definitions were made.

The equivalent conductance is one of the most easily measured properties of an ionic solution which is of theoretical importance, and for this reason, there are probably more data in the literature concerned with the conductance of ionic solutions than any other single property. The methods of measurement are accurate enough to permit a good test of the theory, and much of the experimental work which has been done on the properties of electrolytes in non-aqueous, and mixed-solvent media has been concerned with the measurement and interpretation of the equivalent conductance.

B. History of the Method

The history of conductance measurements has been adequately reviewed in the literature (14,15,16) and only the more important developments will be covered in this thesis.

The first measurements of the resistance of electrolytic solutions employed D.C. methods such as were used to measure the resistance of solids (17,18,19). These methods allowed the formation of concentration gradients in the neighborhood of the electrodes resulting in polarization and non-reproducibility, and as a result these early experiments gave erratic values of the conductance.

Kohlrausch (20) viewed the reaction at the electrodes to be the adsorption of oxygen and hydrogen, which would redissolve in the solution if the polarity were reversed. This idea led him to the use of alternating current sources, and an A.C. Wheatstone bridge for measuring the resistance, with a telephone receiver to detect the null point. To further allow for the reversible adsorption of hydrogen and oxygen at the electrodes, he plated the platinum electrodes with platinum black. Since the specific conductance of a solution is the conductance of a cubic centimeter of solution, the dimensions of the cell were measured to determine the cell constant, d/A. Kohlrausch also realized the importance of the close temperature control which is necessary in conductance. His work was so carefully done that his data, especially on potassium chloride, are still accepted today.

The improvements in conductance measurements which have been made since the time of Kohlrausch have been limited to better design of equipment rather than basic changes in the methods. In 1913, Washburn and Bell (21) introduced the use of a high frequency generator as the source of current, and employed telephone receivers tuned to the frequency of the generator. Taylor and Acree (22) studied the relative merits of induction coils, high frequency generators, and oscillators as sources of the alternating current, and concluded that the Vreeland type oscillator gave better results than either of the other methods. Hall and Adams (23) designed an amplifier which increased the sensitivity of the measurements and introduced the use of the vacuum tube oscillator circuit as a current source. Manufacturers of conductance bridges and cells follow the recommendations of Jones and his co-workers (24,25,26,27) and Shedlovsky (28,29) in design of these instruments. A description of the conductance equipment available from Leeds and Northrup Co. has been given by Dike (30). It is possible to measure the dimensions of the conductance cell to obtain the cell constant $\underline{K = d/A}$, but it is more convenient to employ secondary standards, such as KCl to determine this value. The specific conductance of KCl has been measured by Kohlrausch (20) from the cell dimensions, and by Jones, Bradshaw, and Prendergast (31,32), who used mercury, which is the primary standard of resistance, to calibrate a cell, and obtained the specific conductance of various potassium chloride solutions for use as secondary standards.

In 1923, Parker (33,34) observed that the cell constant varies with the resistance being measured. Shedlovsky (28) and Jones and Bollinger (35) showed that this effect was due to the capacitance of the cell, and designed cells which minimized this effect.

C. Experimental

1. Preparation of materials

The rare earths employed in this research were all obtained as oxides from the rare earth separation group of the Ames Laboratory of the Atomic Energy Commission where they had been separated and purified under the direction of Dr. F. H. Spedding (4,5,6,7,36,37,38,39,40). The purities of the various oxides used are given in Table 1. The oxides were purified further by at least two precipitations from an acid solution with doubly-recrystallized oxalic acid. Before precipitation, chlorine was passed through the solution to remove bromide, and the solution was then boiled. All ignitions of the oxalate were carried out in platinum ware.

The rare earth chloride solutions were prepared in either of two ways:

(1) The oxide was dissolved in an insufficient quantity of redistilled hydrochloric acid, the excess oxide being filtered off. This gave solutions with pH values around 6.0 which contained some colloidal oxide or basic salt, as shown by the Tyndall Cone the solution exhibited when examined with a beam of light, and also by the subsequent titration.

(2) The oxide was completely dissolved in a slight

Table 1.

Purities of the Rare Earth Oxides

Oxide	Purity[a]
Nd_2O_3	Less than 0.2% Sm_2O_3 detected. Slight trace of calcium detected prior to two precipitations from acid oxalate solution.
Dy_2O_3	About 0.02% Y_2O_3, 0.1% Ho_2O_3, 0.05% Er_2O_3, 0.005% Yb_2O_3 detected. Trace of calcium detected prior to two precipitations from acid oxalate solution.
Ho_2O_3	About 0.3% Dy_2O_3, 0.02% Er_2O_3, less than 0.01% Y_2O_3 detected. Trace of calcium detected prior to two precipitations from acid oxalate solution.
Er_2O_3	About 0.1% Ho_2O_3, 0.05% Y_2O_3, 0.02% Tm_2O_3, less than 0.01% Yb_2O_3 detected. Trace of calcium detected prior to two precipitations from acid oxalate solution.
Tm_2O_3	About 0.025% Yb_2O_3, less than 0.025% Y_2O_3 and Er_2O_3 detected. Trace of calcium detected prior to two precipitations from acid oxalate solution.
Yb_2O_3	About 0.02% Tm_2O_3 detected. No other rare earths detected. Trace of calcium detected prior to two precipitations from acid oxalate solution.

[a] All analyses were made by emission spectrography. The limit of detection of the rare earths was about 0.01 to 0.03 per cent. That for the common elements was about 0.01 per cent.

excess of redistilled hydrochloric acid and evaporated to wet crystals which were then redissolved. This process was repeated, and resulted in a solution whose pH value was slightly on the basic side of equivalence and which contained very little colloidal material.

The solution was then diluted to a pre-determined value, and a sample was withdrawn and titrated with dilute hydrochloric acid to determine the equivalence pH value. The bulk of solution was then brought to this pH value with hydrochloric acid. This stock solution was analyzed for both chloride and rare earth, using gravimetric methods. The chloride was weighed as silver chloride, and the rare earth as the oxide following precipitation as the oxalate. The chloride and rare earth analyses agreed in all cases to at least 0.1 per cent. A series of solutions was then made by diluting aliquots of the stock solution in either calibrated or "Normax" brand volumetric flasks. About 15 such solutions were prepared, ranging in concentration from .0003 normal to 0.10 normal.

The potassium chloride solutions for determination of the cell constants of the conductance cells, were made up by weight from twice-recrystallized reagent grade KCl which was fused in a nitrogen atmosphere by the method of Pinching and Bates (41).

2. Apparatus

The apparatus used for measuring the conductances reported in this thesis included a Jones Conductivity bridge, an audio frequency oscillator and tuned amplifier, a cathode-ray oscillograph, three conductivity cells and a constant temperature oil bath. With the exception of the oscillograph and constant temperature bath, all of this equipment was obtained from the Leeds and Northrup Company.

The conductivity bridge (Leeds and Northrup Catalog number 4666) and oscillator and amplifier (catalog numbers 9842 and 9847) were manufactured in accordance with the recommendations of Jones and his co-workers (24,25,26,27) and the bridge is described by Dike (30). A Dumont type 274 A cathode-ray oscillograph was used to detect the null point, and was much easier to use than the conventional earphones.

The conductivity cells (Leeds and Northrup Catalog numbers 4911, 4914, and 4915) were platinized before use by the procedure recommended by Jones and Bollinger (27). A small Parker effect was observed for the two low cells, and so these were calibrated at a number of concentrations with potassium chloride.

The constant temperature bath (A. H. Thomas Company catalog number 9926-D), which was filled with mineral oil to minimize capacitive effects, maintained the temperature at 25° C. $\pm$ 0.02° C. The temperature was determined by a thermometer calibrated in 0.01° C. divisions, which had been certified by the National Bureau of Standards.

3. Procedure

The conductivity cell chosen for use depended upon the concentration of the solution to be measured, and was so chosen that the measured resistance was between 800 and 40,000 ohms. Measurement of the resistance was made on the Jones bridge, and the null point was determined with the oscillograph when the resistance of the solution and capacitance of the circuit had been balanced by the bridge. Two samples were measured at each concentration, and agreed with each other to well within 0.1 per cent in all cases. Each cell constant was determined with at least three concentrations of potassium chloride. A correction for the conductance of the solvent was applied by subtracting the specific conductance of the water from the specific conductance of the solution. A further correction for the conduction of current by the hydrogen ion was calculated from the pH measurements of the solution. This correction will be discussed in more detail later.

4. Results

The data obtained by these measurements were the resistances of the solutions $\underline{R}$. The following calculations were used to determine the equivalent conductances of the solutions:

$$L = (k/R) - L_{H_2O} - L_{H^+} , \tag{57}$$

and

$$\Lambda = \frac{1000\ L}{c} , \tag{58}$$

in which

<u>L</u> is the specific conductance of the solution due only to the solute;

<u>k</u> is the cell constant;

<u>R</u> is the measured resistance in ohms;

$\underline{L_{H_2O}}$ is the specific conductance of the water used in the preparation of the solutions;

$\underline{L_{H^+}}$ is the specific conductance of the hydrogen ion in the solution minus the specific conductance of the hydrogen ion in the water used to prepare the solutions; and

<u>c</u> is the concentration of the solute in equivalents per liter.

The specific conductance of the hydrogen ion in the solution and solvent is calculated from its approximate concentration as measured with a pH meter and its equivalent conductance in the solution as calculated approximately by the Onsager equation.

The equivalent conductance before and after correction for hydrogen ion, and the pH value of the solution for each concentration measured are shown in Tables 2 through 7. The data are included for neodymium, dysprosium, holmium, erbium, thulium and ytterbium chlorides and all data are the average of at least two duplicate determinations. Graphs of these data are shown in Figures 1 and 2. It was necessary to stagger the ordinates of these graphs to separate the various curves.

Values of Λ_0, the equivalent conductance at infinite dilution were obtained by extrapolation using the Onsager limiting law as expressed by equation (51) which for aqueous solutions of 3-1 electrolytes at 25° C. has the form

$$\Lambda = \Lambda_0 - (3.316\ Y \Lambda_0 + 170.3)\ C^{1/2}, \qquad (59)$$

in which C = Normality

$$Y = \frac{0.7500 \Lambda_0 / (\Lambda_0 + 2\lambda^{\circ}_{-})}{1 + 0.7500 \Lambda_0 / (\Lambda_0 + 2\lambda^{\circ}_{-})} \ . \qquad (60)$$

The values of all basic numerical constants used in these calculations, and throughout this thesis, are those recommended by Birge (42,43, p. 586) and Wyman and Ingalls (44). The limiting ionic conductance, λ°_{-} of the chloride ion was taken to be 76.34 mhos/cm/equiv. This value was the average obtained by a combination of conductance and transference number data for the conductance of the chloride ion at

Table 2.

Equivalent Conductances of Neodymium Chloride at 25° C.

Normality	pH[a]	Λ Uncorrected for H^+	Λ Corrected for H^+
0.0003507	5.70	140.6	140.4
0.0005009	5.70	139.6	139.4
0.0007510	5.69	138.2	138.1
0.001002	5.67	137.1	137.0
0.002003	5.61	134.1	134.0
0.003507	5.52	130.4	130.3
0.005009	5.50	128.1	128.0
0.007516	5.47	124.3	124.3
0.01002	5.45	122.1	122.0
0.02003	5.42	115.6	115.6
0.03506	5.38	109.9	109.9
0.05006	5.32	106.4	106.4
0.07516	5.26	102.1	102.1
0.1002	5.14	99.3	99.3

[a] The water used in making the dilutions had a pH value of 5.8.

Table 3.

Equivalent Conductances of Dysprosium Chloride at 25° C.

Normality	pH[a]	Λ Uncorrected for H^+	Λ Corrected for H^+
0.0001722	5.57	140.5	138.3
0.0002929	5.52	139.0	137.4
0.0005166	5.50	136.6	135.6
0.0006888	5.48	136.0	135.2
0.001035	5.46	133.9	133.3
0.001722	5.43	131.8	131.4
0.002929	5.40	128.7	128.5
0.005166	5.37	124.7	124.5
0.006888	5.33	122.6	122.5
0.01034	5.31	119.1	118.9
0.01722	5.27	114.6	114.4
0.02929	5.22	109.3	109.3
0.05166	5.17	103.8	103.7
0.06888	5.14	100.9	100.8
0.1033	5.03	96.8	96.8

[a] The water used in making the dilutions had a pH value of 5.8.

Table 4.

Equivalent Conductances of Holmium Chloride at 25° C.

Normality	pH[a]	Λ Uncorrected for H^+	Λ Corrected for H^+
0.0003411	5.99	138.7	138.0
0.0005120	5.97	137.0	136.5
0.0006826	5.95	136.0	135.6
0.001024	5.78	134.0	133.5
0.001707	5.69	131.8	131.4
0.003411	5.59	128.0	127.8
0.005120	5.67	124.8	124.7
0.006826	5.52	122.6	122.5
0.01024	5.47	119.2	119.1
0.01707	5.37	114.8	114.7
0.05117	5.21	104.0	104.0
0.06826	5.15	101.0	101.0
0.1023	5.02	97.0	97.0

---

[a] The water used in making the dilutions had a pH value of 6.5.

Table 5.

Equivalent Conductances of Erbium Chloride at 25° C.

Normality	pH[a]	Λ Uncorrected for H^+	Λ Corrected for H^+
0.0002720	5.75	139.0	137.6
0.0004082	5.72	137.8	136.8
0.0005442	5.71	136.7	135.9
0.0006804	5.66	136.2	135.4
0.001088	5.55	133.9	133.2
0.002720	5.46	129.3	128.9
0.004082	5.46	126.5	126.3
0.005442	5.43	124.5	124.3
0.006801	5.38	122.7	122.5
0.01088	5.21	118.7	118.5
0.02721	5.18	110.2	110.1
0.04079	5.12	106.1	106.1
0.05442	5.08	103.2	103.1
0.06799	5.01	101.0	100.9
0.1088	5.00	96.1	96.1

[a] The water used in making the dilutions had a pH value of 6.2.

Table 6.

Equivalent Conductances of Thulium Chloride at 25° C.

Normality	pH[a]	Λ Uncorrected for H^+	Λ Corrected for H^+
0.0002602	5.71	138.9	137.6
0.0004226	5.68	137.1	136.2
0.0006509	5.65	135.4	134.7
0.0009759	5.61	133.7	133.2
0.001626	5.58	131.6	131.2
0.002602	5.51	129.2	128.9
0.004226	5.48	126.2	126.0
0.006509	5.38	122.8	122.6
0.009759	5.38	119.3	119.2
0.01626	5.33	114.7	114.7
0.02602	5.29	110.2	110.2
0.04228	5.22	105.5	105.4
0.06515	5.18	101.1	101.1
0.09757	5.09	97.0	96.9

[a] The water used in making the dilutions had a pH value of 6.0.

Table 7.

Equivalent Conductances of Ytterbium Chloride at 25° C.

Normality	pH[a]	Λ Uncorrected for H^+	Λ Corrected for H^+
0.0001815	5.72	139.8	138.0
0.0002948	5.70	138.7	137.5
0.0004538	5.69	137.0	136.2
0.0007487	5.67	135.1	134.5
0.001021	5.64	134.3	133.8
0.001815	5.56	130.7	130.3
0.002948	5.50	128.7	128.5
0.004538	5.45	125.8	125.6
0.007487	5.38	121.7	121.6
0.01021	5.30	119.3	119.2
0.01816	5.22	113.3	113.2
0.02948	5.15	109.3	109.2
0.04541	5.10	104.9	104.9
0.07487	4.98	99.9	99.8
0.1022	4.90	96.8	96.8

[a] The water used in making the dilutions had a pH value of 6.0.

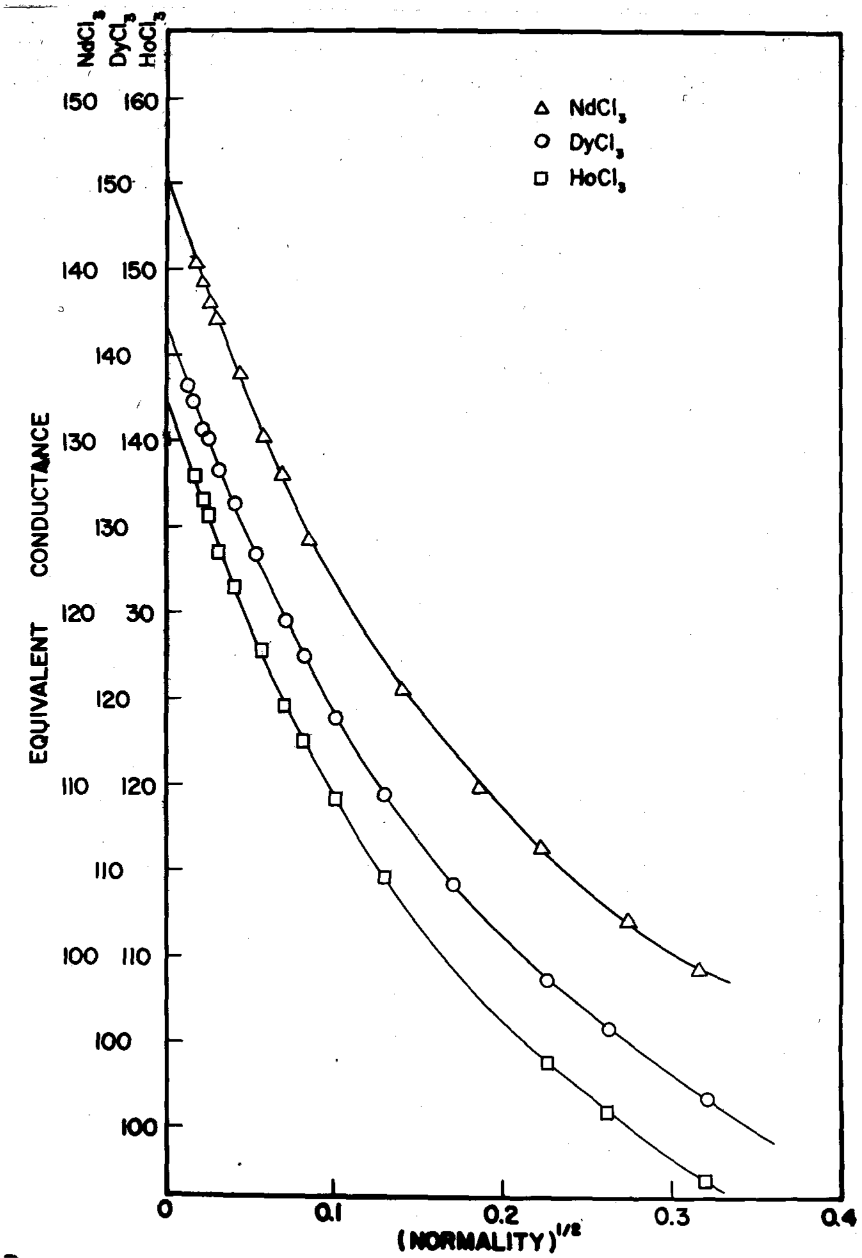


Figure 1. Equivalent Conductances of Neodymium, Dysprosium, and Holmium Chlorides at 25° C.

