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Conductances and transference numbers of some rare earth perchlorates, sulfates and nitrates in aqueous solution

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CONDUCTANCES AND TRANSFERENCE NUMBERS OF SOME RARE EARTH PERCHLORATES, SULFATES AND NITRATES IN AQUEOUS SOLUTION

by

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I. INTRODUCTION

Most of the important modern theories that provide a better understanding of the behavior of strong electrolytes are based on the ionic atmosphere concept as developed by Debye and Hückel. The extended Debye-Hückel limiting law for activity coefficients has been shown to be quite adequate up to one tenth normal solutions for 3-1 electrolytes such as the rare earth halides (1, 2). However, activity coefficients are measured in equilibrium processes. Non-equilibrium properties such as transference numbers and electrolytic conductances for these salts show remarkable variations from theory at low concentrations. The limiting laws for transference numbers hold for these solutes only in very dilute solutions.

The behavior of strong electrolytes is explained only in very dilute solutions because of the many simplifying assumptions necessary to establish the theories and solve the mathematics. Such things as constant ionic mobilities and constant dielectric constant of the solvent may not prevail at higher concentrations. In addition, one should account for the effects of hydration of the ions, the formation of ion pairs and the existance of complex species in solution. Solutes of the uni-univalent type obey the existing limiting laws at moderately dilute concentrations while the few properties that have been measured for some more complex solutes show large deviations from these laws. Many more precise and accurate data should be obtained for polyvalent electrolytes before a complete theoretical explanation can be made to account for these departures from theory.

The study of the electrochemical properties of polyvalent electrolytes is limited because most common highly charged elements exhibit extensive hydrolysis in aqueous solution. Although the rare earths hydrolyze to a slight extent, they present a most desirable series of elements for investigation. The rare earth salts are easy to prepare from the purified rare earth oxides and they are easy to analyze accurately by well defined gravimetric procedures.

The chemistry of the rare earths along with scandium and yttrium differs only slightly from element to element. The only alteration in the series is the filling of the 4f electron shells as the nuclear charge is increased while the valence shells which determine the observed chemical properties remain relatively unchanged. This addition of 4f electrons with increasing atomic number accounts for the decrease in the ionic radius called the Lanthanide Contraction. Thus, the set of elements from lanthanum to lutetium provides an opportunity for studying the effects of ionic radius independently of other factors.

The lack of accurate physical and chemical measurements on the rare earths in the past may be attributed to the unavailability of pure rare earth salts. Since their chemistry is so much alike, they are very difficult to separate and purify in large amounts. In the past numerous and tedious fractionations were necessary to effect satisfactory separation. However, with the development at Iowa State College of excellent ion exchange techniques (3, 4, 5, 6, 7, 8), the rare earth salts have become available in multi-gram amounts and with spectrographic purity.

The purpose of this thesis is to study the electrolytic conductances and transference numbers of some rare earth perchlorates, nitrates and sulfates in order to extend the knowledge of complex unsymmetrical electrolytes. These data should prove invaluable in testing and verifying the applicability of present theories of strong electrolytes. They should also point the way towards extensions and improvements in the theories. Since the perchlorates and nitrates are assumed to be uncomplexed in dilute solutions, it is expected that the properties of these salts should comply with any theory that completely describes any ionic interaction between the rare earths and these anions. Extension of the theory to higher concentrations makes it possible to correlate many properties. This principle was used to evaluate the distances of closest approach of the various ions to each other in rare earth perchlorate and nitrate solutions by the application of an extension in the theory of conductance. Activity coefficients may now be calculated from conductance measurements for these salts even though they cannot be determined directly by experiment.

The rare earth sulfates show such marked deviations from the theories that any insight that would explain their behavior should be a great help towards a better understanding of the nature of electrolytic solutions. It is hoped that the data presented here will play some part in the solution of the many problems in the physical chemistry of electrolytes.

II. THEORIES AND HISTORIES OF METHODS

A. Introduction to the Interionic Attraction Theory

The early investigators in the field of solution chemistry realized that the colligative properties of electrolytes deviated from those of ideal solutions. Measurement of boiling point elevation, freezing point depression and osmotic pressure indicated to them that the number of particles in solution was greater than was expected from the molecular formula of the electrolyte. Arrhenius (9) proposed the classical ionic dissociation theory to explain the presence of these additional particles in solution. These so-called ions contributed to the deviations observed for the colligative properties and the conductances of electrolytes.

J. H. van't Hoff (10) introduced an empirical factor i into the gas law equation for the osmotic pressure of electrolytic solutions to compensate for the unexpected results. The van't Hoff factor is equal to the ratio of the number of molecular particles actually present to the number that would have been in solution if no dissociation occurred. The degree of dissociation calculated from the van't Hoff factor and the Arrhenius theory were in excellent agreement for weak electrolytes. This gave strong support to the idea of ionic dissociation.

However, it was found that the concept of incomplete dissociation did not explain the behavior of strong electrolytes. Therefore, it was proposed that strong electrolytes were completely dissociated in water. They conformed to the simple electrostatic picture of charged spheres in a solvent of given dielectric constant. The deviation from ideal behavior in these solutions could be attributed to the coulombic interactions of these charges. By application of the fundamental concepts of electrostatics, hydrodynamics and statistical mechanics, a theory which describes the properties of electrolytes has been developed.

The following is a brief account of the evolution of the interionic attraction theory. J. J. Van Laar (11) emphasized that electrostatic forces between ions in solution should produce anomalous effects on osmotic pressure, conductance and other properties characteristic of ionic solutions.

In 1904 (12) Noyes studied the optical behavior of solutions of colored strong electrolytes. His observations indicated that the salts were completely dissociated even at high concentrations.