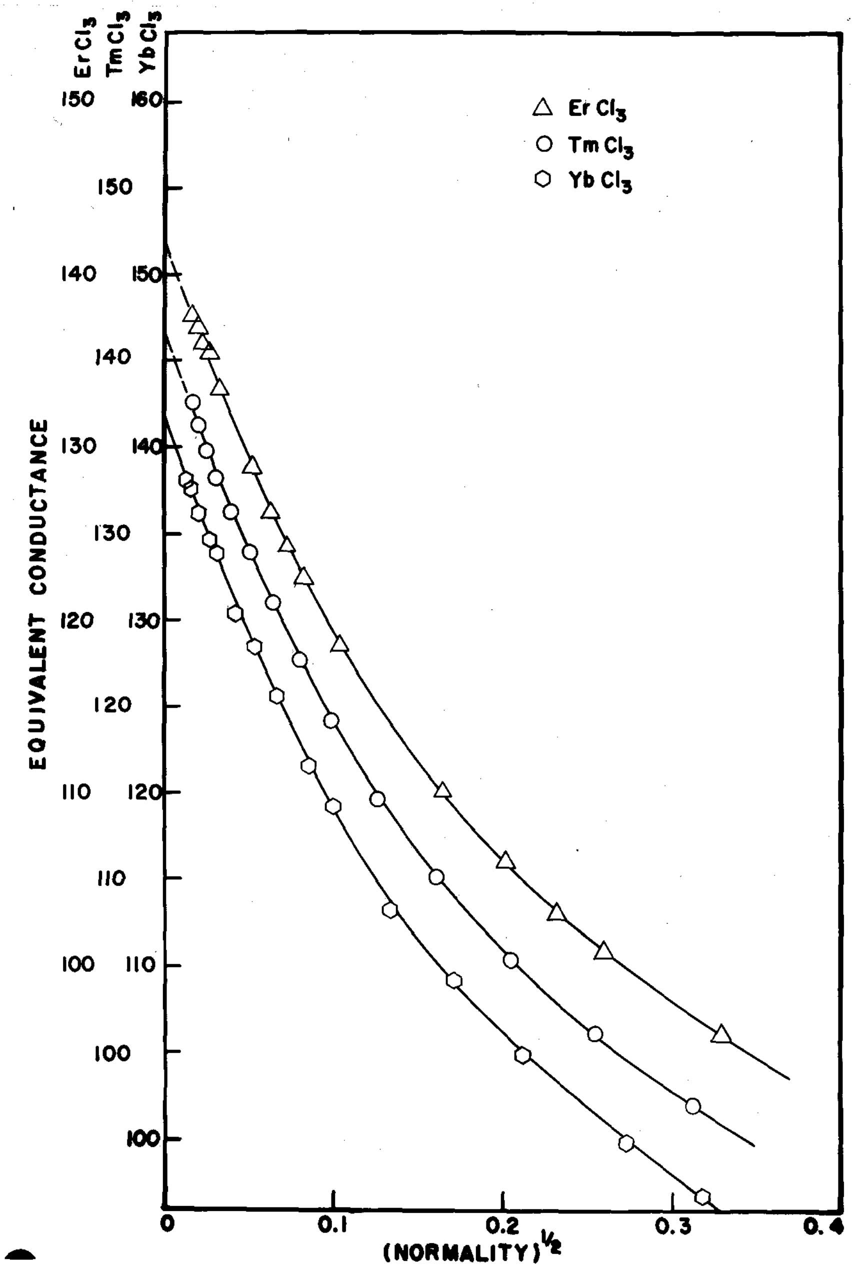


Figure 2, Equivalent Conductances of Erbium, Thulium, and Ytterbium Chlorides at 25° C.

infinite dilution in hydrochloric acid (29,45), sodium chloride (46,47), potassium chloride (46,47), and lithium chloride (29,48).

Using equation (59), the calculated value of Λ_0 designated by Λ_0' was obtained for each experimentally determined Λ value, using successive approximations. As the solution becomes more and more dilute, Onsager's equation should become more applicable and the value of Λ_0' should then approach the true value of Λ_0 and remain constant for the concentration range in which Onsager's equation is valid. A curve of these values will then have zero slope at the axis of zero concentration and will intercept the ordinate at the true value of Λ_0. These extrapolation curves are shown in Figure 3. The ordinates are staggered in order to separate the various curves. The resulting values of Λ_0 are listed in Table 8, along with the cation conductances at infinite dilution, obtained by the following equation:

$$\Lambda_0 = \lambda_+^0 + \lambda_-^0 \quad . \tag{61}$$

D. Discussion of Results

The errors involved in measuring the resistances of the solutions were negligible compared to uncertainties in the concentrations, of about ± 0.1 per cent. In addition to

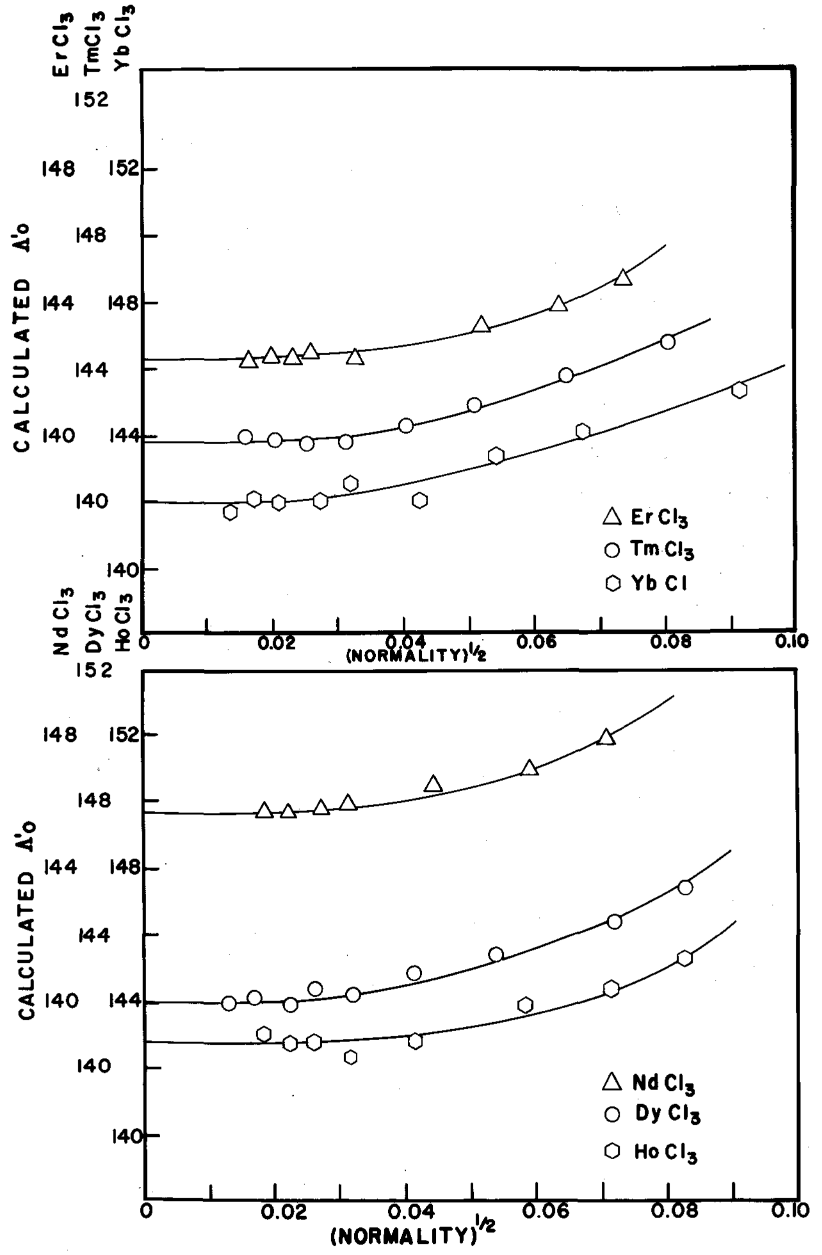


Figure 3. Extrapolation of Equivalent Conductance Data to Infinite Dilution.
Bottom Set - Neodymium, Dysprosium, and Holmium Chlorides.
Top Set - Erbium, Thulium, and Ytterbium Chlorides.

Table 8.

Conductances at Infinite Dilution of Some Rare Earth Chlorides and of Their Cations

Salt	Λ_o	λ_o^+
$NdCl_3$	145.7	69.4
$DyCl_3$	142.0	65.7
$HoCl_3$	142.6	66.3
$ErCl_3$	142.3	66.0
$TmCl_3$	141.8	65.5
$YbCl_3$	142.0	65.7

this source of error, the correction for the conduction of current by the hydrogen ion could have been slightly in error, because of errors in the pH measurements, and may have introduced an additional error in the equivalent conductances of the dilute solutions, of about 0.1 per cent.

Earlier studies in this laboratory (49,50,51) were made with rare earth chloride solutions which were prepared by dissolving the anhydrous chloride of the rare earth in conductance water in a closed system, following the procedure of Jones and Bickford (52). The resulting solutions were clear, and showed no visible evidence of hydrolysis, with pH values slightly greater than six for 0.1 normal solutions. More recent investigations have shown however, that the rare earth chlorides do exhibit a small amount of hydrolysis and have pH values ranging from 5.0 to 6.0 for 0.1 normal solutions. Because of this hydrolysis, the solutions which had been made up by dissolving the anhydrous chloride in water, were examined carefully, and a slight Tyndall cone was found upon examination of the solutions with a light beam. This effect is characteristic of colloidal systems, and indicated that a small amount of colloid was present in the solutions used previously. The effect of this slight lack of equivalence in the solutions was studied by repeating the experimental measurements on the chlorides of neodymium, erbium, and ytterbium. The new solutions were carefully brought to the equivalence pH, to eliminate the possibility of colloid formation.

The conductance values obtained with neodymium chloride, erbium chloride, and ytterbium chloride, show that the previous measurements made with these salts (49,50,51) were slightly in error because of the small amount of colloidal oxide or basic salt which was present in the solutions used in the earlier measurements. On the average, the values obtained for the equivalent conductances were slightly higher for solutions at the equivalence pH than those which contained the colloidal material. The average differences in conductance were 0.10 per cent for neodymium chloride, 0.32 per cent for erbium chloride, and 0.56 per cent for ytterbium chloride. These percentages should be a fair indication of the amount of colloidal material which was present in the earlier solutions, since the colloid is presumably non-conducting.

To obtain correct extrapolation curves of $\underline{\Lambda_0'}$ to infinite dilution, it was necessary to correct for the conduction of current by the hydrogen ion. The concentration of hydrogen ions in the solution was determined approximately with a pH meter. When this correction was used with solutions of the chlorides, satisfactory extrapolation curves were obtained, and the value of $\underline{\lambda_+^0}$ obtained, agreed well with previous work.

When such a correction was attempted for rare earth perchlorate solutions however, the measured pH values gave negligible corrections to the conductance within the error of determining the pH. This difference between chloride and perchlorate solutions is not fully understood, but there are several possible explanations. First, it is possible that the hydrolysis reaction is not merely a reaction between the rare earth ion and water, but involves the anion as a necessary part of the stoichiometry. This does not seem very likely however. Secondly, there could be a difference in the rate of solution of the colloidal oxide depending upon the acid used. If hydrochloric acid dissolves the colloid rapidly, so that there is none present in the solution at equivalence, then the solution would be expected to behave normally and exhibit hydrolysis, which would demand correction of the conductance of the solution because of the hydrogen ion. If, however, perchloric acid attacks the colloidal oxide more slowly than hydrochloric acid, so that there is still a small amount of colloidal material left in the solution at equivalence, the excess hydrogen ions would be depleted by the slow dissolution of the colloid, and no correction would be necessary. These phenomena have not been fully explained as yet, and it may require some careful measurements of the pH values of colloid-free solutions to completely answer these questions.

The values obtained for the equivalent conductances of the rare earth ions at infinite dilution agree quite well with those which have been obtained previously using other rare earth salts. For those salts which have been studied, the values obtained with the chlorides, bromides, nitrates and perchlorates are in good agreement. A plot of $\underline{\Lambda_0}$ against atomic number for the rare earth chlorides is shown in Figure (10) in the transference number section. The low value obtained in the case of dysprosium chloride is unexplained, especially in view of its high transference number. It was thought at first that this discrepancy was due to an incorrect analysis of the solutions, but seven separate analyses all agreed with each other to within ± 0.1 per cent.

This same type of anomaly has been found previously to a lesser degree for samarium chloride (50).

The conductances measured in this thesis obey the Onsager Theory of conductance at concentrations below about 0.0008 normal. It will be shown in a later section that the basic assumptions of the Onsager Theory are valid at concentrations below about 0.008 normal and only a failure in the mathematics of the simple theory causes disagreement below this concentration.

IV. TRANSFERENCE NUMBERS

A. Introduction

The theoretical calculation of the transference numbers of an ionic solution was discussed earlier in this thesis, and the fundamental definitions were given.

Values of the transference numbers and conductances of solutions allow the calculation of individual ionic mobilities and permit the study of Onsager's limiting law for the conductances of the individual ions. Transference number data on the rare earth salts thus makes possible the evaluation of the individual ionic conductances which may prove useful in determining the effect of ionic size, hydration number and other properties of the rare earth ions without the necessity of making arbitrary assumptions about the contribution of the negative ion. Transference numbers offer a more severe test of the Onsager Theory than do equivalent conductances, because a small difference in the contributions to the conductivity of the individual ions is masked in the total equivalent conductance of the salt, but greatly influences the transference number, which is the ratio of the individual ionic conductance to the total conductance.

Measurements of the transference numbers of a salt can be made in three ways:

(1) The Hittorf method, which depends upon concentration changes in the solutions;

(2) The electromotive force method; and

(3) The moving boundary method.

The first method involves a tedious analytical procedure and is now of historical interest only. The second method requires the use of electrodes reversible to both the cation and the anion which greatly limits its applicability. This method cannot be applied to solutions of rare earth salts unless an electrode is devised which is reversible to the rare earth ion. In those cases where this method is applicable it has the advantage that it can be used to measure the transference numbers of dilute solutions. The accuracy is not as great as with the moving boundary method, however. The moving boundary method, while limited in its concentration range, is accurate, and amenable to the study of the transference numbers of aqueous solutions of the rare earth salts. It is the method used in this investigation.

B. History of the Methods

The first indication that the positive and negative ions in a solution do not carry equal amounts of current was given by Daniell (53,54) in 1839, who carried out an electrolysis in a three compartment cell and observed concentration changes in the various compartments.

After the work of Daniell, Hittorf began his quantitative study of transference numbers which covered a span of 50 years(55,56,57). His data are not sufficiently accurate to be useful today, but laid the groundwork for the law of independent ion migration advancedby Kohlrausch in 1876, and the dissociation theory proposed by Arrhenius in 1884.

Progress was made rapidly in the theory and practice of transference number methods when the solutions were finally regarded as solutions of dissociated ions. The three methods mentioned above were then rapidly improved.

The Hittorf apparatus consists of a three compartment electrolysis cell in series with a coulometer. Before passage of current, the concentration of the electrolyte is the same in all three compartments, the anode, cathode, and middle compartments. Because of the migration of the cations toward the cathode and the anions toward the anode, there is observed a different number of equivalents of each ion present in the anode and cathode compartments after electrolysis. By analysis of the solution in the three compartments the transference number of the *jth* ion can be calculated as follows (58):

$$T_j = \frac{N_o - N_f + N_e}{N_e} , \qquad (62)$$

in which $\underline{N_o}$ is the initial number of equivalents of the *jth* ion per gram of solvent, $\underline{N_f}$ is the final number of equivalents of that ion per gram of solvent and $\underline{N_e}$ is the number of equivalents of that ion added to the solvent by the electrode reaction, and is equal to the number of Faradays of current passed through the cell. $\underline{N_e}$ is positive if the ion is added to the solvent by dissolution of the electrode and negative if the ion plates out on the electrode. The concentration in the middle compartment must remain unchanged during the experiment.

The early measurements using the Hittorf method have been summarized by Noyes and Falk (59). These early methods contained enough sources of error to make the results uncertain. More recent work by Jones and Dole (60), MacInnes and Dole (61) and Jones and Bradshaw (62) employed better methods and gave quite good results. The time necessary for such measurements and the comparative ease of the moving boundary method for measuring transference numbers has caused the Hittorf method to fall into disuse in recent years.

The transference number of an ion constituent of a solution may be determined by considering the potentials of E.M.F. cells with and without transference, provided electrodes can be found which are reversible to both the cation and anion. A cell without liquid junctions of the type

$$\text{Ag; AgCl, NaCl}(C_1)\text{; Na(Hg); NaCl}(C_2)\text{, AgCl; Ag} \qquad (63)$$

involves the reversible transport of one equivalent of sodium chloride from the concentration C_1 to C_2 per faraday of current passed through the cell. The operation of a cell of the form

$$\text{Ag; AgCl, NaCl}(C_1)\text{: NaCl}(C_2)\text{, AgCl; Ag} \qquad (64)$$

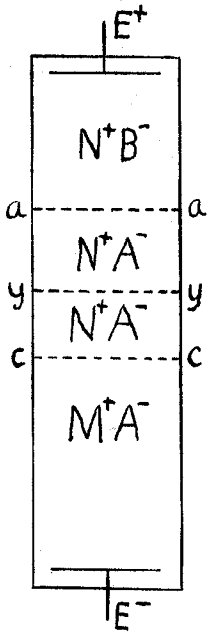
is accompanied by the transfer of T_+ equivalents through the same concentration range. Therefore the transference number is given by

$$T_+ = \frac{E_t}{E} \quad , \qquad (65)$$

in which $\underline{E}$ and $\underline{E_t}$ are the potentials of cells represented by (63) and (64) respectively. This is only true if the transference number is independent of concentration in the range $\underline{C_1}$ to $\underline{C_2}$, and a more detailed analysis requires empirical fitting of the E.M.F. data, or graphical methods. The accuracy is not as great as with the Hittorf and moving boundary methods. The use of cells with and without transference has been studied by MacInnes and Parker (63), MacInnes and Beatie (64), Hammer (65), and Jones and Dole (66).

Before discussing the historical development of the moving boundary method, it is deemed advisable to briefly outline the basis for the method and review the quantities which need to be measured in order to allow calculation of the transference numbers of the constituent ions.

The method consists in forming a boundary between two solutions which may or may not have one ion in common. The initial position of this boundary is represented by (y-y) in the accompanying diagram. A potential difference is applied across the solution by electrodes E^+ and E^- and the motion of the boundary is observed. All of the anions will move toward the positive electrode causing the anions A^- of the compound M^+A^- to cross y-y and form the boundary a-a between the solutions N^+B^-, and N^+A^-. This is called the anion boundary. In exactly the same manner, all the cations will move toward the negative electrode to form the boundary c-c between the solutions N^+A^-, and M^+A^-. For a solution containing c equivalents of a binary salt per liter, the volume swept out per Faraday of current is $1000/c$ milliliters. Of this volume, $T_+ (1000/c)$ milliliters will be due to the motion of the cations, and $T_- (1000/c)$ milliliters will be due to the motion of the anions. If F Faradays of current are passed through the solution, a different volume V_+ will be swept out by the cation boundary and also V_- by the anion boundary. The following relationship will hold:



$$\frac{\mathcal{F}}{T_+ (1000/c)} = \frac{F}{V_+} \quad \text{and} \quad \frac{\mathcal{F}}{T_- (1000/c)} = \frac{F}{V_-} , \qquad (66)$$

where $\mathcal{F}$ is the Faraday. Solving these equations for T_+ and T_- gives:

$$T_+ = \frac{\mathcal{F} V_+ c}{1000 F} \text{ and } T_- = \frac{\mathcal{F} V_- c}{1000 F} \quad . \tag{67}$$

For a constant current of I amperes for t seconds:

$$F = I t , \tag{68}$$

and equation (67) becomes:

$$T_+ = \frac{\mathcal{F} V_+ c}{1000 \ I \ t} \text{ and } T_- = \frac{\mathcal{F} V_- c}{1000 \ I \ t} \quad . \tag{69}$$

There are many excellent reviews available which treat the history and theory of the moving boundary method (43,49,50, 67,68,69) and so only the more important developments will be reviewed here.

The first observations of the motion of individual ions were made in 1886 by Lodge (70) who observed the motion of individual ions in a gelatin gel. He incorporated in the gel an indicator ion which formed either a precipitate or a colored complex with the ion being studied. He measured the velocity of the boundary, but made the erroneous assumption that the potential gradient was constant throughout the gel. This error was pointed out by W.C.D. Whetham (71,72) in 1893, who stated that the gradient depended upon the conductivity of the ionic species and was not the same on the two sides of the boundary. Whetham also objected to the use of a gel to contain the ions and began observations on boundaries between colored and uncolored ions in a gelatin free solution.

The next significant advances in the method of measuring transference numbers by the observation of boundaries were made by Steele (73,74) in 1901, and Denison and Steele (75) in 1906. Steele formed the boundaries at first with the use of gelatin gel plugs. The boundaries were then allowed to move into a gelatin free tube where they were observed. From the work of Lenz (76) and Bein (77) on Schlieren Patterns, Steele conceived the idea of measuring boundaries between two uncolored solutions, making use of differences in the refractive indices to observe the boundaries. A light was placed behind the boundary, and the boundary was observed much as it is today, using a telescope. Denison and Steele eliminated the gelatin plugs which had been used to form the boundaries by the use of a parchment cone to separate the solutions until the boundary was formed. Methods for improving the boundary by other boundary-forming devices were developed by MacInnes and Smith (78), MacInnes and Brighton (79), and Spedding, Porter, and Wright (51). MacInnes and Brighton employed a "shearing disk" apparatus, while Spedding, Porter, and Wright simplified the technique by forming the boundary with a hollow-bore stopcock.

In 1904, Franklin and Cady (80) used a method of forming the boundary which has come to be known as the "autogenic boundary method". This consisted of a metal electrode such as a pool of mercury, or a plug of copper or cadmium in contact with the solution acting as an anode. The electrode reaction

$$M \rightleftharpoons M^{++} + 2e^{-}$$

supplied the indicator cations, which formed the boundary with the cations being studied, and the concentration was automatically adjusted to the Kohlrausch Ratio by the action of the electric field. This method has been used successfully by other investigators also (81,82).

Kohlrausch (83) made the first theoretical treatment of the effect of an electric field on a boundary by considering the equations of continuity. He made some predictions concerning the concentrations of the leading and indicator solutions and the regulation of these concentrations. For the passage of one faraday of current, equation (69) gives

$$T_{+} = cV ,$$

where $\underline{V}$ is the volume in liters swept out by the cations of the leading solution. It is obvious that the cations of the indicator solution must sweep out the same volume in order to keep up to the boundary so that

$$T_{+f} = c_{f}V ,$$

in which $\underline{T_{+f}}$ is the cation transference number of the indicator solution of concentration $\underline{c_f}$ equivalents per liter. Combining these equations gives

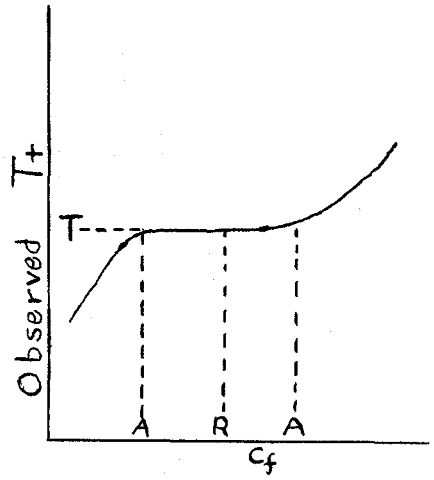
$$T_+/c = T_{+f}/c_f \ . \tag{70}$$

This relationship is known as the "Kohlrausch ratio" and was first derived by Kohlrausch (83).

Kohlrausch also pointed out that because of its higher specific resistance, the indicator solution is in a region of higher potential gradient than the leading solution. If any leading ions diffuse back into the indicator solution, the higher gradient will speed them up until they again enter the leading solution. Conversely, if the indicator ions get ahead of the boundary, they will be slowed down by the lower gradient and again reach the boundary. Thus it is seen that a self-sharpening of the boundary will occur. MacInnes and co-workers (68,84,85,86) have demonstrated that this self-sharpening effect does indeed exist. They were able to reform a boundary that had been made diffuse by shutting off the current for as long as three hours. In addition, observation of the motion of the boundary after re-sharpening led to the correct transference number.

According to the treatment of Kohlrausch, the concentration of indicator electrolyte just behind the boundary, will automatically adjust to that given by the Kohlrausch ratio, equation (70), under the influence of the field. The concentration of the indicator solution can be influenced by the boundary, because the indicator solution moves in to occupy the space left by the leading solution. There is no such influence by the boundary on the leading solution, however. This permits the transference number of the leading solution to be determined accurately even if the indicator solution does not meet with the requirements set by the Kohlrausch ratio.

A study of this effect was made by MacInnes and Smith (78,87). According to Kohlrausch, the transference number obtained should be independent of the concentration of the indicator solution. This was found to be true only for a limited range of concentration of the indicator solution. The observed transference number behaved as shown in the drawing to the right. The flat portion of the curve, *T*, corresponded to the correct value of the transference number; the concentration of the indicator solution predicted by the Kohlrausch ratio is given by *R*, aproximately the midpoint of the plateau; and the width, *A-A*, of the plateau varied from 6 per cent to 15 per cent depending upon the conditions of the experiment. The range of the plateau was found to be

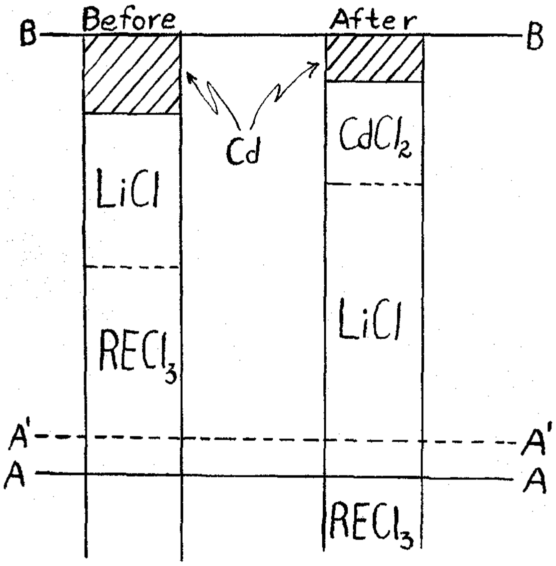


greater for small-bore tubes, dilute solutions, and rising boundaries. These limitations indicate that thermal mixing, which is larger for wide-bore tubes and concentrated solutions, may cause the failure of the solutions to regulate to the concentration given by the Kohlrausch ratio if the initial concentration is off by more than 3 per cent to 8 per cent. The range allowed by the automatic adjustment of concentration makes it possible to measure the transference number of the leading solution when the transference number of the indicator solution is only approximately known.

Since the Hittorf method measures the transference number of an ion with reference to the water of the solution, and the moving boundary method measures the motion relative to a fixed mark on the tube, correction must be made for the motion of the water relative to the tube. This was first proposed by Miller (88) and later calculated quantitatively by Lewis (89). This computation is made quite simply if one side of the cell is left open to the atmosphere and the other side is closed, for then only the volume changes which occur between the boundary and the closed side need be considered.

Consider the cell below employing a falling boundary between lithium chloride and rare earth chloride, and a cadmium metal anode. Before the passage of current, the boundary is at <u>C</u>. Suppose that during the passage of one

Faraday of current, the observed rare earth boundary moves from C to A-A, while if there were no volume change occurring it would have moved to some other point A'-A'. Then we are interested in the volume changes which occur between B-B and A-A during the passage of one Faraday of current. The losses and gains behind A-A are:



1. Loss of one-half mole of Cd metal; $\Delta V = -\frac{V_{Cd}}{2}$

2. Gain of one-half mole of Cd^{++} ions; $\Delta V = +\frac{V_{Cd^{++}}}{2}$ in CdCl$_2$

3. Loss of $\frac{T+}{3}$ moles of RE^{+++} ions; $\Delta V = -\frac{T+\ \bar{V}_{RE^{+++}}}{3}$ in RECl$_3$

4. Gain of one mole of chloride ions in cadmium chloride and loss from lithium chloride; $\Delta V = \bar{V}_{Cl^-}$ in CdCl$_2$ $- \bar{V}_{Cl^-}$ in LiCl

5. Gain of T+ moles of chloride ions in lithium chloride and loss from rare earth chloride; $\Delta V = T+\ \bar{V}_{Cl^-}$ in LiCl $- T+\ \bar{V}_{Cl^-}$ in RECl$_3$

6. Gain of T- moles of chloride ions in lithium chloride by transport; $\Delta V = T- \overline{V}_{Cl^-}$ in LiCl .

Combining the losses and gains (1) through (6) gives

$$\Delta V = - \frac{\overline{V}_{Cd}}{2} + \frac{\overline{V}_{CdCl_2}}{2} - (T+) \frac{\overline{V}_{RECl_3}}{3} . \qquad (71)$$

For the passage of one Faraday, equation (69) becomes

$$T+ = \frac{Vc}{1000} = \frac{(V' - \Delta V)c}{1000} = (T+') - \frac{c\Delta V}{1000} , \qquad (72)$$

in which $\underline{V'}$ is the measured volume in milliliters, $\underline{T+'}$ is the uncorrected or observed transference number and $\underline{\Delta V}$ is the change in volume as calculated by (71). The application of this correction gives the same transference number for a solution determined by the moving boundary method as is obtained using the Hittorf method.

An additional correction was proposed by Longsworth (81). He observed that in dilute solutions the sum of the cation transference number and anion transference number was not exactly one. He concluded that this was due to the small fraction of the total current which was carried by impurities in the solvent, and derived the following expression to correct for these impurities:

$$\Delta T+ = T+ \text{ (L solvent / L solution)} , \qquad (73)$$

in which T+ is the correct transference number, L solvent is the specific conductance of the solvent, and L solution is the specific conductance of the solution. The final equation for the true transference number then becomes:

$$T+ = \frac{\mathfrak{F}\, cV}{1000\ It} - \frac{c\Delta V}{1000} + T+ \frac{L\ \text{solvent}}{L\ \text{solution}} \quad . \tag{74}$$

The first correction term is more important in concentrated solutions and the second in dilute solutions.

It will be worth while to summarize at this point the properties which are required of the indicator solution.

(1) The solution must not react with the ion under investigation.

(2) The transference number of the indicator ion must be less than that of the leading ion.

(3) The following, or indicator solution, must be lighter than the leading solution for falling boundaries, and vice versa for rising boundaries.

(4) There must be sufficient difference in some property of the two solutions, such as color or refractive index, to permit the boundary to be observed and followed.

If these conditions are met, and the proper concentration of indicator solution is used, the moving boundary method for determination of transference numbers is capable of a high degree of accuracy.

C. Experimental

1. Preparation of materials

The preparation of the rare earth chloride solutions was described previously in this thesis in the section on conductance.

Lithium chloride was used as the indicator electrolyte for these measurements. A stock solution of this salt was prepared as recommended by Scatchard and Prentiss (90). A solution of c.p. lithium carbonate was treated with hydrochloric acid and flushed with nitrogen until the pH value of the solution was 6.6. The solution was analyzed by taking aliquots, evaporating to dryness with sulfuric acid, igniting to 800° C., and weighing as sulfate. Solutions to be used as indicator solutions were prepared from the stock solution by dilution. As was the case for all solutions used in this research, conductance water was used as the solvent.

2. Apparatus

The sheared boundary technique was used to measure the transference numbers reported in this thesis. A modification of the equipment of MacInnes and Longsworth (68) was used, and has been described completely by Spedding, Porter, Wright, and Yaffe (49,50,51,69). It consisted of:

(1) An electrolytic cell;

(2) A timing device;

(3) A device for observing the boundary;

(4) A constant temperature bath;

(5) A constant-current source; and

(6) A device for measuring the current through the cell.

The electrolytic cell is pictured in Figures 4 and 5. Two such cells were constructed of Pyrex brand glass, and consisted of a hollow-bore stopcock which formed the sheared boundary, connected at the middle opening to the calibrated measuring tube and at the end opening to the anode compartment. The cathode compartment was sealed to the bottom of the measuring tube by means of a connecting U-tube. One of the measuring tubes consisted of a two-milliliter Pyrex brand pipette graduated in 0.1 ml intervals. The other tube was made from a similar pipette which had been coated with wax and placed in a lathe in which fine grooves were cut in the wax. This pipette was then etched with hydrofluoric acid to form the graduations. Both measuring tubes were calibrated with mercury as recommended by Longsworth (81). The anode and cathode compartments were equipped with female ground glass joints to accommodate the male joints into which the electrodes were sealed. The electrode compartments also had overflow tubes which could be closed with stopcocks. Removable glass electrode cups were used to prevent the

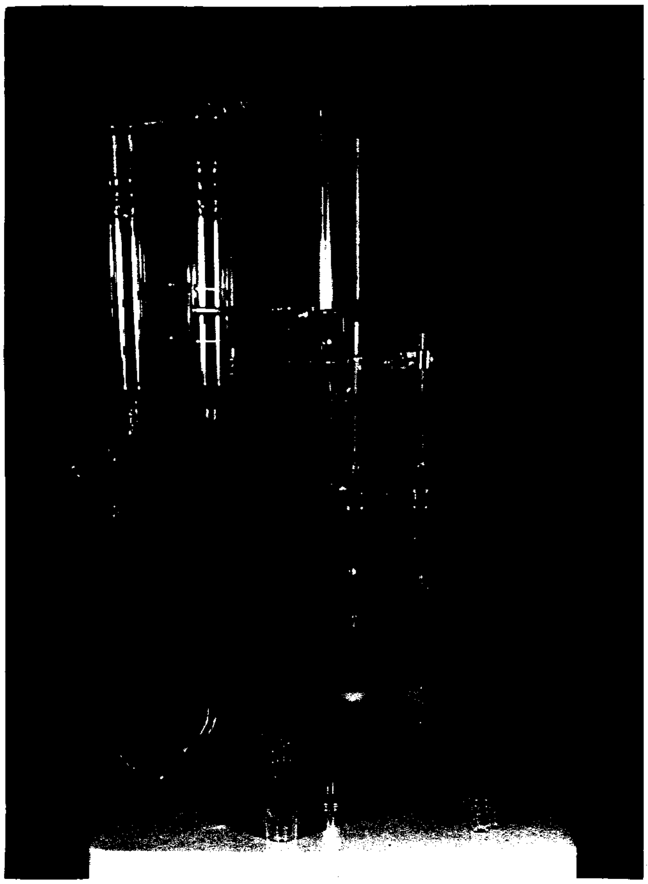


Figure 4. Unassembled Moving Boundary Electrolytic Cell.

Figure 5. Assembled Moving Boundary Electrolytic Cell.

products of the electrode reactions from reaching the measuring tube.

The anode consisted of a plug of cadmium into which was sealed a copper wire surrounded by a glass tube. The glass tube was sealed with Apiezon wax into a standard-taper ground glass joint which fit into the electrode compartment. The cadmium plug was made by melting c.p. cadmium metal in a test tube under helium, inserting the copper wire and glass tube and breaking away the test tube after solidification of the cadmium.

The cathode consisted of a silver-silver chloride electrode which was purchased from the Klett Manufacturing Company. It consisted of a smooth silver sheet wound around a central hollow silver tube, with corrugated silver sheet separating the various layers of smooth silver. The central silver tube was sealed through a standard-taper glass joint with Apiezon wax. This electrode was plated with silver chloride by electrolyzing in a one normal solution of hydrochloric acid.

The position of the boundary was detected by means of a narrow slit of light placed behind the transference tube with a telescope focused on the tube from the front. The detection was based on the fact that while a beam of light striking the interface between two substances with different refractive indices is generally only refracted; if the angle of incidence is small enough it will be totally reflected rather than refracted. Thus if the light source is placed so that all the light comes from slightly below the boundary, there will be a narrow angle on the opposite side of the tube into which light is neither reflected nor refracted. This will appear as a dark line when viewed from the proper position.

The apparatus used for observing the boundary is illustrated in Figure 6. The light source employed two 25-watt light bulbs mounted in a box, which was suspended from the shaft of a motor by a flexible wire. The front of the box had a two-centimeter wide slit covered with a pane of frosted glass. The slit of light could be moved up and down by the motor with a switch placed to be convenient for the operator. The telescope was mounted so that it could be moved vertically to follow the movement of the boundary. To time the movement of the boundary, two stopwatches mounted in a box with a hinged lid were used. The lid extended over the watches in such a way that one watch could be started and the other stopped by pressing down on the lid. The stopwatches were checked on a "Watchmaster" manufactured by American Time Products, Incorporated, and were accurate to within five seconds over a 24-hour period.

The water bath was a large aquarium-type, glass-sided. bath, which maintained the temperature at $25.00 \pm 0.05^{\circ}$ C. as determined by a thermometer calibrated by the National Bureau of Standards.

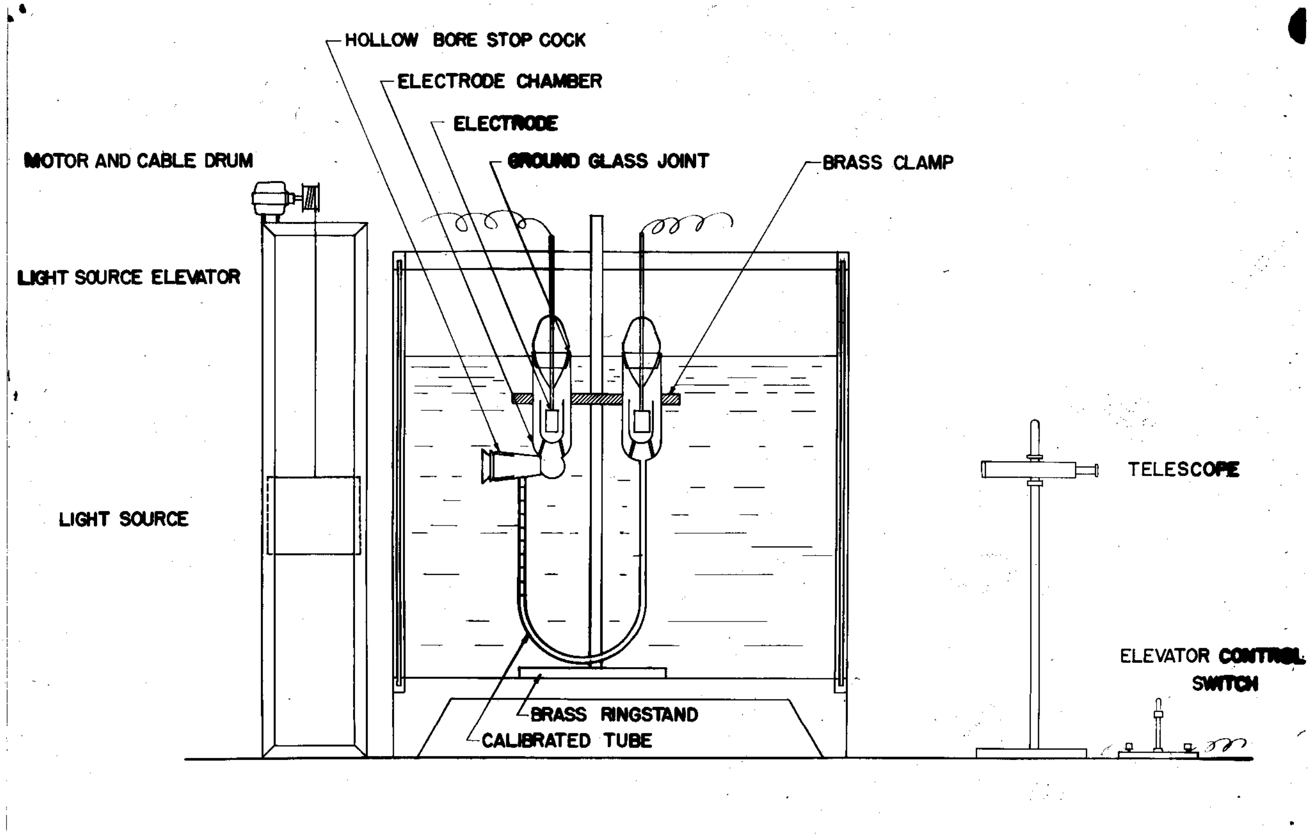


Figure 6. Apparatus Assembly for Determination of Transference Numbers.