The first attempt to calculate the approximate magnitude of the effects of ionic interactions was made by Sutherland in 1907 (13). He concluded that coulomb forces alone could produce all of the observed effects such as the decrease in conductance of an electrolyte with an increase in concentration.

Hertz (14) and Ghosh (15) attempted to give the effects of interionic attraction mathematical expression, but the basis of their treatments proved to be inadequate. However, Milner (16) successfully analyzed the problem and developed a mathematical theory that was essentially correct. He treated the problem by statistical methods and graphical solutions, but the mathematics proved to be too cumbersome to be practical and easily used.

Debye and Hückel (17) introduced the concept of the ionic atmosphere and the use of Poisson's equation and effected a mathematical short cut in the solution of Milner's equations. Only a brief account of the development of the theory will be included here since Harned and Owen have described the theory in great detail in their text (18).

The important fundamental assumptions of the Debye-Hückle theory were:

1.) All of the deviations from ideal behavior in moderately dilute electrolytic solutions may be attributed to the results of coulombic interactions. Because of the attraction between electrical charges of unlike sign and repulsions of charges of like sign, a given ion will be surrounded by an ionic atmosphere in which there are on the average more ions of an opposite sign than those of like sign.

2.) The solvent medium is assumed to be continuous with a constant dielectric constant.

3.) The time average charge distribution is such that the Boltzman factor gives the distribution of the ions in the ionic atmosphere.

4.) The Poisson equation is valid for systems of ions in a solvent.

5.) The solution of the potential equation is effected by expansion of the Boltzman exponential and, since the series converges rapidly, higher terms are neglected. The solution of the equation results in the electrostatic potential in the neighborhood of an ion.

Let us consider a solution with n_1, n_2, ...n_i, ...n_s ions of different kinds per cubic centimeter with charges $z_1\epsilon$, $z_2\epsilon$, ...$z_i\epsilon$, ...$z_s\epsilon$ either positive or negative in which ϵ is the charge on the electron or positron. The density of the ions of the ith kind in the neighborhood of a given ion is given by the Boltzman factor as

$$n_i e^{-z_i\frac{\epsilon\psi}{kT}}$$

in which ψ is the electrostatic potential, k is the Boltzman constant and T is the absolute temperature.

The electrical density, ρ of the ionic atmosphere is

$$\rho \quad = \quad \epsilon\,\Sigma n_i z_i e^{-z_i\frac{\epsilon\psi}{kT}} \, .$$

Expansion of the exponentials and retension of only the first two terms gives

$$\rho \quad = \quad \epsilon\,\Sigma n_i z_i (1 - z_i\frac{\epsilon\psi}{kT}) \, .$$

Since electrical neutrality requires that

$$\sum_s n_i z_i \epsilon \quad = \quad 0 \, ,$$

the charge density becomes

$$\rho \quad = \quad -\epsilon\,\Sigma n_i z_i^2 \frac{\epsilon\psi}{kT} \, .$$

Now the Poisson equation, in spherical polar coordinates and for radial dependence only, is

$$\nabla\cdot\nabla\psi = \frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{d\psi}{dr}\right) = -\frac{4\pi\rho}{D}$$

in which r is the radial distance from the central charge and D is the dielectric constant of the medium.

If

$$\kappa = \left(\frac{4\pi\epsilon^2}{DkT}\,\Sigma\, n_i z_i^2\right)^{1/2}$$

then

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{d\psi}{dr}\right) = \kappa^2\psi$$

which integrates to

$$\psi = A\frac{e^{-\kappa r}}{r} .$$

A may be evaluated if one considers that the charge $z_i\epsilon$ on an ion is equal and opposite to the charge in the field surrounding it. This field starts at the distance of closest approach, a_i, which is an average of the radii of the charged ions in contact, and extends to infinity. Thus, for a spherically symmetrical field

$$-z_i\epsilon = \int_{a_i}^{\infty} 4\pi r^2\rho\, dr = \int_{a_i}^{\infty} D\kappa^2 r A e^{-\kappa r} dr .$$

Integration by parts and rearrangement yields

$$A = \frac{z_i \epsilon}{D} \frac{e^{\kappa a_i}}{1 + \kappa a_i} .$$

Now when $r = a_i$,

$$\psi = \frac{z_i \epsilon}{D a_i} - \frac{z_i \epsilon}{D} \frac{\kappa}{1 + \kappa a_i} .$$

The first term on the right is the potential due to the charge on the central ion and is independent of concentration. The second term, called ψ_i, arises from the ionic atmosphere and is dependent on the concentration.

The quantity $\frac{1}{\kappa}$ in the second term has the dimensions of length and is analagous to r in the first term. This quantity is called the Debye length and represents the distance from the central ion at which a maximum in potential occurs. This implies that the ionic atmosphere has its greatest density at a distance $\frac{1}{\kappa}$ from a given ion.

The limiting law for the activity coefficients may be derived from the potential of the ion atmosphere and a consideration of the free energy change in charging the system up to that potential.