The current through the cell was also passed through a high-precision standard resistor which was calibrated by the National Bureau of Standards. The potential drop across this standard resistor was measured on a Rubicon Type B High Precision potentiometer, in series with either an automatic Brown recording potentiometer or a Leeds and Northrup Type E galvanometer (catalog number 2430-D) with a sensitivity of 0.0004 microamperes per millimeter of scale deflection. When the Brown recording potentiometer was used, all but five to ten millivolts of the potential drop were balanced by the Rubicon potentiometer; the remaining voltage was continuously recorded on the chart of the Brown recorder. When the galvanometer was used, readings of the Rubicon potentiometer were taken just after the boundary had passed each mark, with the galvanometer used to detect the null point.

The constant-current apparatus was designed by A. A. Read and his colleagues at the Electronics Shop of the Ames Laboratory of the Atomic Energy Commission. A circuit diagram of the controller is shown in Figure 7. During a determination, the total resistance of the cell increased as the indicator, or following solution, replaced the leading solution in the narrow tube; this was compensated for by the electronic current controller.

3. Procedure

The transference cell was cleaned with acid cleaning

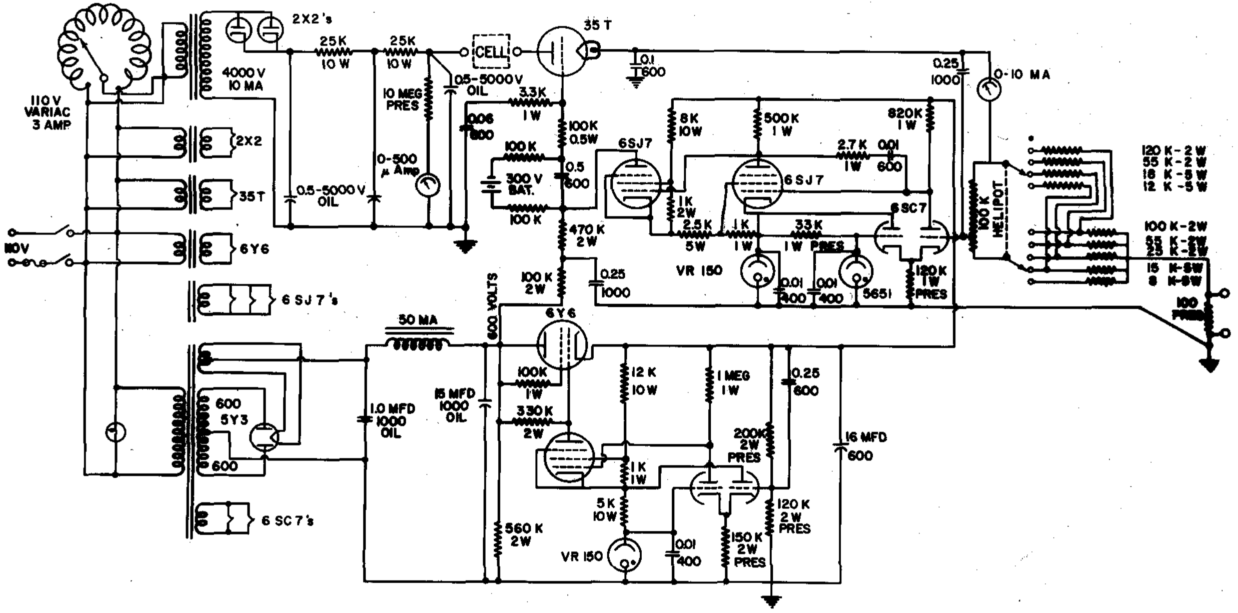


Figure 7. Circuit Diagram of the Current Controller.

solution before the determination of a transference number. It was necessary to do this only once for each two or three determinations. The cell was filled with distilled water after cleaning and rinsing, and allowed to stand at least 12 hours to insure the complete removal of acid from the glass. The hollow-bore plug and stopcock were dried and gently warmed with a cool flame. While still warm the plug was coated thinly and uniformly with a silicone lubricant and inserted into the stopcock. With the stopcock open, the cathode compartment was rinsed at least three times with the solution to be measured and filled to the level of the stopcock, which was then closed, taking care that no air bubbles were trapped in the tube. The cathode compartment was then filled with the solution to be measured, the electrode cup and silver-silver chloride electrode inserted and the side arm stopcock closed. The anode compartment was then rinsed with water, and lithium chloride solution. The lithium chloride solution was made up to the concentration given by the Kohlrausch ratio from an estimate of the transference number of the rare earth chloride. The anode compartment was filled with the lithium chloride solution; the cups and electrodes were inserted and the side arm stopcock closed. The outside of the cell was then washed with distilled water to remove any salts which could have caused a short to the water bath.

The cell was placed in the water bath in such a position that the light, measuring tube, and telescope were in a straight line, with the divisions of the tube clearly visible in the telescope. The system was checked for electrical leaks using a vacuum tube ohm-meter. After balancing the Rubicon potentiometer against a standard cell, the leads were connected to the cell, the stopcock opened, and the current turned on. It was not necessary to wait for temperature equilibrium before beginning a run, because at least 45 minutes always elapsed between the time the stopcock was opened, and the time that the boundary reached the first mark on the tube. The current was adjusted to such a value that the boundary required between 180 and 350 seconds to traverse the distance between two marks. The time required for the boundary to pass each mark successively was determined with the stopwatches.

The densities of the solutions were measured using a calibrated 50 ml pycnometer. These densities were necessary for the calculation of the partial molar volumes of the rare earth chlorides. These partial molar volumes were needed for the calculation of the volume correction on the transference number.

4. Results

The transference numbers of neodymium, dysprosium, holmium, erbium, thulium and ytterbium ions in chloride solution were calculated from the data using equation (69). The indicator solution used was lithium chloride, whose concentration was determined in advance from the Kohlrausch ratio using the transference number data of L. G. Longsworth (81). The concentrations of lithium chloride were well within the prescribed limits and this was checked in several cases by changing the concentration of lithium chloride several per cent after a determination, and repeating the run. The same transference number was obtained, showing that the indicator solution concentration was still within the prescribed limits. The transference number data are presented in Tables 9 through 14, and are plotted in Figures 8 and 9. It was necessary to stagger the ordinates of Figure 9 in order to separate the various curves.

The volume correction was calculated by equation (71) using the following values:

$\overline{V}_{Cd} = 13.0$ ml (reference 91);

$\overline{V}_{CdCl_2} = 23.24 + 8.82\,(\text{Molality})^{1/2}$ (reference 92).

The densities of the solutions of the rare earth chlorides were determined using a calibrated 50 ml. pycnometer and are described by the following expressions:

Table 9.

Cation Transference Numbers for Neodymium Chloride at 25° C.

Normality	(Normality)$^{1/2}$	T_+ Observed	Volume Correction	Solvent Correction	T_+ Corrected	Deviation[a]
0.1002	0.3166	0.4394	-0.0002	0.0000	0.4392	-0.0004
0.07516	0.2742	0.4455	-0.0001	0.0000	0.4454	+0.0007
0.05006	0.2237	0.4505	-0.0001	0.0001	0.4505	-0.0004
0.03506	0.1872	0.4553	0.0000	0.0001	0.4554	+0.0002
0.02003	0.1415	0.4604	0.0000	0.0002	0.4606	-0.0001

[a] Deviation from the least-squares straight line; $T_+ = 0.4776 - 0.120 \sqrt{c}$.

Table 10.

Cation Transference Numbers for Dysprosium Chloride at 25° C.

Normality	(Normality)$^{1/2}$	T_+ Observed	Volume Correction	Solvent Correction	T_+ Corrected	Deviation[a]
0.1033	0.3214	0.4271	-0.0002	0.0000	0.4269	+0.0002
0.06888	0.2625	0.4340	-0.0001	0.0000	0.4339	+0.0001
0.05166	0.2273	0.4375	0.0000	0.0000	0.4375	-0.0006
0.02929	0.1711	0.4449	0.0000	0.0001	0.4450	+0.0001
0.01722	0.1312	0.4490	0.0000	0.0001	0.4491	-0.0006
0.01034	0.1017	0.4536	0.0000	0.0002	0.4538	+0.0005

[a] Deviation from the least-squares straight line; $T_+ = 0.4655 - 0.120 \sqrt{c}$.

Table 11.

Cation Transference Numbers for Holmium Chloride at 25° C.

Normality	(Normality)$^{1/2}$	T_+ Observed	Volume Correction	Solvent Correction	T_+ Corrected	Deviation[a]
0.1023	0.3199	0.4205	-0.0002	0.0000	0.4203	-0.0006
0.06826	0.2613	0.4288	-0.0002	0.0000	0.4286	+0.0003
0.05117	0.2262	0.4335	-0.0001	0.0000	0.4334	+0.0007
0.03411	0.1847	0.4367	0.0000	0.0001	0.4368	-0.0012
0.01706	0.1306	0.4450	0.0000	0.0002	0.4452	+0.0004
0.01024	0.1012	0.4481	0.0000	0.0003	0.4484	-0.0001

[a] Deviation from the least-squares straight line; $T_+ = 0.4613 - 0.126 \sqrt{c}$.

Table 12.

Cation Transference Numbers for Erbium Chloride at 25° C.

Normality	$(\text{Normality})^{1/2}$	T_+ Observed	Volume Correction	Solvent Correction	T_+ Corrected	Deviation[a]
0.1088	0.3300	0.4189	-0.0003	0.0000	0.4186	-0.0002
0.06799	0.2608	0.4279	-0.0002	0.0000	0.4277	+0.0003
0.04078	0.2020	0.4345	-0.0001	0.0001	0.4345	-0.0003
0.02721	0.1650	0.4388	0.0000	0.0001	0.4389	-0.0005
0.01088	0.1043	0.4472	0.0000	0.0002	0.4474	+0.0004

[a] Deviation from the least-squares straight line; $T_+ = 0.4601 - 0.125\sqrt{c}$.

Table 13.

Cation Transference Numbers for Thulium Chloride at 25° C.

Normality	(Normality)$^{1/2}$	T_+ Observed	Volume Correction	Solvent Correction	T_+ Corrected	Deviation[a]
0.09757	0.3124	0.4236	-0.0002	0.0000	0.4234	+0.0000
0.06515	0.2551	0.4310	-0.0002	0.0000	0.4308	+0.0006
0.04228	0.2056	0.4360	-0.0001	0.0001	0.4360	-0.0001
0.02602	0.1613	0.4409	0.0000	0.0001	0.4410	-0.0003
0.01626	0.1275	0.4455	0.0000	0.0002	0.4457	+0.0004

[a] Deviation from the least-squares straight line; $T_+ = 0.4604 - 0.118 \sqrt{c}$.

Table 14.

Cation Transference Numbers for Ytterbium Chloride at 25° C.

Normality	$(\text{Normality})^{1/2}$	T_+ Observed	Volume Correction	Solvent Correction	T_+ Corrected	Deviation[a]
0.1022	0.3196	0.4203	-0.0002	0.0000	0.4201	-0.0003
0.07487	0.2736	0.4271	-0.0002	0.0000	0.4269	+0.0007
0.04541	0.2131	0.4341	-0.0001	0.0001	0.4341	+0.0003
0.02948	0.1717	0.4380	-0.0001	0.0001	0.4380	-0.0009
0.01816	0.1348	0.4435	0.0000	0.0002	0.4437	+0.0001
0.01021	0.1010	0.4477	0.0000	0.0003	0.4480	+0.0002

[a] Deviation from the least-squares straight line; $T_+ = 0.4604 - 0.125 \sqrt{c}$.

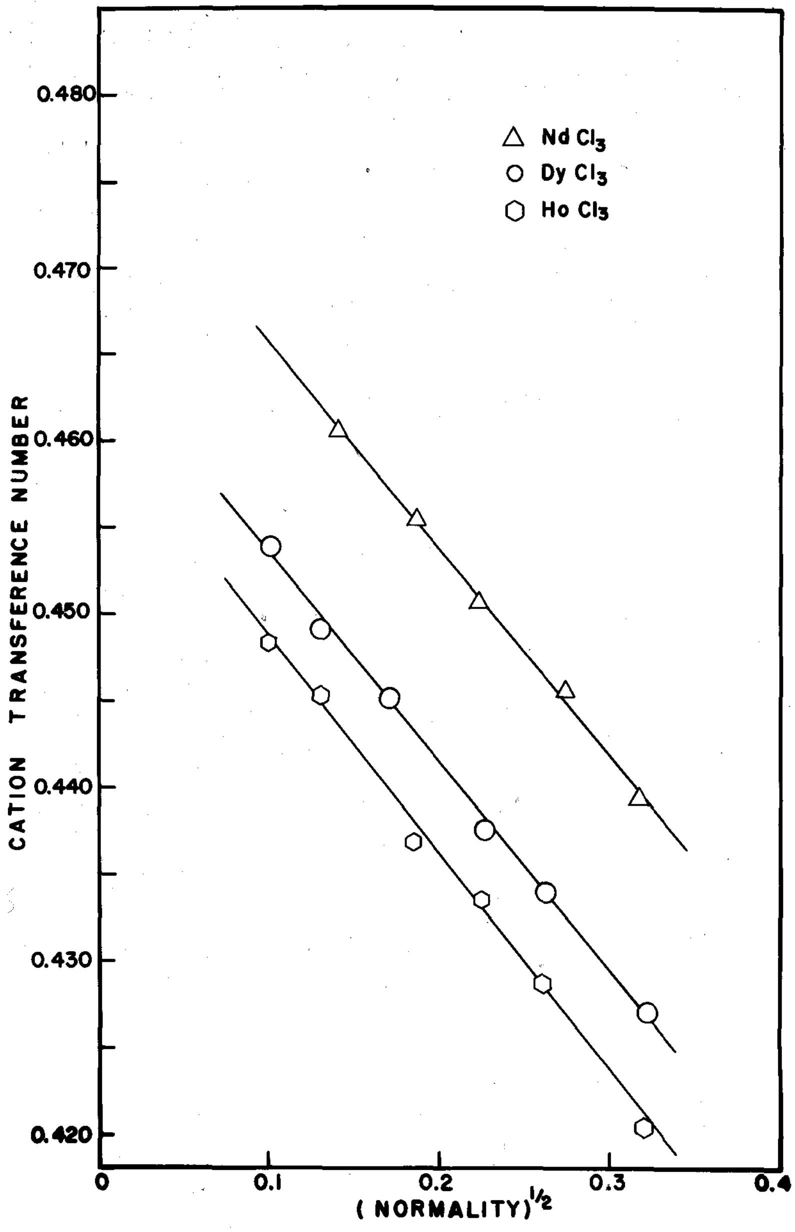


Figure 8. Cation Transference Numbers of Neodymium, Dysprosium, and Holmium Chlorides at 25° C.

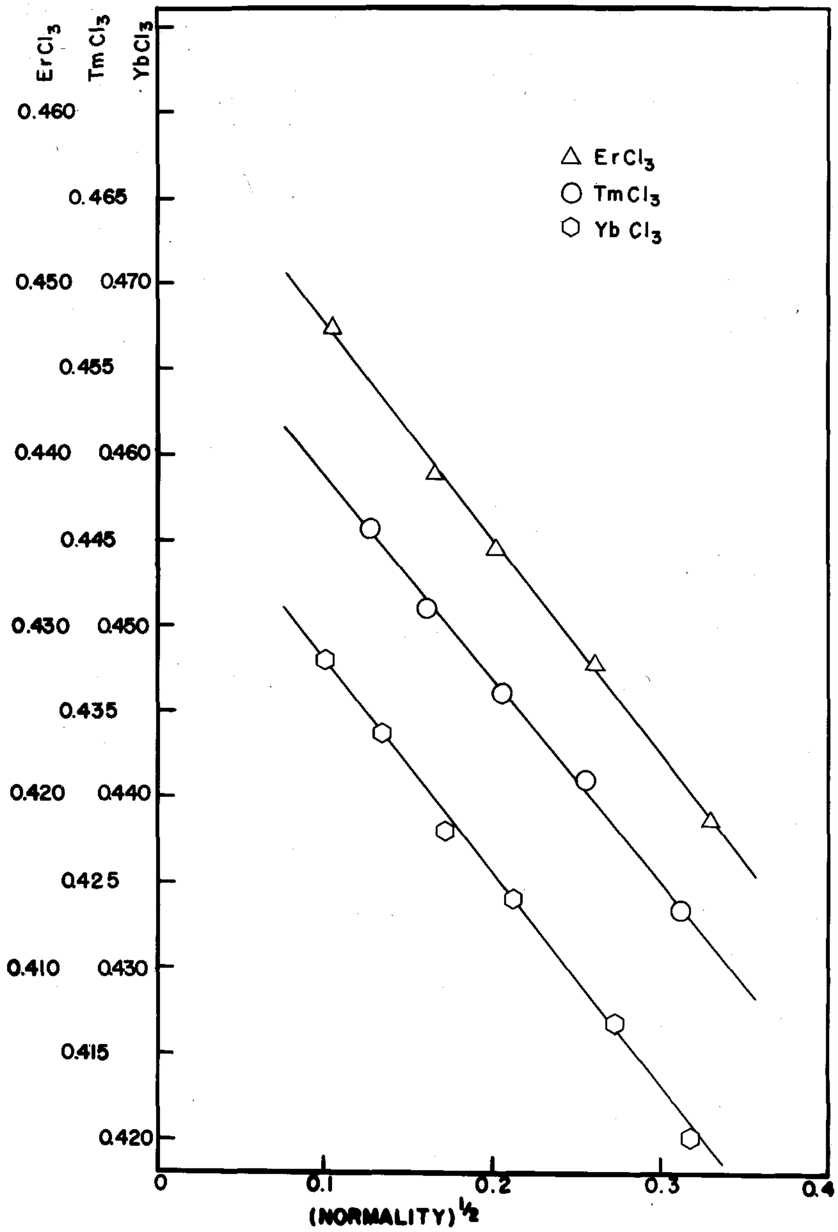


Figure 9. Cation Transference Numbers of Erbium, Thulium, and Ytterbium Chlorides at 25° C.

$$\begin{aligned}
NdCl_3&: \quad \rho = .99707 + 0.0785c = .99707 + .2355C \\
DyCl_3&: \quad \rho = .99699 + 0.0839c = .99699 + .2517C \\
HoCl_3&: \quad \rho = .99695 + 0.0863c = .99695 + .2589C \\
ErCl_3&: \quad \rho = .99711 + 0.0879c = .99711 + .2637C \\
TmCl_3&: \quad \rho = .99703 + 0.0865c = .99703 + .2598C \\
YbCl_3&: \quad \rho = .99709 + 0.0883c = .99709 + .2649C \ ,
\end{aligned} \qquad (75)$$

in which c as usual is the normality, and C is the molarity of the solution. All of these equations were obtained by a least squares treatment of the density data. The transference number curves were also fitted by a least squares method to a straight line. The equations for these lines are given below the corresponding tables of data.

D. Discussion of Results

There are four factors which influence the accuracy of determination of the transference numbers. These involve the correct measurement of:

(1) The time required for the boundary to travel the distance between two marks on the tube.

(2) The current which passes through the solution.

(3) The volume of the tube between each set of marks.

(4) The concentration of the solution.

While any one of these factors is known to at least ± 0.1 per cent, it is conceivable that the total error could be greater than this figure. The amount of deviation of the measured transference numbers from the straight line,

$$T_+ = a + b\sqrt{c} \quad , \tag{76}$$

indicates that, except in rare cases, the precision of any given run was about ± 0.1 per cent so that the first three sources of error mentioned above must have been kept at a minimum. The concentrations were known to ± 0.1 per cent. From these considerations, the overall accuracy of any experimental point, is estimated to be ± 0.2 per cent, and the accuracy of the smoothed values is estimated to be ± 0.1 per cent.

The values of the transference numbers of the rare earth chlorides at $\underline{\sqrt{c} = 0.3}$ are plotted against atomic number in Figure 10. At a given concentration, the transference number remains nearly unchanged from rare earth to rare earth in the light end of the rare earth series, from lanthanum through samarium, undergoing a relatively large change from samarium to holmium, then remaining nearly unchanged again from holmium through ytterbium. This change with atomic number is similar to the change shown by the equivalent conductance at infinite dilution, as is illustrated by Figure 10. This behavior is believed to be due to changes in hydration number, but has not yet been checked by other data, such as the crystal structures of the hydrated chlorides for the heavier members of the series.

The high value obtained for the transference number of

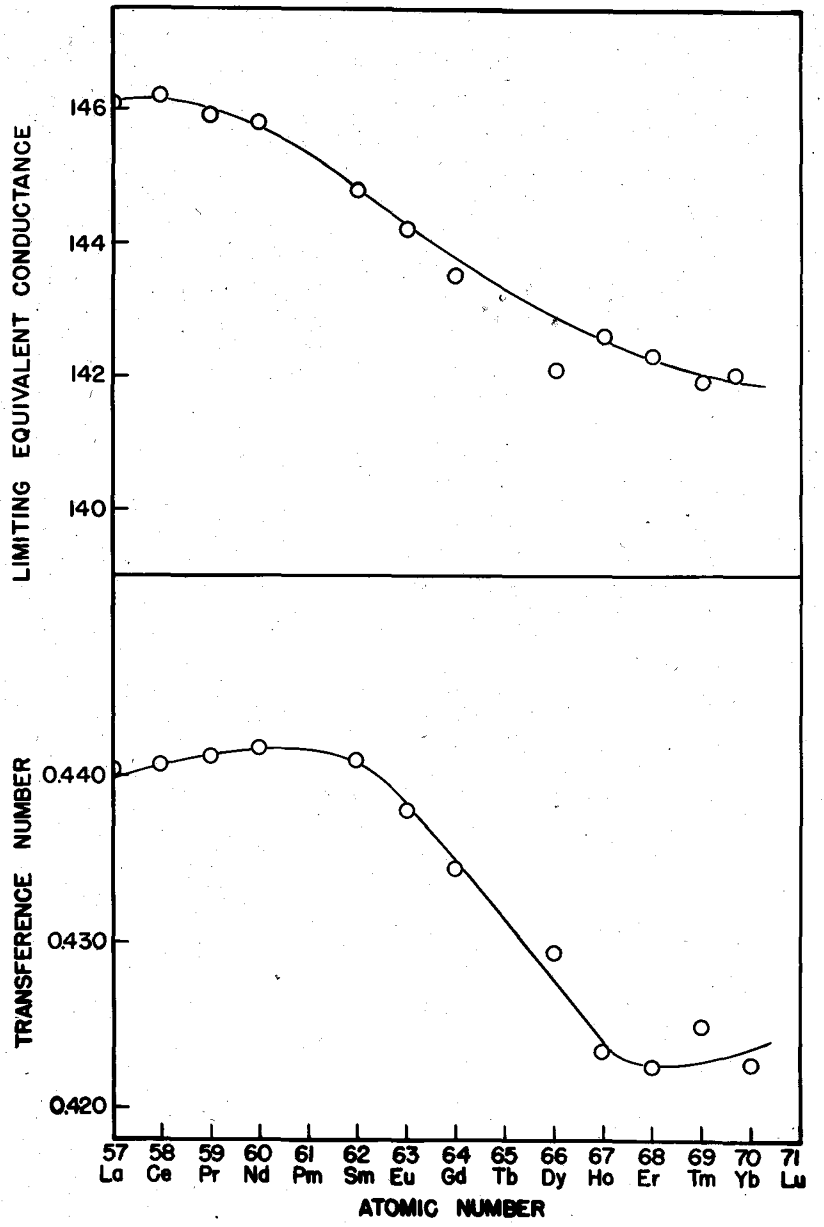


Figure 10. Change in Limiting Equivalent Conductance, (Top Curve), and Transference Number at $\sqrt{c} = 0.3$ (Bottom Curve) for Rare Earth Chlorides.

thulium chloride is unexplained. It was thought at first to be due to an error in the determination of the concentration of the solution, but repeated analysis showed this to be highly unlikely, because six separate analyses agreed to within ± 0.1 per cent. It will be interesting to note whether this anomaly for thulium chloride and the anomaly in the conductance of dysprosium chloride at infinite dilution are found when measurements are made on salts of thulium and dysprosium other than the chlorides.

The transference numbers of neodymium chloride, erbium chloride and ytterbium chloride were repeated to determine the effect of the slight deviation from equivalence due to the colloid present in the solution. The transference numbers measured were slightly lower than those previously obtained, for erbium chloride (0.47 per cent) and ytterbium chloride (0.54 per cent), but agreed with the values obtained previously for neodymium chloride. Again, these percentages are a fair measure of the amount of colloidal oxide or basic salt which was present in the solutions used for the previous measurements.

The Theory of Onsager as originally deduced predicts transference numbers for the rare earth chlorides which are far lower than are obtained by experiment. This anomaly had been previously unexplained. Another section of this thesis extends the mathematics of the Onsager Theory, and shows much better agreement with experiment.

V. ACTIVITY COEFFICIENTS

A. Introduction

The theory and thermodynamic definition of activity coefficients were discussed earlier in this thesis.

The calculation of thermodynamic quantities from electromotive force measurements can be made provided that the net result of all chemical changes occurring in the cell is known, and also provided that the changes occurring are reversible. The second condition is fulfilled if:

(1) No changes take place in the cell without the passage of current.

(2). Every change which takes place during the passage of current may be reversed by reversing the direction of the current.

Although the activity coefficients of solutions of electrolytes may be measured in a number of ways, only the use of cells with transference will be discussed in this thesis, since the other methods are adequately reviewed elsewhere (15,43,67,93,94).

B. History of the Method

The nature of the E.M.F. of concentration cells with transference was first considered by Helmholtz (95) in 1877, who made calculations on the free energy changes involved, which were essentially correct although he assumed the transference numbers to be constant. This work of Helmholtz inspired research on the E.M.F. of cells with transference, and his ideas were confirmed roughly by the work of Moser (96,97) and Miesler (98,99). Nernst (100) also made calculations relating the E.M.F. of cells to the osmotic pressure and his measurements as well as those of Jahn (101) showed reasonable agreement with the theory of Nernst. With the introduction of the concepts of fugacity and activity by G. N. Lewis (8), the calculations were brought to their modern form. In 1915, D. A. MacInnes and K. Parker (63) became interested in the possibility of measuring transference numbers from the E.M.F. of cells with transference. MacInnes and Beattie (64) first took into account the variation of transference number with concentration.

The calculations involved in the determination of activity coefficients from E.M.F. measurements using cells with transference may be illustrated by considering the following general cell,

$$M - MX \left| A_{\nu_+}^{z_+} X_{\nu_-}^{z_-} (m_1) \,\vdots\, A_{\nu_+}^{z_+} X_{\nu_-}^{z_-} (m_2) \right| MX - M \ , \qquad (77)$$

in which $M - MX$ is an electrode reversible to the X^- ions, and m_1 is greater than m_2. Consider the changes which occur in the left hand side of the cell when one Faraday of current, $\mathcal{F}$, is passed. T_+ equivalents of A^{z_+} will be lost by migration across the boundary; T_- equivalents of X^{z_-} will be gained by migration of that ion; one equivalent of X^{z_-} will be lost due to deposition on the electrode. The net result is the transfer of T_+ equivalents of $A_{\nu_+}^{z_+} X_{\nu_-}^{z_-}$ from the left side of the electrode at concentration m_1 to the right side at concentration m_2.

The free energy change for a transfer such as that depicted by (77), if m_1 and m_2 differ only infinitesimally, is

$$dF = n\, RT\, d(\ln a) = \frac{T_+}{\nu_+ z_+} RT\, d(\ln a) \ , \qquad (78)$$

in which n is the number of moles of the electrolyte undergoing the change, and a is the activity of the electrolyte, da being the change in activity experienced in the transfer. Since $dF = -\mathcal{F} d\mathcal{E}$ where $\mathcal{E}$ is the potential of the cell,

$$d\mathcal{E} = -\left[\frac{T_+\ RT}{\nu_+ z_+ \mathcal{F}}\right] d(\ln a) \ , \qquad (79)$$

and

$$\frac{d}{T_+} = -\left[\frac{RT}{\nu_+ z_+ \mathcal{F}}\right] d(\ln a) \ , \qquad (80)$$

so that, integrating over the total concentration change gives

$$\int_{m_1}^{m_2} \frac{d\mathcal{E}}{T_+} = - \left[\frac{RT}{\nu_+ z_+ \mathcal{F}}\right] \int_{m_1}^{m_2} d \ln a = - \left[\frac{RT}{\nu_+ z_+ \mathcal{F}}\right] \ln \frac{a_2}{a_1} \ . \quad (81)$$

The integral on the left cannot be determined analytically because the transference number is a function of concentration. For this purpose the following function is devised:

$$\delta = \frac{1}{T_+} - \frac{1}{T_{+(ref)}} \ , \quad (82)$$

where now $\underline{m_1}$ refers to the reference solution. This leads to

$$\frac{RT}{\nu_+ z_+} \ln \frac{a}{a(ref)} = \frac{-\mathcal{E}}{T_{+(ref)}} - \int_0^{\mathcal{E}} \delta \, d\mathcal{E} \ . \quad (83)$$

It was shown previously, equation (7), that

$$a = (a_{\pm})^{\nu} \ . \quad (84)$$

So equation (83) becomes

$$\frac{\nu RT}{\nu_+ z_+ \mathcal{F}} \ln \frac{a_{\pm}}{a_{\pm(ref)}} = - \frac{\mathcal{E}}{T_{+(ref)}} - \int_0^{\mathcal{E}} \delta \, d\mathcal{E} \ , \quad (85)$$

or, converting to activity coefficients and common logarithms

$$\log \frac{y_{\pm}}{y_{\pm(\mathrm{ref})}} = \log \frac{C\ \mathrm{ref}}{C} \quad +$$

$$- \frac{\nu_+ z_+ \mathcal{F}\, \mathcal{E}}{2.303\, \nu RT\ T_{+(\mathrm{ref})}} - \frac{\nu_+ z_+ \mathcal{F}}{2.303\, \nu RT} \int_0^{\mathcal{E}} d\mathcal{E} \quad . \qquad (86)$$

For the rare earth chlorides, $\underline{\nu_+ = 1}$, $\underline{z_+ = 3}$, $\underline{\nu = 4}$.

It is seen that, from experimental data on the E.M.F. of cells with transference, and transference numbers, one can calculate the ratio $\underline{y_{\pm} / y_{\pm(\mathrm{ref})}}$. To calculate the individual values of $y_{\pm}$, one needs to obtain the activity coefficient of the reference solution. This is done using the extended Debye-Hückel equation (31) in the form

$$\log y_{\pm} = \frac{-A\sqrt{C}}{1 + \mathring{a}\, B \sqrt{C}} \quad , \qquad (87)$$

where A and B are constants at a given temperature; $\mathring{a}$ is the distance of closest approach of the ions; and C is the molar concentration. A term involving the densities, which converts $f_{\pm}$ to $y_{\pm}$ was neglected since it is small in the concentration range used. By subtracting log $\underline{y_{\pm(\mathrm{ref})}}$ from both sides of the above equation and multiplying both sides by $\underline{(1 + \mathring{a}\, B \sqrt{C}\,)}$, and rearranging terms, one obtains

$$\left[\log \frac{y_{\pm}}{y_{\pm(\mathrm{ref})}} + A\sqrt{C}\right] = -\log y_{\pm(\mathrm{ref})} + $$

$$-\overset{\circ}{a}\,B\left[\sqrt{C}\left(\log y_{\pm(\mathrm{ref})} + \log \frac{y_{\pm}}{y_{\pm(\mathrm{ref})}}\right)\right] . \qquad (88)$$

A plot of the bracketed term on the right, denoted by *x*, against the bracketed term on the left called *Z*, gives $\underline{-\log y_{\pm(\mathrm{ref})}}$ as an intercept. In order to obtain this value, a successive approximation method must be used, since $\underline{\log y_{\pm(\mathrm{ref})}}$ appears in the bracket on the right. A least squares treatment of the data is generally used.

Before this method may be used to determine activity coefficients, it must be ascertained that the measured potentials are dependent only upon the concentration of the solutions in contact with the electrodes, and are independent of the distribution of concentration gradients in other parts of the cell, *i.e.*, at the junction. This has been well tested since the inception of this method and these requirements are indeed fulfilled provided suitable electrodes are used.

Cummings and Gilchrist (102), MacInnes and Parker (63), and Lewis, Brighton, and Sebastian (103) showed that reproducible potentials are obtained provided the area of the junction is large enough (at least four millimeters diameter).

MacInnes and Beattie (64) and Brown and MacInnes (104) showed that the potentials are independent of the solution concentration at the junction, so long as the solution in contact with the electrodes remains unchanged in composition. The inclusion of a third compartment, with solutions of different concentration than existed in either electrode compartment, produced no change in the E.M.F. observed.

The design of apparatus necessary for these measurements is simple. The cell must be made so that junction can be made between the dilute and concentrated solutions, without diffusion into the electrode compartments. The junctions are most easily made by using a hollow bore stopcock, although other, more elaborate devices have been made (63,104). The potentials of the cells are measured with a high precision potentiometer.

C. Experimental

1. Preparation of materials

The rare earth chloride solutions were prepared as described in the section on conductance.

The potassium chloride for soaking the electrodes was prepared by the method of Pinching and Bates (41). C. P. potassium chloride was dissolved in conductance water and chlorine was bubbled through the solution to remove traces of bromide. The solution was boiled to remove the bromine and the potassium chloride was then recrystallized twice from conductance water and fused in platinum ware under an atmosphere of nitrogen. These precautions were necessary because bromide contamination greater than .001 per cent caused the electrodes to be erratic in nature.

The silver oxide used for the preparation of electrodes was prepared by adding a dilute solution of carbonate-free sodium hydroxide to a solution of reagent-grade silver nitrate (105) and washing the precipitate at least 40 times with boiling conductance water.

2. Apparatus

The apparatus used for the measurement of the E.M.F. of concentration cells with transference consisted of suitable concentration cells, pictured in Figure 11, silver-silver chloride electrodes, a potentiometer, a galvanometer, standard cells and a constant temperature bath.

The cells and electrodes were of the same design as used by Spedding, Porter and Wright (51). Each cell had two compartments joined by a high-vacuum hollow-bore stopcock. Each of the two compartments had two ground glass joints to hold the electrodes. A trap was placed between one of the compartments and the stopcock to prevent diffusion.

The silver-silver chloride electrodes were prepared by the thermal-electrolytic method described by Smith and Taylor (106). The platinum spirals were each made from three inches of number 26 C. P. platinum wire sealed into a 12/30

Figure 11. Concentration Cell with Transference.

male standard taper. The spirals were made by winding the wire on two-millimeter glass rod, and were wound fairly tightly. They were cleaned by alternately heating the wire to a red heat and plunging into concentrated nitric acid, and rinsing with conductivity water. They were then coated with a paste of silver oxide which was ignited to silver at 400° C. This was repeated three or four times until a complete covering of silver was obtained. The electrodes were then filled with mercury and plated with silver chloride by electrolyzing in a one normal solution of redistilled hydrochloric acid using a platinum cathode. The electrolysis was carried on for 45 minutes with a current of eight milliamperes per electrode.

A Rubicon Type B High Precision potentiometer was employed for measuring the potentials developed in the cells. A Leeds and Northrup Type E galvanometer (catalog number 2430-d) with a sensitivity of .00042 microamperes per millimeter of scale deflection was used as a null point indicator. The potentiometer was checked at intervals against an Eppley-type standard cell which had been calibrated by the National Bureau of Standards. The constant temperature bath was the same type as was employed for conductance measurements except that water was used as a bath medium.

3. Procedure

After electrolysis, the silver-silver chloride electrodes were connected in parallel and allowed to stand in 0.1 normal bromide-free potassium chloride for at least 24 hours until they reached a constant potential when checked against each other. If this potential was greater than 0.02 millivolts from the mean of the other electrodes, the electrode was discarded. The electrodes were soaked in conductivity water overnight followed by two one hour soakings in the solution to be measured before being placed in the cell.

The electrode compartment containing the trap, connected to the center opening of the stopcock, was rinsed with at least three portions of solution and filled with the more dilute solution and the electrodes inserted. This procedure was then followed for the other compartment with the more concentrated solution. No stopcock grease was used on the stopcock, the ground glass plug being tight enough to prevent diffusion. The cell was placed in the water bath, and at least one hour was allowed for the cell to come to thermal equilibrium with the bath. The stopcock was then opened and the E.M.F. determined with the potentiometer. To correct for differences in the individual electrodes, the electrodes were switched. That is, the electrodes which were in the dilute solution were soaked in the more concentrated solution and placed in fresh concentrated solution in the cell and vice versa for the other two electrodes. Since four electrodes were used, eight readings were obtained, or four average readings after switching. The E.M.F. value reported was the average of these four readings. All dilutions of the rare earth chloride were measured against the same dilution, termed the reference concentration.

4. Results

The potentials of cells with transference were measured for solutions of neodymium, dysprosium, holmium, erbium, thulium, and ytterbium chlorides. A typical set of data is shown in Table 15.

For the special case of rare earth chlorides, equation (86) has the form

$$\log \frac{y_{\pm}}{y_{\pm r}} = \log \frac{C_r}{C} - \frac{3\mathfrak{F}\mathcal{E}}{9.212\ RT\ T_{+}} - \frac{3\mathfrak{F}}{9.212\ RT} \int_{0}^{E} \delta\ dE\ , \qquad (89)$$

in which the subscript $\underline{r}$ refers to the indicated quantities of the reference solution. Employing the Debye-Hückel equation in the form (88), values of log $y_{\pm r}$ and $\underline{\overset{\circ}{a}B}$ were obtained by a least-squares method. Equation (88) is repeated here for clarity.

$$\left[\log \frac{y_{\pm}}{y_{\pm r}} + A\sqrt{C}\right] = -\log y_{\pm r} - \overset{\circ}{a}B \left[\sqrt{C}\left(\log y_{\pm r} + \log \frac{y_{\pm}}{y_{\pm r}}\right)\right] \ . \qquad (88)$$

Figure 12 shows a typical plot of the left side of this

Table 15.

A Typical Set of E.M.F. Data for a Concentration Cell with Transference

Salt: Holmium Chloride
Concentration: 0.001137 molar
Reference Concentration: 0.01136 molar

Electrodes	E.M.F. millivolts	Average E.M.F. millivolts
C vs. 19	29.893	29.864
19 vs. C	29.835	
C vs. F	29.902	29.872
F vs. C	29.843	
18 vs. F	29.902	29.887
F vs. 18	29.873	
18 vs. 19	29.912	29.890
19 vs. 18	29.869	
	Average:	29.878 mv.
	Average deviation:	0.010 mv.
	Maximum deviation:	0.014 mv.