The electrical contribution to the work content, ΔA, of

n_i ions and their atmospheres is given by

$$W_{(el)} = \Delta A_{(el)} = \sum_{i=1}^{n_i} \int_0^{z_i \epsilon} \psi_i de$$

in which $W_{(el)}$ is the electrical work, e is the instantaneous charge and ψ_i is the potential due to the ionic atmosphere. Partial differentiation with respect to n_i at constant V and T yields

$$\Delta\mu_{i(el)} = \left(\frac{\partial \Delta A_{(el)}}{\partial n_i}\right)_{V,T} = \int_0^{z_i \epsilon} \psi_i de$$

in which μ_i is the chemical potential. This relation was first pointed out by Güntelberg (19) in 1926. Upon integration one obtains

$$\Delta\mu_{i(el)} = -\frac{z_i^2 \epsilon^2}{2D} \frac{\kappa}{1 + \kappa a_i} .$$

By definition

$$\mu_i = \mu_i^\circ + RT\ln X_i + RT\ln f_i$$

in which X_i is the mole fraction and f_i is the activity coefficient. This can be divided into two parts so that

$$\Delta\mu_i(\text{ideal}) = RT\ln X_i$$

and

$$\Delta\mu_{i(el)} = RT\ln f_i \quad .$$

For a single ion

$$\Delta\mu_{i(el)} = kT\ln f_i$$

which can be combined with the above equations to give

$$\ln f_i = -\frac{z_i^2\epsilon^2}{2DkT}\,\frac{\kappa}{1+\kappa a_i} \quad .$$

In the expression for κ is the quantity $\Sigma n_i z_i^2$ which is related to the stoichiometric concentration c_i by

$$\frac{N}{1000}\Sigma c_i z_i^2$$

in which N is Avogadro's number. This expression differs from the ionic strength, ω, of Lewis and Randall (20) only by a numerical factor. The ionic strength concept was a very useful empirical function. It is a great triumph for the ionic strength that the Debye-Hückle law gives it theoretical significance.

By incorporating

$$\omega = \tfrac{1}{2}\,\Sigma c_i z_i^2$$

into the expression for κ and substituting this into the equation for the activity coefficient, one obtains

$$-\ln f_1 = \frac{z_1^2 A \omega^{1/2}}{1 + B a_1 \omega^{1/2}}$$

in which

$$A = \frac{\epsilon^3}{(DkT)^{3/2}} \left(\frac{2\pi N}{1000}\right)^{1/2}$$

and

$$B = \left(\frac{8\pi N \epsilon^2}{1000 DkT}\right)^{1/2}.$$

One may obtain the mean ion activity coefficient for a binary electrolyte by using the relation

$$f_{\pm}^{\nu} = f_{+}^{\nu_+} f_{-}^{\nu_-}$$

in which ν is the total number of ions produced upon solution, ν_+ is the number of positive ions, ν_- is the number of negative ions and $f_{\pm}$ is the mean ion activity coefficient.

The result is

$$-\log f_{\pm} = \frac{z_+ z_- A \omega^{1/2}}{1 + B a_1 \omega^{1/2}}.$$

This is the most useful form of the Debye-Häckle limiting law.

B. Conductances

1. Introduction and theory

Conductance in electrolytic solutions is due to the movement of the ions under the influence of an impressed field. Each ion carries a portion of the current and thus effects the transfer of electricity.

Some of the fundamental definitions that describe the conductance of electrolytes are:

1.) The conductance, K, of a conductor is equal to the reciprocal of the resistance.

2.) The resistance, R, of a conductor is the property which converts electrical energy into heat. The resistance of a homogeneous substance of uniform cross-sectional area, A, and length, l, is

$$R = \Gamma \frac{l}{A}$$

in which Γ is the specific resistance. Γ is equal to the resistance between two opposite sides of a unit cube of the substance.

3.) The specific conductance, L, is equal to the reciprocal of the specific resistance and is a characteristic property of the conductor.

4.) The equivalent conductance, Λ, is the conductance of a solution containing one gram equivalent of solute when measured between parallel electrodes which are one centimeter apart. It may be expressed as

$$\Lambda = 1000\frac{L}{C}$$

in which C is the concentration in equivalents.

5.) The molar conductance, Λ_m, is, similarly, the conductance of a solution containing one mol of solute under the conditions defined above and may be obtained from the relation

$$\Lambda_m = 1000\frac{L}{C_m}$$

in which C_m is the molar concentration.

The molar conductance depends on the number of particles, their electrical charges and their velocities in solution. The charge on each ion, $z\epsilon$, is a multiple of the charge on the electron, ϵ. Z is an interger corresponding to the valence of the ion. The velocities will be equal to the components of the velocities in the direction of the electric force superimposed on the random motion of the ions. This is related to the mobilities, U_i, which are the velocities of the ions under a potential gradient of one volt per centimeter. From these considerations, the general expression for the molar conductance becomes

$$\Lambda_m = \Sigma n_i U_i z_i \epsilon \ .$$

Since a gram molecular weight of a salt can dissociate into only $N\sum_i \nu_i$ ions, in which N is Avogadro's number, the expression for the molar conductance of a completely dissociated solute is

$$\Lambda_m = N\epsilon \sum_i \nu_i z_i U_i \ .$$

For an incompletely dissociated solute with one degree of dissociation, α, the equation becomes

$$\Lambda_m = N\epsilon\alpha\Sigma \nu_i z_i U_i \ .$$

In 1887, Arrhenius (9) proposed a method for computing α. According to his method, the degree of dissociation is found by the simple formula

$$\alpha = \frac{\Lambda}{\Lambda_\circ}$$

in which Λ is the equivalent conductance at the concentration in question and Λ_o is the equivalent conductance at infinite dilution.

For weak electrolytes, the above relation gives nearly correct results. The value of α computed by this method agrees generally with that obtained from the colligative properties of solutions.