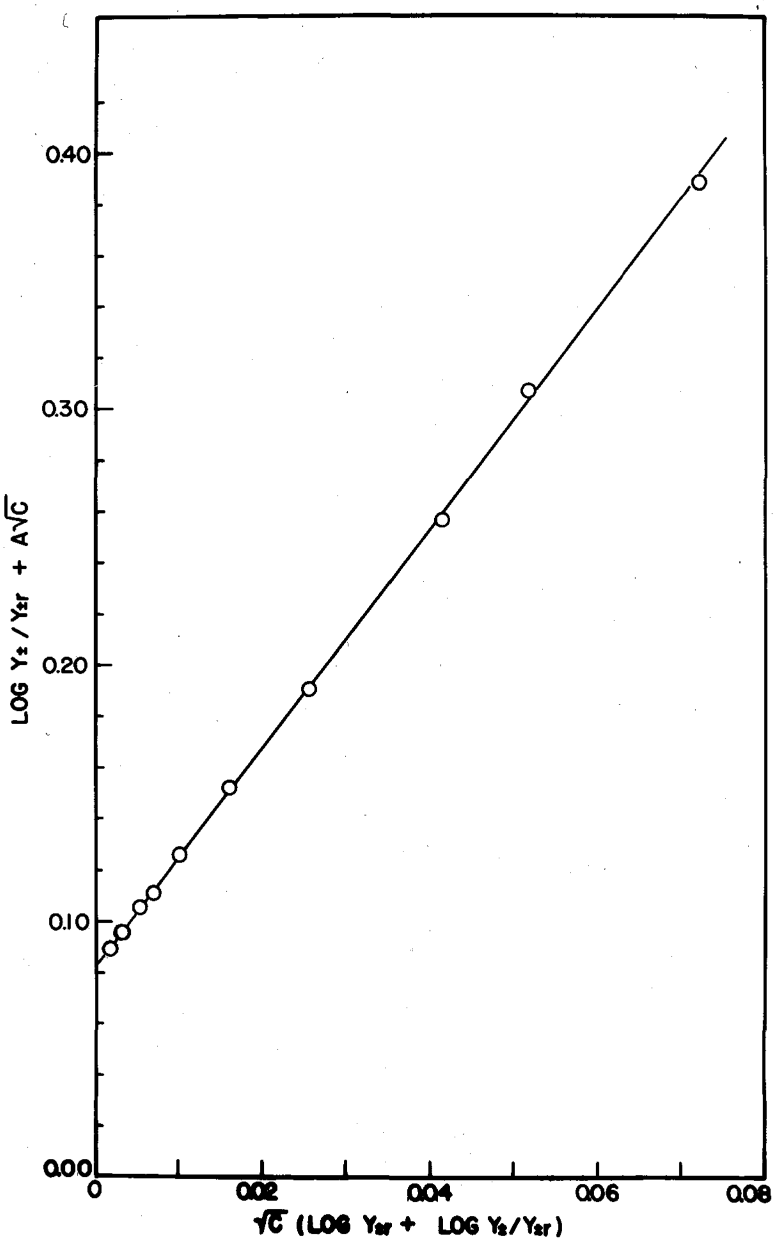


Figure 12. Debye-Hückel Straight Line for Dysprosium Chloride at 25° C. (Equation 88).

equation against the bracketed term on the right. This plot is taken from data on dysprosium chloride. The intercept at zero concentration is the value of $\log y_{\pm r}$, and the slope is $\mathring{a}B$. From the ratio, $\log y_{\pm} / y_{\pm r}$ and the value of $\log y_{\pm r}$, values of $y_{\pm}$ were obtained for each solution. These data are tabulated in Tables 16 through 21, and a typical example is plotted in Figure 13. This plot is taken from data on thulium chloride. The molal quantities listed in the tables were obtained by the use of equation (10), and the densities are given by equation (75).

The values of $\mathring{a}$ are listed in these tables also. Using these values of $\mathring{a}$, the mean molal activity coefficients, $\gamma_{\pm}$, were calculated from the Debye-Hückel equation (87). These calculated values are listed with the experimental values in Tables 16 through 21.

D. Discussion of Results

The measurement of the potentials of cells with transference as described in this thesis was accurate to about $\pm$ 0.1 per cent. Because the experimental values of the potentials are involved in sums, and log terms in the calculation of the activity coefficients, this degree of accuracy may not carry through to the final values of interest, the activity coefficients. Indeed, comparison with the values predicted by the Debye-Hückel Theory indicates a precision of

Table 16.

E.M.F. Data and Activity Coefficients of Neodymium Chloride at 25° C.

Molarity	Molality	E.M.F. millivolts (average)	$y_{\pm}$	$\gamma_{\pm}$	$\gamma_{\pm}$ (Debye-Hückel)[a]
0.03340	0.03352	51.272	0.4180	0.4178	0.4179
0.02505	0.02514	47.919	0.4467	0.4466	0.4477
0.01669	0.01674	43.230	0.4941	0.4940	0.4919
0.01169	0.01172	38.843	0.5320	0.5319	0.5321
0.006676	0.006696	31.872	0.5972	0.5972	0.5959
0.003340	0.003350	22.778	0.6731	0.6731	0.6723
0.002505	0.002513	18.817	0.7004	0.7004	0.7022
0.001670	0.001675	13.231	0.7413	0.7413	0.7419
0.001169	0.001172	8.196	0.7751	0.7751	0.7741
0.0006676[b]	0.0006696	0.000	0.8166	0.8166	0.8187

[a] The least-squares value of $\overset{o}{\underline{a}}$ is 5.49 Angstroms.

[b] Reference concentration.

Table 17.

E.M.F. Data and Activity Coefficients of Dysprosium Chloride at 25° C.

Molarity	Molality	E.M.F. millivolts (average)	$y_{\pm}$	$\gamma_{\pm}$	$\gamma_{\pm}$ (Debye-Hückel)[a]
0.03444	0.03456	52.198	0.4092	0.4090	0.4097
0.02296	0.02304	47.806	0.4556	0.4554	0.4526
0.01722	0.01728	44.366	0.4825	0.4824	0.4844
0.009763	0.009794	37.716	0.5483	0.5482	0.5494
0.005740	0.005758	31.263	0.6122	0.6122	0.6106
0.003445	0.003455	24.703	0.6677	0.6676	0.6673
0.002296	0.002303	19.303	0.7082	0.7082	0.7098
0.001722	0.001727	15.463	0.7386	0.7386	0.7380
0.0009763	0.0009793	7.602	0.7894	0.7894	0.7885
0.0005740[b]	0.0005757	0.000	0.8286	0.8286	0.8292

[a] The least-squares value of $\overset{\circ}{\underline{a}}$ is 5.32 Angstroms.

[b] Reference concentration.

Table 18.

E.M.F. Data and Activity Coefficients of Holmium Chloride at 25° C.

Molarity	Molality	E.M.F. millivolts (average)	$y_{\pm}$	$\gamma_{\pm}$	$\gamma_{\pm}$ (Debye-Hückel)[a]
0.03411	0.03423	-12.689	0.4307	0.4305	0.4320
0.02275	0.02283	- 8.110	0.4715	0.4714	0.4722
0.01707	0.01712	- 4.902	0.5058	0.5057	0.5021
0.01137[b]	0.01140	0.000	0.5466	0.5466	0.5458
0.005689	0.005707	8.509	0.6224	0.6224	0.6214
0.003412	0.003423	15.049	0.6768	0.6767	0.6755
0.002275	0.002282	20.410	0.7167	0.7167	0.7162
0.001707	0.001712	24.308	0.7427	0.7427	0.7434
0.001137	0.001141	29.878	0.7786	0.7786	0.7790

[a] The least-squares value of $\overset{\circ}{\underline{a}}$ is 6.04 Angstroms.

[b] Reference concentration.

Table 19.

E.M.F. Data and Activity Coefficients of Erbium Chloride at 25° C.

Molarity	Molality	E.M.F. millivolts (average)	$\underline{\underline{y_{\pm}}}$	$\underline{\gamma_{\pm}}$	$\gamma_{\pm}$ (Debye-Hückel)[a]
0.03628	0.03640	46.284	0.4220	0.4218	0.4225
0.02266	0.02273	41.028	0.4698	0.4697	0.4695
0.01814	0.01819	38.460	0.4932	0.4931	0.4928
0.01360	0.01364	35.110	0.5248	0.5247	0.5239
0.009069	0.009096	30.297	0.5705	0.5705	0.5684
0.003626	0.003637	18.794	0.6692	0.6692	0.6679
0.002267	0.002274	12.595	0.7150	0.7150	0.7156
0.001814	0.001819	9.609	0.7368	0.7368	0.7369
0.0009065[b]	0.0009091	0.000	0.7929	0.7929	0.7969

[a] The least-squares value of $\overset{\circ}{\underline{a}}$ is 5.92 Angstroms.

[b] Reference concentration.

Table 20.

E.M.F. Data and Activity Coefficients of Thulium Chloride at 25° C.

Molarity	Molality	E.M.F. millivolts (average)	$\underline{y}_{\pm}$	$\underline{\gamma}_{\pm}$	$\gamma_{\pm}$ (Debye-Hückel)[a]
0.02172	0.02178	47.866	0.4710	0.4708	0.4713
0.01409	0.01414	42.821	0.5167	0.5166	0.5177
0.008673	0.008700	37.097	0.5739	0.5738	0.5716
0.005421	0.005437	31.266	0.6256	0.6255	0.6236
0.003253	0.003263	24.708	0.6795	0.6795	0.6783
0.002170	0.002176	19.353	0.7198	0.7198	0.7191
0.001409	0.001413	13.505	0.7599	0.7599	0.7594
0.0008673	0.0008699	6.745	0.7989	0.7988	0.7999
0.0005421[b]	0.0005437	0.000	0.8291	0.8291	0.8344

[a] The least-squares value of $\overset{\circ}{\underline{a}}$ is 5.81 Angstroms.

[b] Reference concentration.

Table 21.

E.M.F. Data and Activity Coefficients of Ytterbium Chloride at 25° C.

Molarity	Molality	E.M.F. millivolts (average)	$y_{\pm}$	$\gamma_{\pm}$	$\gamma_{\pm}$ (Debye-Hückel)[a]
0.03405	0.03393	51.380	0.4266	0.4264	0.4279
0.02496	0.02490	47.918	0.4585	0.4583	0.4589
0.01514	0.01509	42.303	0.5164	0.5163	0.5117
0.009828	0.009798	37.102	0.5617	0.5616	0.5591
0.006053	0.006035	30.991	0.6088	0.6087	0.6125
0.003403	0.003393	23.822	0.6772	0.6772	0.6744
0.002496	0.002488	19.718	0.7070	0.7070	0.7060
0.001513	0.001508	12.961	0.7531	0.7531	0.7534
0.0009828	0.0009799	7.051	0.7919	0.7919	0.7904
0.0006049	0.0006032	0.000	0.8179	0.8179	0.8271

[a] The least-squares value of $\overset{\circ}{a}$ is 5.90 Angstroms.

[b] Reference concentration.

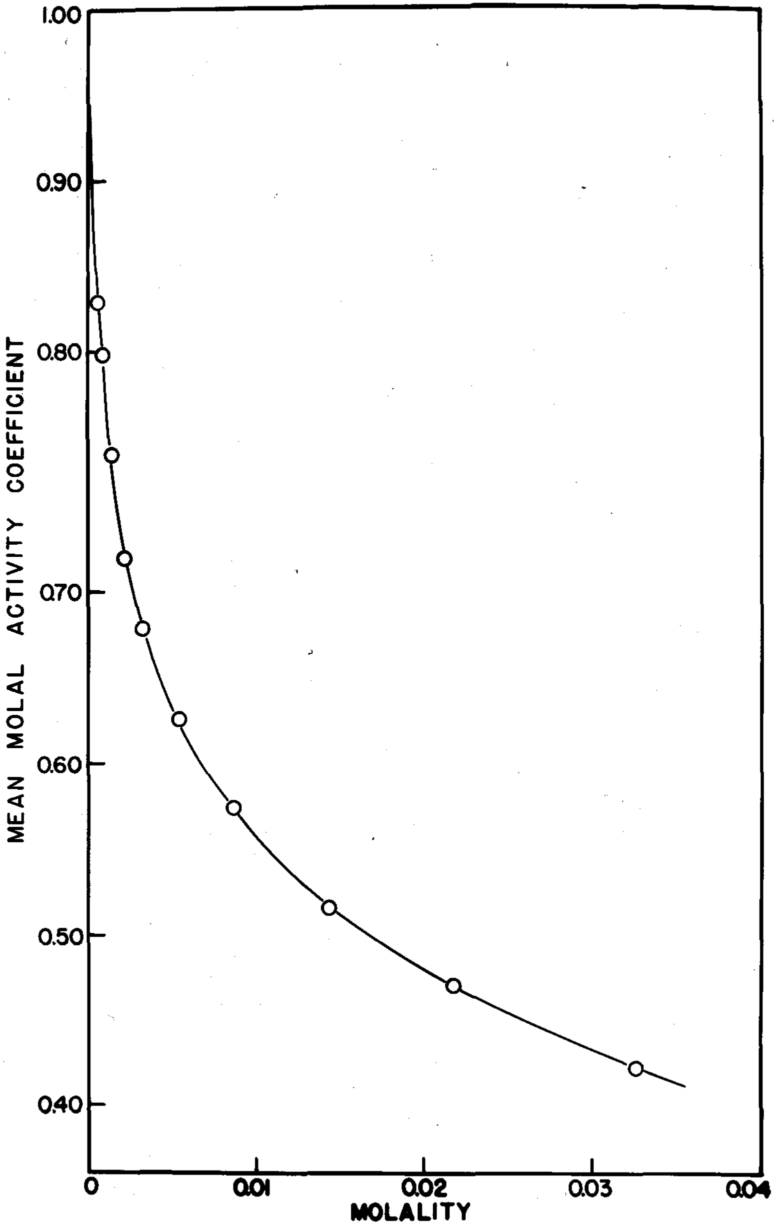


Figure 13. Mean Molal Activity Coefficient of Thulium Chloride at 25° C.

about 0.2 per cent, although some of this "error" may come about because the theory is not entirely adequate to describe the activity coefficients over the whole range of concentrations.

The values of $\overset{o}{\underline{a}}$, the mean distance of closest approach of the ions, do not show the regularity that one would expect from the precision of the data. In general, however, the higher molecular weight rare earth chlorides have larger values of $\overset{o}{\underline{a}}$ than the lower members of the series. In spite of this, dysprosium chloride has the lowest value of $\overset{o}{\underline{a}}$ of any member of the series. This is not believed to be due to an error in the measurements since the precision in this case was quite good as is shown by Figure 12. It is possible that the activity variations described above are real, and due to differences in the electrostatic fields about the ions, or it may just be that the values of $\overset{o}{\underline{a}}$ are more sensitive to experimental error than was believed to be the case. It will be of interest to examine partial molar volume data in this connection when it becomes available.

VI. PROPOSED EXTENSION OF THE MATHEMATICS OF ONSAGER'S THEORY OF CONDUCTANCE AND TRANSFERENCE

A. Introduction

It has been noted in this thesis and elsewhere (56, p. 163,123), that Onsager's equation fails when applied to the transference numbers of 2-1, 1-2, and 3-1 electrolytes, even though it predicts satisfactorily the transference number behavior of 1-1 electrolytes. Because of this dependence of the agreement of theory and experiment upon charge type, it was deemed advisable to re-examine the mathematical development of Onsager's theory of conductance and transference. When this was done, it was found that the expansion of the exponential in equation (39) and the subsequent neglect of terms higher than first order, becomes invalid even at low concentrations for unsymmetrical electrolytes. For this reason, a treatment of the mathematics was carried out, which accounted, to a large degree, for the discrepancy which had existed between the calculated and experimental transference numbers of unsymmetrical electrolytes. Instead of expanding equation (39) and integrating analytically, this equation was put into a form which permitted graphical integration.

B. Development of the Theory

In the section of this thesis dealing with the general theory, there was developed the following equation relating the velocity of the ionic atmosphere to the distance from the ion under consideration:

$$dV_j = \frac{dF}{6\pi\eta r} = \frac{2Xr}{3\eta}\left[\sum_{i=1}^{s} e_i(n_{ji} - n_i)\right] dr \ , \qquad (90)$$

in which

η is the viscosity of the solvent.

r is the distance from the central, j, ion.

X is the potential gradient in volts per cm.

e_i is the charge on the ith ion, and is positive for positive ions, and negative for negative ions.

n_{ji} is the concentration of ions of the ith kind near the central j ion, and is different from n_i, the average concentration of i ions in the solution, only because of the field of the j ion and its atmosphere.

The total velocity change due to the movement of the atmosphere is the integral of (90) from the distance of closest approach, a, to infinity:

$$\Delta V_j = \frac{2X}{3\eta}\int_a^{\infty} r\left[\sum_{i=1}^{s} (n_{ji} - n_i)e_i\right] dr \ . \qquad (91)$$

Utilizing the equations relating the velocity of an ion to its ionic equivalent conductance,

$$u_j = V_j/300\ X \quad , \qquad (920$$

and

$$\lambda_j = 96{,}500\ u_j \quad , \qquad (93)$$

we obtain the following equation for the electrophoretic correction, $\Delta\lambda_j$, to the ionic equivalent conductance of the jth ion:

$$\Delta\lambda_j = \frac{96{,}500}{450\,\eta}\int_a^{\infty} r\left[\sum_{i=1}^{s}(n_{ji} - n_i)e_i\right]\ dr. \qquad (94)$$

Employing equations (39) and (28), which are

$$n_{ji} = n_i\ \exp\left[-\frac{e_i\,\psi_j^o}{kT}\right] , \qquad (39)$$

and

$$\psi_j^o = \left[\frac{e_j\ e^{\kappa a}}{D\ (1 + \kappa a)}\right]\cdot\left[\frac{e^{-\kappa r}}{r}\right] , \qquad (28)$$

we obtain, by combination with equation (94),

$$\Delta\lambda_j = \frac{96{,}500}{450\,\eta}\int_a^{\infty} r\left\{\sum_{i=1}^{s} n_i e_i\left[\exp\left(-\frac{e_i e_j\ e^{\kappa a}}{DkT(1+\kappa a)}\ \frac{e^{-\kappa r}}{r}\right) - 1\right]\right\} dr\ . \qquad (95)$$

Define the following quantities:

$\rho = \kappa r$

$x = \kappa a$

ϵ is the charge on the electron.

z_i has the sign of the charge on the *ith* ion, and a magnitude equal to the number of electronic charges carried by the *ith* ion.