The law of mass action apparently holds for electrolytes that are only slightly dissociated. For the dissociation

$$CA = C^+ + A^-$$

the ionization constant, K', may be written

$$K' = \frac{[C^+][A^-]}{[CA]}$$

in which the brackets indicate molar concentrations. If C_m is the original molar concentration of the solute and αC_m is the resulting concentration of both C^+ and A^-, the expression may be written

$$K' = \frac{\alpha^2 C_m}{(1 - \alpha)} .$$

This is called the Ostwald dilution law. Substitution of the Arrhenius equation for α gives

$$K' = \frac{\Lambda^2 C_m}{\Lambda_o(\Lambda_o - \Lambda)} .$$

If the Arrhenius theory and the Ostwald dilution law hold, the ionization constant should be strictly a constant and not a function of concentration. MacInnes and Shedlovsky (21) observed that K' is fairly constant for weak electrolytes such as acetic acid, but a drift in the constant is quite evident for chloroacetic acid and the law fails completely for hydrochloric acid. The fact that the ionization constant does not vary with concentration for weak electrolytes indicates that the activity coefficients for these solutes are nearly unity and that the mobilities of the ions do not change markedly with concentration.

However, the causes of the deviations for strong electrolytes were soon recognized after the failure of the Arrhenius theory and the Ostwald dilution law. These deviations may be attributed to the marked change in the mobilities of the ions because of the interaction of the ions with their ionic atmospheres.

Onsager (22) applied an extension of the interionic attraction theory to conductance and evolved his important limiting law. He postulated that the lowering of ionic mobilities with increasing concentrations is due to two effects.

These are the electrophoretic effect and the time of relaxation effect.

The electrophoretic effect arises as a consequence of the ionic atmosphere that surrounds an ion. When a potential gradient of intensity E is applied to a solution, a given ion will tend to move with a velocity, v_1, in the direction of the field and superimposed on the thermal motion. This velocity is related to the ion's limiting mobility U_o. However, the ionic atmosphere being of opposite charge will tend to move in a reverse direction. This produces a drag on the central ion and effects a decrease in its net velocity.

By making use of the potential field distribution around an ion,

$$\psi = \frac{z_1 \epsilon}{D} \frac{e^{\kappa a_1}}{1 + \kappa a_1} \frac{e^{-\kappa r}}{r} ,$$

and the Poisson relation,

$$\nabla \cdot \nabla \psi = - \frac{4\pi \rho}{D} ,$$

the corresponding distribution of space charge in the ion atmosphere may be obtained as

$$\rho = - \frac{z_1 \epsilon e^{\kappa a_1}}{4\pi(1 + \kappa a_1)} \kappa^2 \frac{e^{-\kappa r}}{r} .$$

The force per unit volume on each element of the ion atmosphere will be

$$F = \rho E = -E \frac{z_1 \epsilon e^{\kappa a_1}}{4\pi(1 + \kappa a_1)} \kappa^2 \frac{e^{-\kappa r}}{r} =$$

$$-A' \frac{e^{-\kappa r}}{r} .$$

If the atmosphere is arranged around the ion in spherical shells of thickness dr, the total force acting on such a shell will be

$$d\bar{F} = 4\pi r^2 F dr .$$

The velocity of a sphere of radius r in a fluid of viscosity η moving under a force $\bar{F}$ is given by Stokes' law as

$$v = \frac{\bar{F}}{6\pi\eta r} .$$

Combination of the above relations gives the contribution dv_2 of a spherical shell of thickness, dr to the velocity, v_2 as

$$dv_2 = -\frac{2A'}{3\eta} e^{-\kappa r} dr .$$

Upon integration between the distance of closest approach and infinity one obtains

$$v_2 = -\frac{E\epsilon z_1}{6\pi\eta}\,\frac{\kappa}{1 + \kappa a_1}\ .$$

This is the retardation due to the electrophoretic effect.

The time of relaxation effect may be described as follows. Around a selected ion the atmosphere has spherical symmetry. When the ion is suddenly moved the ion atmosphere will tend to move with it, but will not be able to adjust to the new position instantaneously. Thus, the atmosphere will be momentarily arranged asymmetrically with respect to the ion. The adjusted portion of the atmosphere will tend to exert an electrostatic attraction in the opposite direction to which the ion is moving. For an ion moving steadily, a permanent distortion will be effected. This produces a further decrease in the velocity that the ion attains in a given field.

Onsager's equation for the equivalent conductance of an ion constituent in a binary electrolyte is

$$\lambda = \lambda_\circ - \left[\frac{0.9834\text{x}10^6}{(DT)^{3/2}}\,\omega\,\lambda_\circ + \frac{28.94z_1}{(DT)^{1/2}\eta}\right]\left[(z^+ + z^-)C\right]^{1/2}$$

in which C is the concentration in equivalents of the solute per liter, D is the dielectric constant and η is the viscosity of the solvent and T is the absolute temperature.

$$\omega = z_+ z_- \frac{2q}{1 + (q)^{1/2}}$$

and

$$q = \frac{z_+ z_- (\lambda_o^+ + \lambda_o^-)}{(z_+ + z_-)(z_+ \lambda_o^- + z_- \lambda_o^+)}$$

in which λ_o^+ and λ_o^- are the limiting equivalent conductances and z_+ and z_- are the valences of the positive and negative ions. The first term in the brackets accounts for the time of relaxation effect and the second for the electrophoretic effect. A complete derivation of the equation can be found in Onsager's original paper (22).

2. History of conductance measurements

The first accurate measurements of electrolytic conductances were made by F. Kohlrausch in 1868 (23). His work was so precise that it stands even to this day as a model of experimental ingenuity. A few of the details of his technique are included here because of the importance of his contribution to the measurement of conductances.

Kohlrausch used alternating current of 1000 cycles per second and measured the resistances on a modified Wheatstone bridge which included a telephone earpiece as a null indicator. He believed that when alternating current passed between platinum electrodes hydrogen and oxygen alternately deposited and the electrolysis was chemically and thermodynamically reversible (24). The effective capacitance of the cell was compensated for by connecting a condenser in parallel with the resistance on the other arm of the bridge (25).

The electrodes were platinized with chloroplatinic acid (26) in order to increase their surface and reduce polarization effects. In addition, the cell was designed so that the resistance measured would be high since Kohlrausch and Holborn (27) found that polarization effects were negligible if the resistance was greater than fifty divided by the area of the electrodes. The cell constant was obtained by actually measuring the geometry of the cell (28) after which seven standard reference solutions were prepared as secondary standards. As a final precaution, Kohlrausch used accurate temperature control (29).

Further study on the improvement of conductance measurements was made by Taylor and Acree (30) in 1916. They compared various oscillators and concluded that the Vreeland oscillator was superior. After experimenting with bridge and cell design and the preparation of solutions, they were able to make measurements with a precision of 0.001 per cent.

Washburn (31) investigated the design of cells and the characteristics of telephone receivers and other null indicators. Hall and Adams (32) perfected an amplifier to be used with the detector and improved the sensitivity of the measurements. Several additional studies were made of the bridge design, shielding, oscillators and the construction of conductance cells. Among the more important contributors were Morgan and Lammert (33), Jones and Josephs (34), T. Shedlovsky (35), Jones and Bollinger (36) and Jones and Christian (37). A result of these investigations is the highly accurate Jones bridge which is used in this laboratory.

The early investigators realized that in order to obtain accurate conductance measurements, the geometry of the cell must be known. The cell constant, k, is a measure of the cell dimensions since

$$L = \frac{1}{R}\frac{l}{A} = \frac{k}{R}$$

in which L is the specific conductance, l is the distance between electrodes and A is the area of the electrodes. Therefore,

$$k = \frac{l}{A} .$$

The simplest method of obtaining the cell constant is to measure the resistance of a solution of known specific conductance and k may be obtained from the relation

$$k = RL \quad .$$

Kohlrausch (28) used potassium chloride for this purpose by first measuring $\frac{1}{A}$ physically and obtaining precise potassium chloride values which were used in subsequent cell calibrations. These potassium chloride values were slightly improved by Parker and Parker (38) and Jones and Bradshaw (39).

Jones and Predergast (40) used pure mercury as a primary standard at 0°C. The constants for a series of cells of decreasing cell constant were obtained and the specific conductances of concentrated sulfuric acid were measured so that the acid could be used as a secondary standard for cell calibration.

Complete cell calibration must include provision for the Parker effect (41) which is the variation of the cell constant with the resistance measured. H. C. Parker believed that this effect was due to absorption at the electrodes. However, Shedlovsky (42) and Jones and Bollinger (36) correctly attributed the effect to capacitance between the cell leads. In order to minimize this capacitance, cell leads are placed as far apart as is practical.

C. Transference Numbers

1. Introduction and theory

The transference number of an ion in solution is the proportion of the current carried by that ion when an electric current is passed through the solution. This quantity is of singular importance in the calculation of absolute ionic mobilities since it is a measure of the behavior of an ion species as it is related to the total behavior of the solution.

In an electric field an ion will migrate with a velocity which depends on its mobility. Since the mobilities of different ions are characteristic of the species, the different kinds of ions in solution will not, in general, transport equal amounts of current. The transference number will depend on the number of ions or equivalent concentration, c_i; the charge on the ion, z_i; and its mobility, U_i. Thus, the transference number of the ith ion, T_i, is the ratio of the current, i, carried by it to the total current, I, carried by the entire system

$$T_i = \frac{i}{I} = \frac{c_i z_i U_i}{\sum_s c_s z_s U_s} .$$

For a binary electrolyte, for which $c_+ z_+ = c_- z_-$, the expression reduces to

$$T_+ = \frac{U_+}{U_+ + U_-}$$

for the transference number of the positive ion.

Since the mobility is related to the ionic equivalent conductance, λ , by the faraday, F,

$$\lambda_+ = U_+F \ ,$$

$$\lambda_- = U_-F$$

and

$$T_+ = \frac{\lambda_+}{\lambda_+ + \lambda_-} = \frac{\lambda_+}{\Lambda} \ .$$

This important relation permits the calculation of individual ionic equivalent conductances from a knowledge of transference numbers and total equivalent conductances. It also points to the relationship between transference phenomena and the conductance of ions in solution.

If the above relation is substituted into the Onsager equation for the conductance of a binary electrolyte, one obtains

$$T_+ = T_+^\circ + S_{(T)}C^{1/2}$$

in which

$$S_{(T)} = \left[\frac{T^{\circ}_{+}(|z_+| + |z_-|) - |z_+)}{(|z_+| + |z_-|)\Lambda_{\circ}} \right] B^{*}$$

and

$$B^{*} = \frac{28.98(|z_+| + |z_-|)^{3/2}}{\eta \, (DT)^{1/2}} \; .$$

This relation is for the special case of a binary electrolyte and gives good agreement with experiment only for uni-univalent electrolytes in extremely dilute solutions. Much better agreement between theory and experiment is obtained when the extended Onsager equation is used. However, in order to use the extended Onsager equation one must know the distance of closest approach, a_1. The above equation may only be used to obtain the limiting slope of the transference number as a function of the square root of the equivalent concentration. A further discussion of this relation will be made in the section on the evaluation of experimental results later in the thesis.

There are three general procedures for measuring transference numbers. They are the Hittorf method, the e.m.f. method and the moving boundary method.

The Hittorf method consists of electrolyzing a solution of a solute in a three compartment cell. The cell is constructed so that there is an anode compartment, a middle compartment and a cathode compartment from which samples can be removed and analyzed after the passage of a known amount of current. The electrodes are made of a material which is reversible to the ions in solution. A simple formula for the computation of transference numbers from the experimental data has been developed by Washburn (43).