Employing these definitions and equation (95), one obtains the general expression for the electrophoretic correction to the conductance of the *jth* ion:

$$\Delta\lambda_j = \frac{96{,}500}{450\eta\kappa^2}\int_x^\infty \rho\left\{\sum_{i=1}^{s} n_i e_i\left[\exp\left(-\,z_i z_j\,\frac{\kappa e^x \epsilon^2}{DkT(1+x)}\,\frac{e^{-\rho}}{\rho}\right)-1\right]\right\}d\rho. \tag{96}$$

For an electrolyte which dissociates into ν ions by the scheme

$$M_{\nu_+}A_{\nu_-} \longrightarrow \nu_+ M^{z_+} + \nu_- A^{z_-},$$

we may specialize equation (96). Let

$$P = \frac{\kappa e^x \epsilon^2}{DkT(1+x)}. \tag{97}$$

It is to be noted that by virtue of $x = \kappa a$, and the definition of κ, P is dependent upon the concentration of the electrolyte, the distance of closest approach, the dielectric constant, and the temperature. For the electrophoretic correction to the conductance of the positive ion of an electrolyte which dissociates into only two kinds of ions, equation (96) then becomes

$$\Delta\lambda_+ = \frac{96{,}500}{450\eta\kappa^2}\int_x^{\infty}\left\{ n_+e_+\,\rho\left[\exp\left(-\,z_+z_+P\,\frac{e^{-\rho}}{\rho}\right)-1\right] + \right.$$

$$\left. +\,n_-e_-\,\rho\left[\exp\left(-\,z_+z_-P\,\frac{e^{-\rho}}{\rho}\right)-1\right]\right\}d\rho\,. \tag{98}$$

Furthermore, for an electrolyte of this type,

$$z_- = -|z_-|\ ; \qquad n_+e_+ = \frac{\nu_+z_+CN\epsilon}{1000}\ ; \qquad n_-e_- = \frac{\nu_-z_-CN\epsilon}{1000}$$

and

$$\nu_+z_+ = -\,\nu_-z_-\ ,$$

in which C is the concentration in moles per liter, and N is Avogadro's number. Utilizing these quantities, equation (98) becomes

$$\Delta\lambda_+ = \frac{96{,}500\ CN\epsilon\,\nu_+z_+}{10^3\cdot 450\eta\kappa^2}\int_x^{\infty}\rho\left\{\exp\left[-\,(z_+)^2\,P\,\frac{e^{-\rho}}{\rho}\right]\right.$$

$$\left. -\,\exp\left[|z_+z_-|\,P\,\frac{e^{-\rho}}{\rho}\right]\right\}d\rho\ . \tag{99}$$

The definition of κ^2, which is given by equation (24) is

$$\kappa^2 = \frac{4\pi\epsilon^2}{DkT} \sum_{i=1}^{s} n_i z_i^2 = \frac{4\pi\epsilon^2 NC}{10^3 DkT} \left[\nu_+ z_+^2 + \nu_- z_-^2 \right] , \qquad (100)$$

and we may define

$$M = \frac{96{,}500 \; CN \epsilon \, \nu_+ z_+}{10^3 \cdot 450 \, \eta \, \kappa^2} = \frac{96{,}500 \; CN \epsilon \, \nu_+ z_+}{10^3 \cdot 450 \, \eta} \cdot \frac{10^3 \; DkT}{4\pi\epsilon^2 NC(\nu_+ z_+^2 + \nu_- z_-^2)} ,$$

and introducing the relationship

$$|\nu_+ z_+| = |\nu_- z_-| ,$$

we obtain

$$M = \frac{96{,}500 \; DkT}{1800 \; \pi \eta \epsilon (|z_+| + |z_-|)} . \qquad (101)$$

The final expression for the electrophoretic correction to the conductance of the positive ion of the salt $\underline{M_{\nu_+} A_{\nu_-}}$ is

$$\Delta\lambda_+ = M \int_x^\infty \rho \left\{ \exp\left[-(z_+)^2 P \frac{e^{-\rho}}{\rho} \right] - \exp\left[|z_+ z_-| P \frac{e^{-\rho}}{\rho} \right] \right\} d\rho , \qquad (102)$$

and the correction for the negative ion is

$$\Delta\lambda_- = M \int_x^\infty \rho \left\{ \exp\left[-(z_-)^2 P \frac{e^{-\rho}}{\rho} \right] - \exp\left[|z_+ z_-| P \frac{e^{-\rho}}{\rho} \right] \right\} d\rho . \qquad (103)$$

We may let the integrands of equations (102) and (103) be represented by G_+ and G_- respectively. The correction can then be determined at any specified concentration, by the graphical integration of a plot of G_+ against ρ, and G_- against ρ, from $x = \kappa a$ to infinity. It must be remembered that M is dependent upon the charge type of the electrolyte, and P is dependent also on the value of the distance of closest approach and the concentration. A typical plot of G_+ and G_- against ρ is shown for 0.00333 molar neodymium chloride, in Figure 14.

One can obtain the area under the curve from a large value of ρ to infinity analytically instead of graphically, thus eliminating a possible source of error. Let F_+ be the area under the curve G_+ from a large value of ρ, say B, to infinity. Then by equation (102)

$$F_+ = M \int_B^{\infty} \rho \left\{ \exp - \left[|z_+|^2 \, P \, \frac{e^{-\rho}}{\rho} \right] - \exp \left[|z_+ z_-| \, P \, \frac{e^{-\rho}}{\rho} \right] \right\} d\rho \ . \qquad (104)$$

For large values of ρ, $e^{-\rho}/\rho$ becomes very small, and we may expand the exponentials in power series, and neglect all terms higher than the first order. This gives

$$F_+ = M \int_B^{\infty} \rho \left[1 - \left(|z_+|^2 \, P \, \frac{e^{-\rho}}{\rho} \right) - 1 - \left(|z_+ z_-| \, P \, \frac{e^{-\rho}}{\rho} \right) \right] d\rho$$

$$F_+ = - M \, P \, (|z_+|^2 + |z_+ z_-|) \, e^{-B} \ . \qquad (105)$$

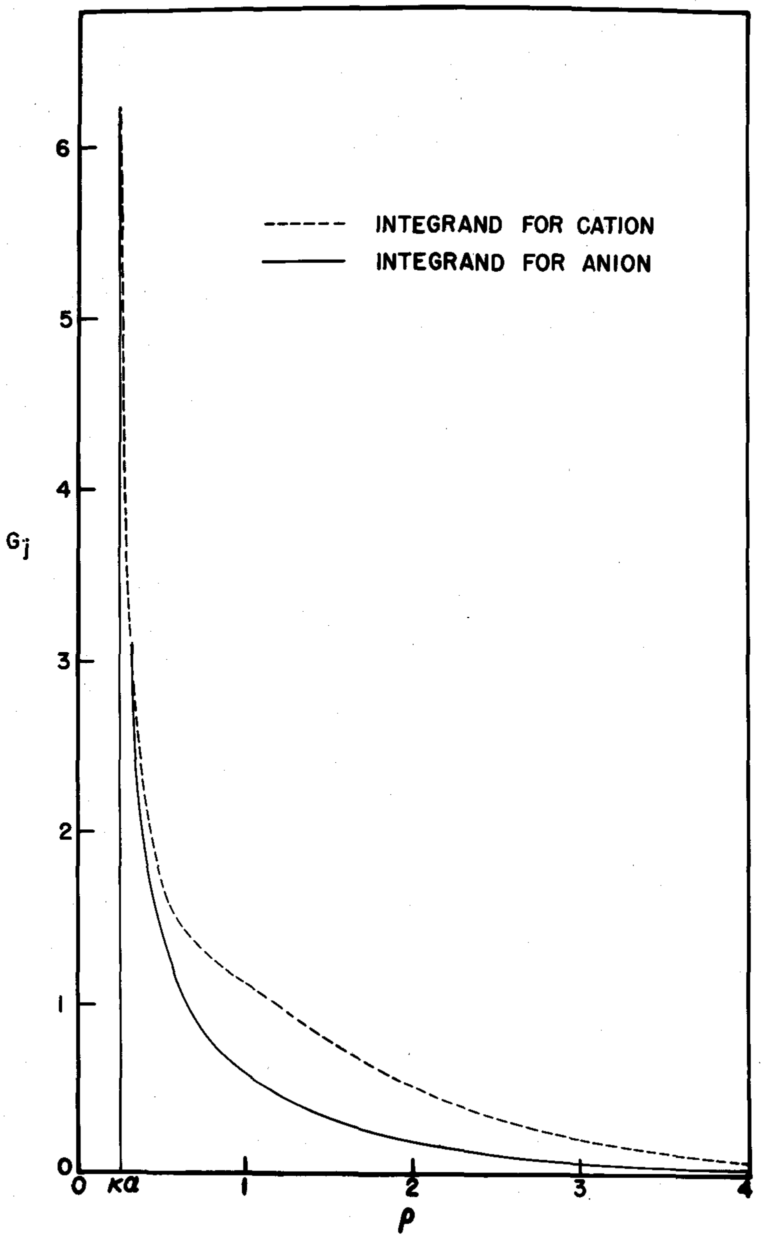


Figure 14. Typical Integrands of the Equations Expressing the Electrophoretic Correction to the Anionic and Cationic Conductances of a 3-1 Electrolyte. $\overset{\circ}{\underline{a}}$ = 5.49 Angstroms; C = 0.00333 Molar.

It is not necessary to perform new graphical integrations for each value of a used in this treatment. To determine the electrophoretic correction at a value of a different from that used in obtaining the graph, one uses the same graphical integration but with a different lower limit, and at a slightly different concentration. This concentration is determined from κ in the expression for P. For the case of 3-1 electrolytes,

$$P = 7.135 \times 10^{-8} \frac{\kappa e^{\kappa a}}{(1 + \kappa a)} \quad . \qquad (106)$$

The same value of P that was used in the original graphical integration is used to solve for κ by successive approximations, using the new value of a, and equation (106). The integral from the old lower limit of ρ, $\kappa' a'$, to the new lower limit, κa, is determined graphically. This method was used to determine the corrections for erbium chloride from the graphs prepared for neodymium chloride.

Having obtained expressions for $\Delta\lambda_+$ and $\Delta\lambda_-$ due to electrophoresis, we may combine them with the time of relaxation corrections as was done in equation (46) and obtain expressions for the individual ionic conductances, λ_+, and λ_-, from which Λ and T_+ can be obtained. The theoretical quantities determined by this method can thus be compared with experiment.

C. Comparison with Experiment

The values of $\underline{\lambda_+}$, $\underline{\lambda_-}$, $\underline{\Lambda}$, and $\underline{T_+}$, for neodymium chloride, erbium chloride, and calcium chloride, were calculated by the method outlined above, using values of a obtained from activity coefficient measurements.

The values of a used for neodymium chloride and erbium chloride were taken from data reported in the section of this thesis dealing with activity coefficients. Transference and conductance data, for comparison purposes, were also taken from this thesis.

The value for a for calcium chloride is listed as 4.575×10^{-8} cm. by McLeod and Gordon (107) and was obtained from measurements of the E.M.F. values of cells with transference. Transference data for calcium chloride were obtained from measurements by Allgood, LeRoy, and Gordon (108) and Longsworth (109). Conductivity data for calcium chloride were obtained from measurements by Shedlovsky and Brown (110).

Tables 22 and 23 give the values of the conductances and transference numbers of neodymium chloride, erbium chloride, and calcium chloride, calculated by this method as well as those calculated using the simple Onsager Equation. The smoothed experimental values are also listed as well as the per cent deviations of the calculated values from experiment. The table for calcium chloride transference numbers gives the average of the values obtained by Allgood, LeRoy, and

Table 22.

Comparison of Theoretical and Observed Conductances of Neodymium Chloride, Erbium Chloride, and Calcium Chloride at 25° C.

Salt	Normality	Measured conductance	Calculated conductance		Per cent deviation	
			Onsager	Extended	Onsager	Extended
$NdCl_3$	0.00009294	143.1	142.91	143.05	0.14	0.03
	0.0003340	137.1	136.88	137.37	0.16	0.20
	0.003507	130.4	129.14	130.53	1.00	0.10
	0.01002	122.1	117.72	121.05	3.6	0.80
	0.03506	109.9	93.35	103.87	15.0	5.5
	0.07520	102.1	69.06	89.50	32.3	12.3
$ErCl_3$	0.00009291	139.7	139.64	139.77	0.04	0.05
	0.0009993	134.0	134.22	133.59	0.33	0.16
	0.003489	127.5	126.03	127.72	1.2	0.17
	0.009945	119.3	114.84	118.76	3.8	0.42
	0.03423	108.2	91.37	102.73	15.5	1.1
	0.07257	99.6	68.15	89.44	31.6	10.2
$CaCl_2$	0.0001000	134.1	134.06	134.08	0.03	0.01
	0.0009000	130.6	130.53	130.76	0.05	0.12
	0.002114	128.0	127.71	128.09	0.24	0.07
	0.01000	120.3	118.16	119.38	1.7	0.76
	0.02000	115.6	110.85	113.49	4.1	1.7
	0.04000	110.3	100.50	105.47	8.9	4.3

Table 23.

Comparison of Theoretical and Observed Transference Numbers of Neodymium Chloride, Erbium Chloride, and Calcium Chloride at 25° C.

Salt	Normality	T_+ measured	T_+ calculated		Per cent deviation	
			Onsager	Extended	Onsager	Extended
$NdCl_3$	0.00009294	----	0.4731	0.4738	---	---
	0.0003340	----	0.4655	0.4695	---	---
	0.003507	----	0.4551	0.4657	---	---
	0.01002	0.4650	0.4370	0.4592	4.8	1.2
	0.03506	0.4542	0.3833	0.4469	14.2	1.6
	0.07520	0.4440	0.2924	0.4339	32.6	2.3
$ErCl_3$	0.00009291	----	0.4605	0.4610	---	---
	0.0009993	----	0.4524	0.4563	---	---
	0.003489	----	0.4411	0.4522	---	---
	0.009945	0.4471	0.4217	0.4451	5.7	0.45
	0.03423	0.4366	0.3658	0.4318	16.2	1.1
	0.07257	0.4262	0.2723	0.4182	36.1	1.9
$CaCl_2$	0.0001000	----	0.4361	0.4364	---	---
	0.0009000	----	0.4322	0.4329	---	---
	0.002114	----	0.4289	0.4313	---	---
	0.01000	0.4271	0.4167	0.4245	2.4	0.60
	0.02000	0.4226	0.4060	0.4206	3.9	0.50
	0.04000	0.4167	0.3850	0.4120	7.6	1.1

Gordon (108), and Longsworth (109). The transference numbers as calculated and measured are plotted in Figures 16 through 18. The calculated and observed conductances of erbium chloride are plotted in Figure 15. The calculated results for the conductance of neodymium chloride and calcium chloride are in similar agreement with experiment.

D. Discussion of Results

Figures 15, 16, 17, and 18, and Tables 22 and 23 show that the new calculated values for the transference numbers agree with experiment much better than those calculated using the simple Onsager Equation, while the fit of conductance data is also improved. The calculation of the individual ionic conductances using the extended equation, results in quite different values than are obtained using the simple equation, even at low concentrations where the simple equation begins to give the correct total conductance. If the distance of closest approach, $\overset{\circ}{\underline{a}}$, is not neglected in the original Onsager Equation (42), much better agreement with the total conductance is obtained, while there is little improvement in the agreement with the individual ionic conductances. This is shown in Figure 19 where the electrophoretic contribution to the conductance of neodymium chloride is plotted as a function of concentration, for the anion, the cation, and the total salt. It is seen that while the

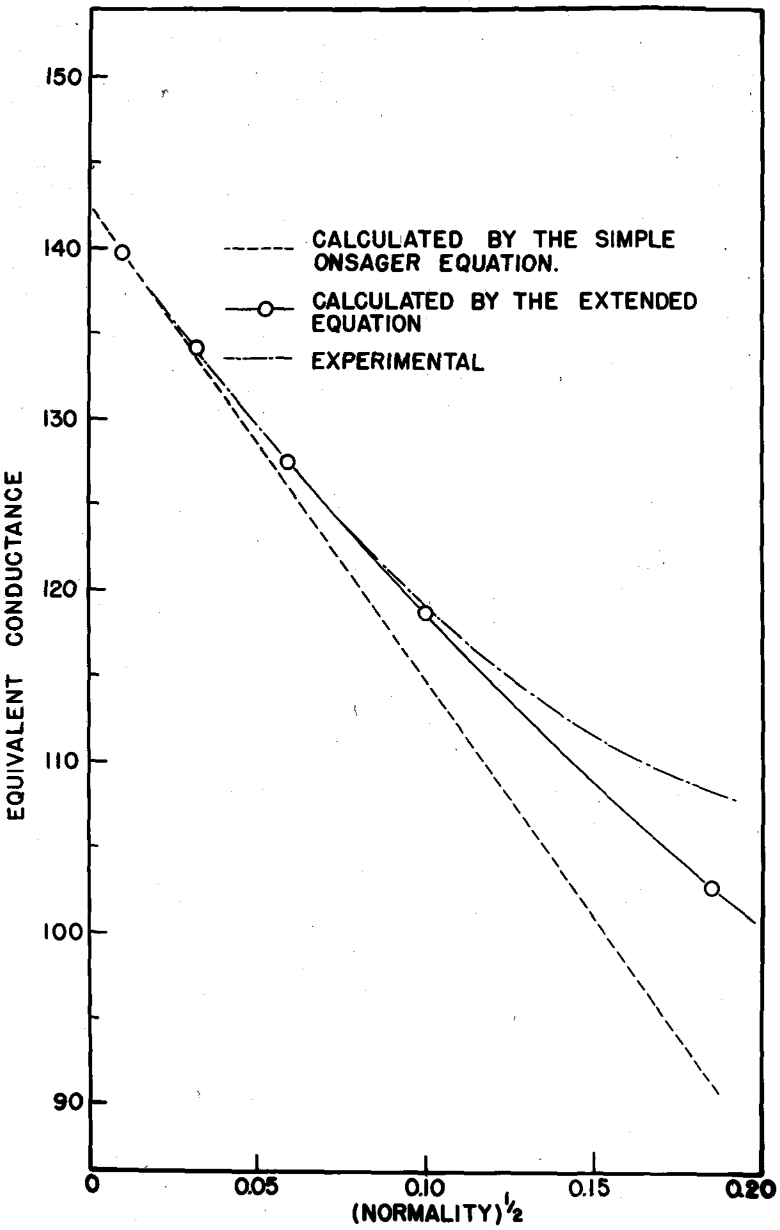


Figure 15. Comparison of Theoretical and Observed Equivalent Conductances of Erbium Chloride at 25° C.

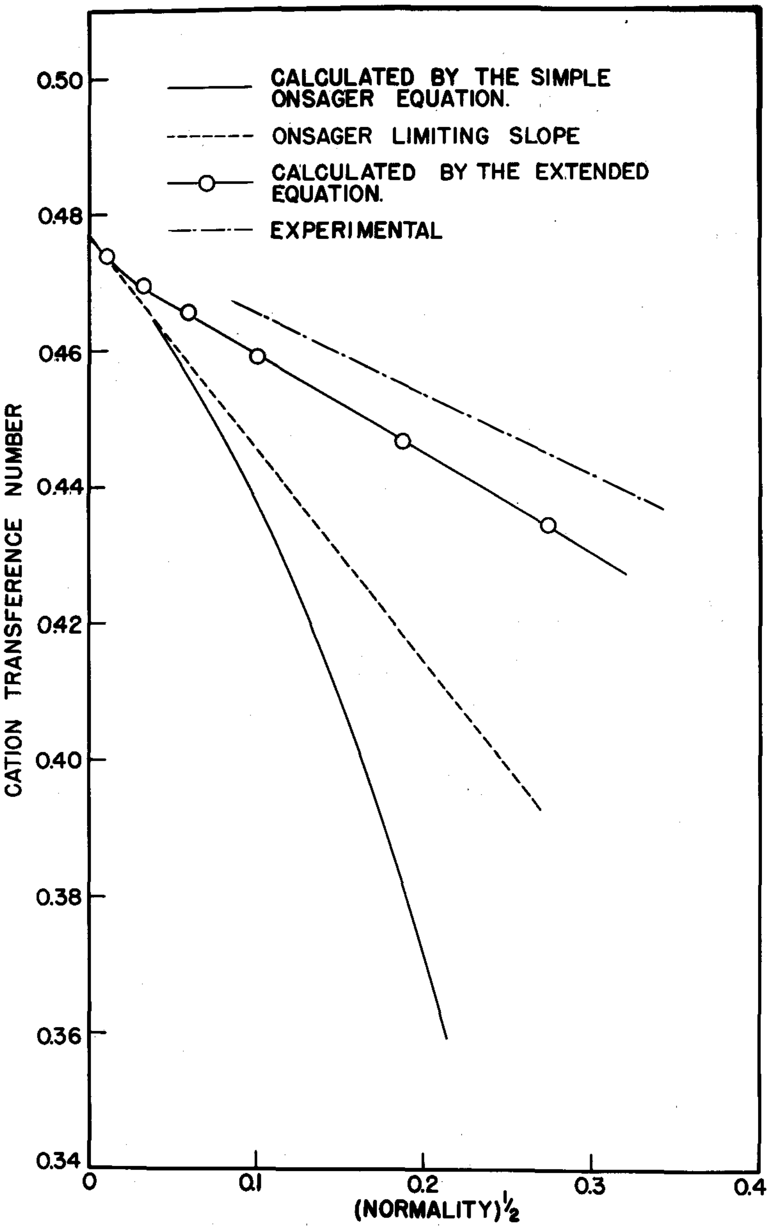


Figure 16. Comparison of Theoretical and Observed Transference Numbers of Neodymium Chloride at 25° C.