The number of equivalents of an ion, N_f, left in a given weight of solvent, for example in the anode compartment, after electrolysis must be equal to the number of equivalents, N_o, present before the experiment plus the number of equivalents, N_e, introduced by the electrode reaction minus the number of equivalents, N_eT, lost by ionic migration

$$N_f = N_o + N_e - N_eT \ .$$

Thus, the transference number, T, can be obtained from the equation

$$T = \frac{N_o - N_f + N_e}{N_e} \ .$$

N_e may be obtained from the number of faradays passed during the experiment and N_o and N_f are found by analysis of the solution before and after the electrolysis.

The e.m.f. method for transference numbers involves the use of concentration cells. The potential of a concentration cell with liquid junction is measured and the potential of a concentration cell without liquid junction, but with the same concentrations of solutes, is compared with it. For a concentration cell with liquid junction

$$-FdE_t = Td\mu ,$$

in which F is the faraday, E_t is the potential for the cell with transference and μ is the chemical potential. The corresponding expression for a concentration cell without liquid junction is

$$-FdE = d\mu .$$

Therefore, the transference number can be obtained from the relation

$$\frac{dE_t}{dE} = T .$$

This method is the least accurate of the three and has found very little application.

The moving boundary method has been used in this work because it is the simplest to perform and capable of the most accuracy. It consists of placing the solution to be measured in a calibrated tube of uniform cross-section and narrow bore. An indicator electrolyte is placed above this and is separated from it mechanically. An anode is placed in the indicator solution and a cathode is placed in the solution to be measured. When a potential is applied across the cell and the solutions are brought into contact, the cations of the leading electrolyte will migrate towards the cathode with a characteristic velocity. The indicator cations will follow the leading cations, but will not pass them because of the slower mobility of the indicator ions. An interface or boundary will be formed between the two solutions. This boundary will move with the velocity of the leading ions and become sharp and visible if the solutions have different colors or sufficiently different indices of refraction. The boundary will remain sharp because of the potential gradients developed in the tube. These potentials may be represented as a function of the distance along the tube as shown in Figure 1.

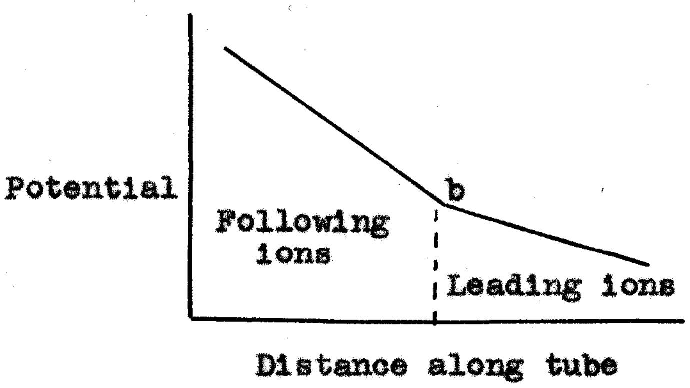
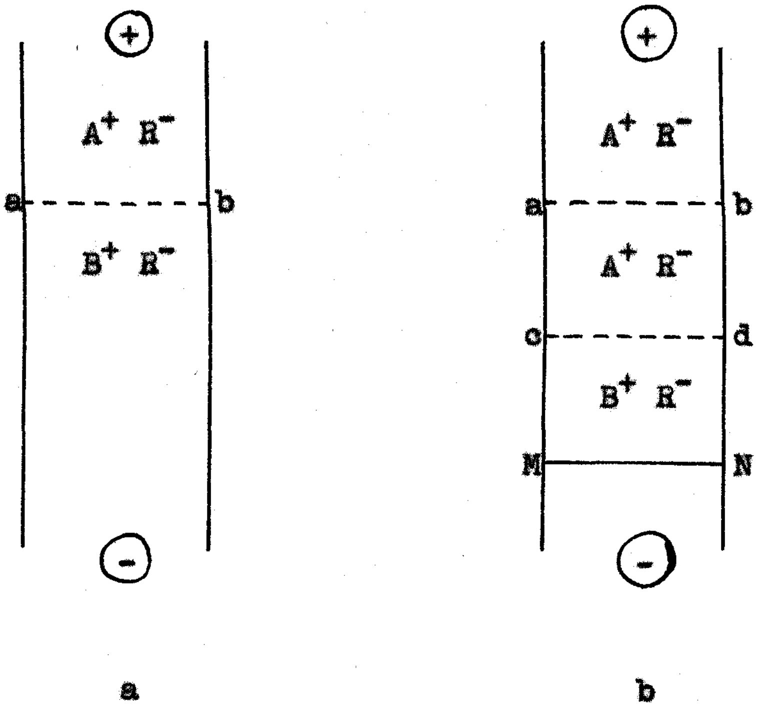


Figure 1. Potential Gradients in Transference Cell.

When the slower moving following ions get ahead of the boundary at b in Figure 1, they find themselves in too small a potential gradient and are slowed down. Also, when the leading ions drop behind the boundary they are in too great a potential gradient and are speeded up. Thus, the boundary remains sharp.

By observing the time it takes for the boundary to pass through a given volume under the influence of a given current, one can calculate the transference number of the leading ion.