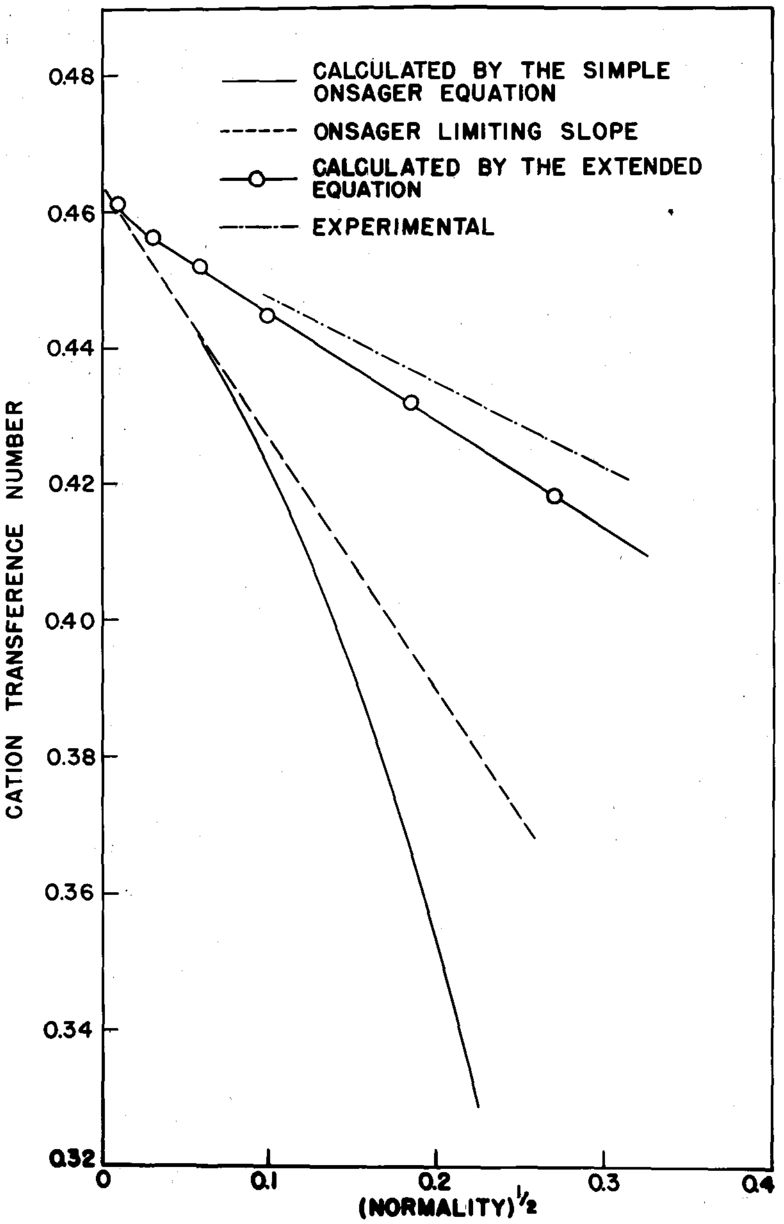


Figure 17. Comparison of Theoretical and Observed Transference Numbers of Erbium Chloride at 25° C.

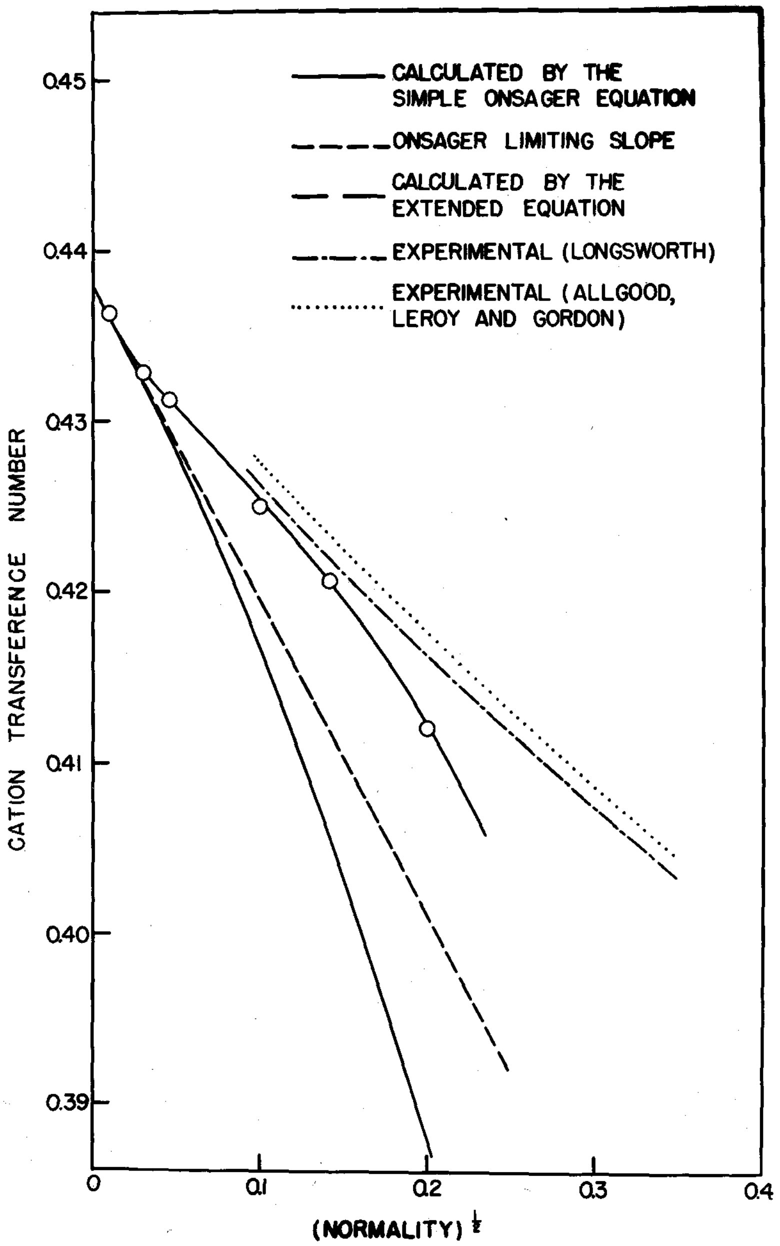


Figure 18. Comparison of Theoretical and Observed Transference Numbers of Calcium Chloride at 25° C.

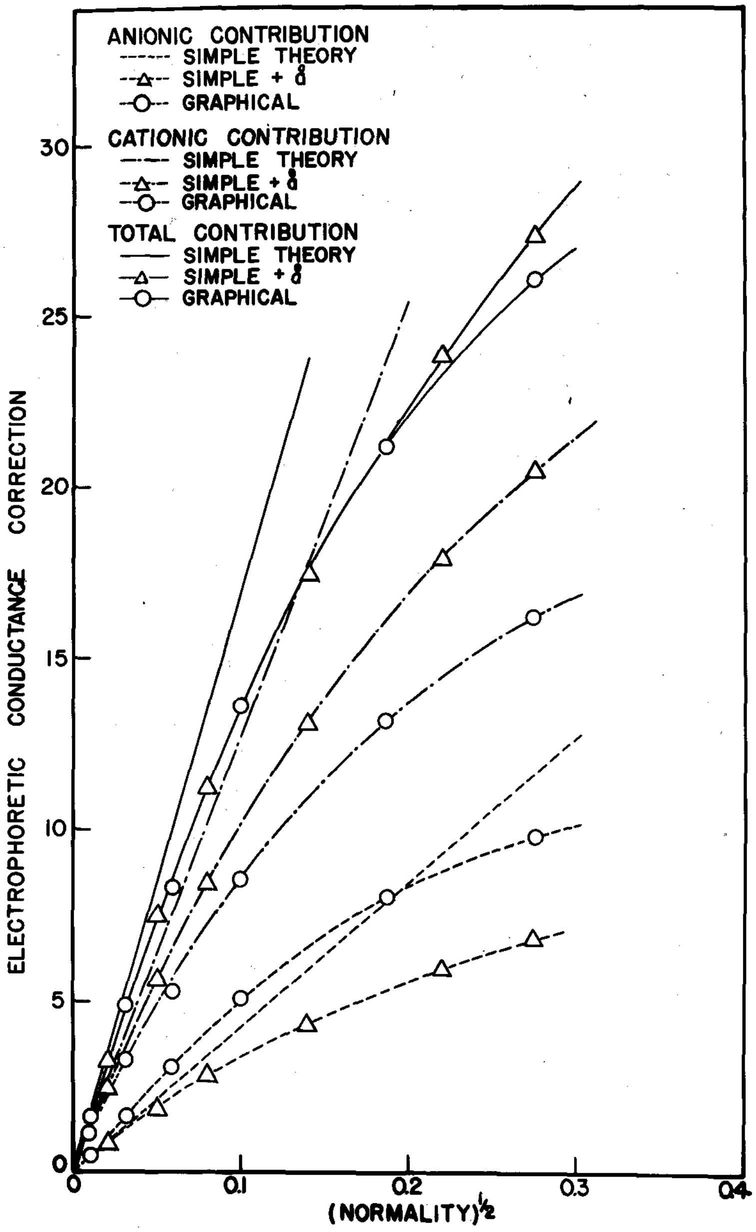


Figure 19. Calculated Electrophoretic Correction to the Conductance of a 3-1 Electrolyte; å = 5.49 Angstroms.

extended calculations agree with the simple Onsager Equation when it includes $\underline{\overset{\circ}{a}}$ (called, simple theory plus $\underline{\overset{\circ}{a}}$), for the total conductance, there exist large discrepancies for the individual ionic conductances.

The term, referred to as $\underline{\text{simple} + \overset{\circ}{a}}$, is also the first term of an expansion of the exponential in the general expressions (102) and (103), and because of the close fit for the total conductance, it was desired to know whether the agreement was accidental, or a consequence of the mathematics. A plot of the integrand of the complete equation (102 plus 103), and also of only the first term ("simple + $\overset{\circ}{a}$") of an expansion of the exponential, as a function of $\underline{\rho}$, is given for 0.01169 molar neodymium chloride in Figure 20. From this it is seen that the integrals are equal only because the shaded areas are approximately equal, and that the integrands of the two equations are not the same. Because of this, it seems that the agreement is good in the simple case because of a fortuitous cancellation of areas, rather than a necessary consequence of the theory. In addition, calculations of this type for other values of $\underline{\overset{\circ}{a}}$, do not show the same agreement that was obtained for this case of $\underline{\overset{\circ}{a} = 5.49\ \text{Å}}$. It seems that such agreement is obtained only for values of $\underline{\overset{\circ}{a}}$ around six Angstroms, and is not a general phenomenon.

The contribution of the electrophoretic effect to the conductance of a salt depends upon the value of $\underline{\overset{\circ}{a}}$, which is the same parameter that is used in the Debye-Hückel Theory of

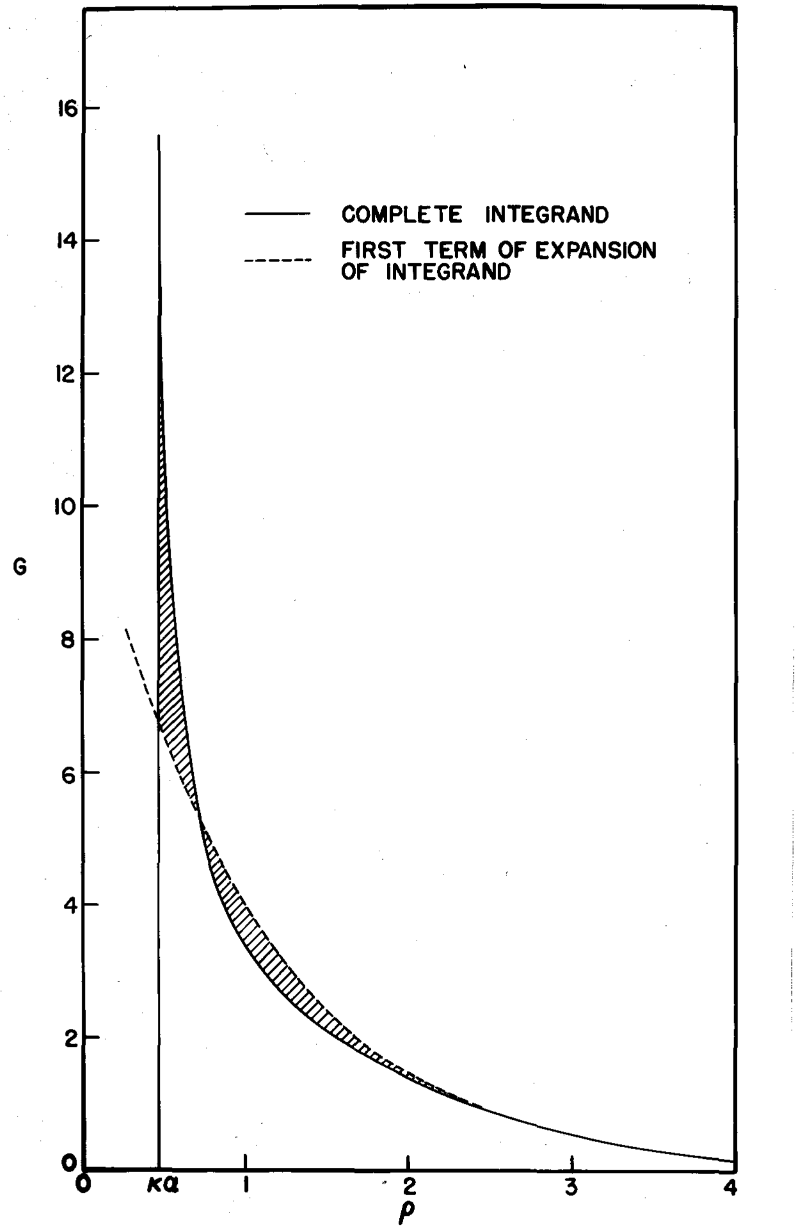


Figure 20. Comparison of the Integrand of the Simple Onsager Equation (Including $\mathring{\underline{a}}$) with the Total Integrand for a 3-1 Electrolyte. $\mathring{\underline{a}}$ = 5.49 Angstroms; C = 0.01169 Molar.

activity coefficients. It may be possible to determine $\overset{o}{\underline{a}}$ from conductance measurements by finding the best fit of the conductance data of solutions with concentrations below about 0.008 normal where the extended equation holds for the chlorides. This method is being applied to the conductances of rare earth nitrates and perchlorates (111).

The original Onsager Equation explains the transference number behavior of 1-1 electrolytes quite well. This is because the low charges on the ions result in small exponents in the integrand of equations (102) and (103), and also because the second term, and all even terms of an expansion of the exponent, disappear for a symmetrical electrolyte. Another factor which contributes to the good agreement of theory with transference number data for 1-1 electrolytes is that, for symmetrical electrolytes, both the simple and the extended equation demand equal contributions to the conductance from the cation and anion.

The calculations described in this section are of value because they show that the underlying assumptions made by Onsager are valid at higher concentrations than was previously thought to be the case. It will be necessary to know the extent of validity of the present physical assumptions when an attempt is made to extend present theories of conductance.

VII. GENERAL SUMMARY

The conductances, transference numbers, and activity coefficients of aqueous solutions of some rare earth chlorides at the equivalence pH, were measured at concentrations up to 0.1 normal. The measurements were made on the chlorides of neodymium, dysprosium, holmium, erbium, thulium, and ytterbium. In addition to these measurements, a new mathematical treatment of the electrophoretic part of the Onsager Theory of conductance was carried out. This resulted in better agreement between the theoretical and experimental values of the transference numbers and conductances. The rare earth chloride solutions were brought to the equivalence pH value before measurement of the properties was undertaken. This equivalence pH value was determined by titration of an aliquot of the stock solution with acid. The titration was followed with a pH meter. It was found that the clear "solutions", at pH values of 6 to 6.5, which had been previously made by dissolving anhydrous rare earth chlorides in water in a closed system, actually contained small amounts of colloidal oxide or basic salt. This was negligible for the light members of the rare earth series, but exceeded by a small amount the normal experimental errors for the heavier members of the series. The small effect of this deviation was demonstrated by repeating the measurements which had been made previously, on neodymium chloride, erbium chloride, and ytterbium chloride.

The conductances were measured, using a Jones bridge and its accessories, for solutions ranging from 0.003 normal to 0.1 normal in concentration. Since these measurements were made at the equivalence pH values, which were below the neutral point, a correction for conduction of current by the hydrogen ion was necessary for low concentrations. The equivalent conductances obeyed the simple Onsager Equation up to about 0.0008 normal and agreed with the new mathematical treatment of Onsager's Theory up to about 0.008 normal.

The transference numbers were determined by the moving boundary method for solutions from 0.01 normal to 0.1 normal in concentration. The simple Onsager Equation predicted much lower transference numbers than were measured. When the mathematical extension of the theory of Onsager was developed, however, the theory agreed with the experimental values much more closely.

The conductances and transference numbers both exhibit similar changes with atomic number. The experimental values of both the transference numbers and the equivalent conductances at any concentration remain nearly unchanged for the first five or six rare earth chlorides. A relatively large change in these properties then takes place between samarium chloride and holmium chloride, and again the values remain nearly unchanged for holmium, erbium, thulium and ytterbium chlorides. This probably is due to changes in the hydration number of the rare earth ion, but has not been fully explained as yet. It would be of interest to study further the structure of the hydrated chlorides in this connection.

The activity coefficients were determined by a measurement of the E.M.F. of cells with transference in the concentration range, 0.002 normal to 0.1 normal. The experimentally obtained activity coefficients were found to agree with the predictions of the Debye-Hückel Theory throughout this range with a precision of about ± 0.2 per cent. The values of $\overset{o}{a}$, the distance of closest approach of the ions, indicate that the rare earth ion has one layer of water molecules which adheres rather firmly to the central ion. The $\overset{o}{a}$ values obtained from the experiments do not increase or decrease in a regular fashion throughout the series, but are larger for the high atomic number rare earth chlorides than for the lower members of the series.

A new mathematical treatment of the electrophoretic part of Onsager's Theory of conductance is described, which employs graphical methods to evaluate integrals which were only approximately evaluated by Onsager. The approximate methods, while satisfactory for 1-1 electrolytes, are unable to explain the transference number behavior of unsymmetrical electrolytes. The extension of the mathematics resulted in much better agreement of experiment with theory for the transference numbers of unsymmetrical electrolytes. This treatment of the theory was applied to the conductances and transference numbers of neodymium chloride, erbium chloride, and calcium chloride. The calculated conductances agreed with the experimental values up to about 0.008 normal, compared with agreement to about 0.0008 normal in the case of the simple theory. The calculated transference numbers agreed well enough with the experimental values to explain the large discrepancy which had existed between theory and experiment for the transference numbers of unsymmetrical electrolytes. In addition, the possibility of determining the mean distance of closest approach of the ions, $\overset{\circ}{\underline{a}}$, from conductance measurements was recognized. This would make it possible to calculate activity coefficients from conductance measurements using the equation of Debye and Hückel which includes the parameter $\overset{\circ}{\underline{a}}$. These calculated activity coefficients should certainly be better than those obtained from the simple limiting law, since the theoretical basis for the inclusion of $\overset{\circ}{\underline{a}}$ in the theories of both activity coefficients and conductances, demands a single value for $\overset{\circ}{\underline{a}}$.

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