The equation for calculating the transference number was derived by Miller (44) in the following manner. Consider the cell initially containing two solutes AR and BR with a boundary at a-b in Figure 2a. After the passage of current for a time t, the boundary will be located at c-d in Figure 2b and would have swept out a volume V. The flow of one faraday causes a number of equivalents of the ion constituent B^+, equal to that originally contained in the volume V, to pass a fixed plane M-N in the unchanged portion of the solution. Thus, the number of equivalents of B^+ passing the plane M-N will be VC_{B^+} in which C_{B^+} is the equivalent concentration of B^+. At the same time the anions R^- are moving towards the anode with their characteristic velocity. The B^+ ions will always be in an atmosphere of R^-



a b

Figure 2

Motion of Solutes in Transference Cell

ions so that the equivalent concentration of B^+ is equal to that of BR. This number of equivalents will be equal to the transference number,

$$T_{B^+} = VC_{BR} .$$

When a smaller number of coulombs, f, is passed through the tube, the boundary moves through a smaller volume, v, such that

$$\frac{v}{V} = \frac{f}{F} .$$

Eliminating V from the equations above yields

$$T_{B^+} = \frac{vC_{BR}F}{f} .$$

The number of coulombs, f, is equal to the current times the time in seconds. Therefore,

$$T_{B^+} = \frac{vC_{BR}F}{It} .$$

In this expression the volume is in liters, the concentration is in equivalents per liter, the time is in seconds and the current is in amperes.

There are three kinds of transference numbers. The Hittorf transference number, the Nernst transference number and the moving boundary number. The Hittorf transference number measures the velocity of the solute ions relative to the solvent. The Nernst transference number measures the velocity of the ions relative to molecules of an inert solute which is not influenced by the field. An inert solute like raffinose is added to the solution and the motion of the solvent may be determined by analysis for the raffinose. The third type of transference number measures velocities relative to fixed points on the cell. These methods give rise to different transference numbers because of the different amounts of solvent transported during an experiment. However these differences may be resolved to give the "true" transference number if the amount of solvent transported is taken into account in the calculations. A description of how this correction is made in the moving boundary method is included in the next section.

2. History of transference number measurements

Among the earliest investigators to discover that the positive and negative ions in solution do not transport the same amount of current were Daniell (45) and Hittorf (46). Daniell used a three compartment cell separated by diaphragms of bladder. After electrolysis, he observed that the concentration changes occurred unequally in the cathode and anode compartments. Hittorf's work from 1853-1903 confirmed Daniell's conclusions and afforded a wealth of data which helped to lead to Kohlrausch's independent migration theory and Arrhenius' dissociation theory.

However, extensive accurate studies of transference were made later using the Hittorf method with vast improvements in analytical technique, current measurement and cell design. MacInnes and Dole (47) and Jones and Bradshaw (48) obtained a high degree of accuracy with the method.

The moving boundary method was originated by Lodge (49) who attempted a study of absolute ionic velocities using a gelatin gel medium through which the ions migrated. In 1893, W. C. D. Whetham (50) demonstrated that Ohm's law applied in moving boundary systems and was able to obtain a uniform potential drop through the measuring tube.

In 1897, Kohlraush (51) derived an important relation between the concentration changes and the motion of the concentration gradient at the boundary. This limiting law is known as the Kohlrausch ratio,

$$\frac{T}{C} = \frac{T'}{C'} ,$$

in which T is the transference number of the leading ion and C its concentration, while T' is the transference number of the following ion and C' its concentration. If the concentrations of the solutions do not adjust to this ratio, the velocity of the boundary will not be constant. Kohlrausch believed that the adjustment took place automatically in any system, but recent work shows that the range of concentrations over which this relation will operate is about 3-5 per cent.

Although Weber (52), Nernst (53) and Planck (54) improved the theory by introducing the effects of diffusion, the greatest contribution was made by Masson (55). By observing the cation and anion boundaries simultaneously, he was able to conclude that the conditions listed below must be fulfilled:

1.) The concentrations of the indicator solution must be such that the Kohlrausch ratio will hold.
2.) The indicator ion must have a lower mobility than the leading ion.
3.) The indicator solution must not react chemically with the leading solution.
4.) No fast ions should be produced at the electrodes.
5.) The solution on top must be less dense than the one on the bottom to prevent mixing.

These rules are still used in order to obtain good boundaries.

MacInnes and Smith (56, 57) made an extensive study of the Kohlrausch ratio and the adjusting of the boundary due to potential gradients in the tube. They were able to verify the Kohlrausch ratio experimentally. By plotting the transference number of a given concentration of leading electrolyte against the concentration of following solution, the following graph is obtained.

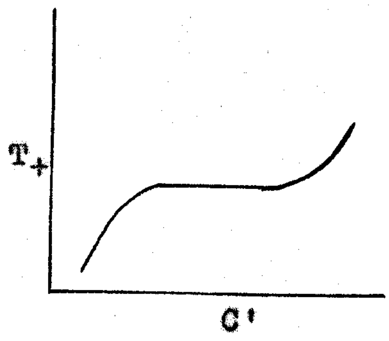


Figure 3
Range of Validity of Kohlrausch Ratio

The plateau portion of the curve indicates the range over which the Kohlrausch ratio is operating. MacInnes and Smith estimated that this range was about 3 per cent. However, the range is greater for dilute solutions and greater for rising boundaries.

In the early work transference numbers were measured by observing the movement of the boundary through a gelatin gel which was previously saturated with an indicator that showed the progress of the leading ions. Lenz (58) and Bein (59) pointed out that boundaries may be visible in colorless solutions by reason of differences in refractive indices. B. D. Steele (60) used this knowledge to advantage in observing aqueous boundaries with a telescope cathetometer. Gelatin plugs were still used to separate the solutions. Steele noted that by using low current densities and indicator solutions with as high a mobility as possible, he could eliminate much of the heating which caused mixing by convection. Falling boundaries were observed to give rise to less mixing since the rising heat does not affect the boundary as much when the boundary is moving away from the convection currents.

The method was further improved by Denison (61), who made corrections for electoendosmosis through the gelatin plugs. Franklin and Cady (62) in 1904 originated the autogenic boundary method which eliminated the need for choosing an indicator solution. In a rising boundary experiment the solution to be measured was placed in a calibrated tube and an anode was sealed at the bottom of the tube. When the current was turned on the electrolysis at the anode gave rise to cations of the metal that acted as the indicator ions and formed the boundary. The indicator solution was self generated and hence called autogenic.

Denison and Steele (63) in 1906 eliminated the need for gelatin plugs in forming the initial boundary. They used a parchment cone to cover the boundary tube. When the current was turned on, the leakage around the parchment was sufficient to allow the boundary to form. When the boundary was sharp, the parchment was removed. Henceforth, mechanical means instead of gelatin were used to form the boundaries and completely aqueous systems were used.

By this time the advantages of the moving boundary method were becoming recognized. However, the transference numbers obtained by this method did not agree with those measured by the Hittorf method. Therefore, a study of the process was made to discover the explanation of the differences.

W. L. Miller (44) considered the moving boundary method as a Hittorf experiment with the concentration changes in the electrode compartments corresponding to penetration of indicator solution into one compartment. He derived the Kohlrausch ratio very simply as follows. Since

$$T = \frac{VCF}{1000It}$$

and

$$T' = \frac{VC'F}{1000It}$$

and since the volume swept out, the current and the time are the same for indicator and leading solution, the ratio between the transference numbers of the indicator and the leading solutions is

$$\frac{T}{T'} = \frac{C}{C'}$$

which is the Kohlrausch ratio.

Lewis (64) showed that a correction must be made for the volume changes occurring during electrolysis. These changes effectively produce a movement of the entire solution whereas the boundary velocity is being measured relative to fixed points on the tube. Lewis was able to make the large volume correction on Steele's experiments and obtain better agreement with the Hittorf values. The validity of the volume correction was tested and confirmed by Smith (65) and MacInnes and Longsworth (66).

The volume correction as it is used in this work may be described as follows. Consider the moving boundary tube in which the anode compartment is closed to the atmosphere so that all volume changes will occur relative to the partial molal volume changes above the boundary in a falling boundary experiment.

Before any current is passed the situation may be pictured as in Figure 4a. However, after the passage of a faraday the following changes, pictured in Figure 4b, occur. An equivalent of Cd metal is lost from the anode and an

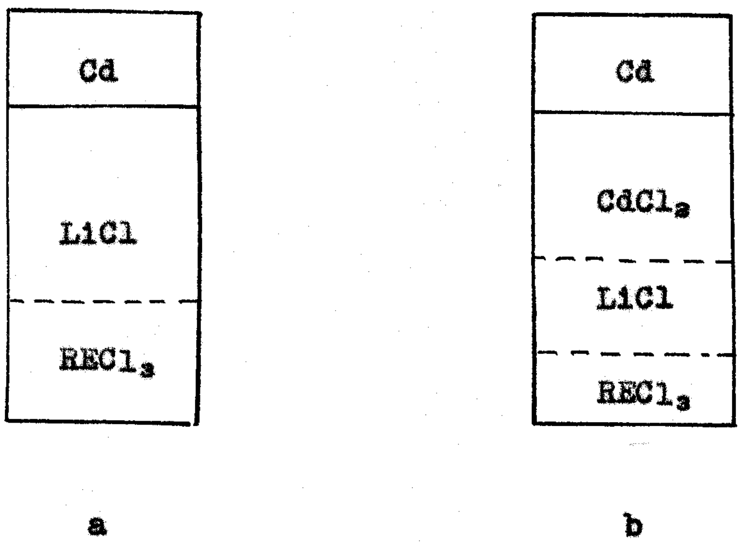


Figure 4
Volume Changes in Transference Cell

equivalent of Cd^{++} ions is gained in the $CdCl_2$ solution. Also an equivalent of Cl^- ions is gained in the $CdCl_2$ solution while an equivalent of Cl^- ions is lost from the LiCl solution. However, T_- equivalents of Cl^- ions are gained in the LiCl solution due to the migration of Cl^- ions towards the anode and T_+ equivalents of Cl^- ions are gained in the LiCl solution due to the downward motion of the boundary. In the meantime, $\frac{T_+}{3}$ equivalents of RE^{+++} ions are lost in the region above the boundary by migration towards the cathode and T_+ equivalents of Cl^- ions are lost from the $RECl_3$ solution. The net change in volume, ΔV, may be described as follows:

$$\Delta V = \frac{-\bar{V}_{Cd}}{2} + \frac{\overset{\underline{CdCl_2}}{\bar{V}_{Cd^{++}}}}{2} + \overset{\underline{CdCl_2}}{\bar{V}_{Cl^-}} - \overset{\underline{LiCl}}{\bar{V}_{Cl^-}} + \overset{\underline{LiCl}}{(T_-)\bar{V}_{Cl^-}} +$$

$$\overset{\underline{LiCl}}{(T_+)\bar{V}_{Cl^-}} - \overset{\underline{RECl_3}}{\frac{T_+}{3}\bar{V}_{RE^{+++}}} - \overset{\underline{RECl_3}}{(T_+)\bar{V}_{Cl^-}} .$$

Since $T_+ + T_-$ equals one by definition,

$$(T_- + T_+)\bar{V}_{Cl^-} = \bar{V}_{Cl^-}$$

and the above expression may be simplified to:

$$\Delta V = \frac{-\bar{V}_{Cd}}{2} + \frac{\bar{V}_{CdCl_2}}{2} - \frac{T_+}{3}\bar{V}_{RECl_3} .$$

The corrected transference number would account for this volume change by inserting it into the expression

$$T = \frac{(V - \Delta Vn)CF}{1000It}$$

in which n is the number of faradays passed. Since $\frac{nF}{It}$ is equal to one in this case, the correction may be applied by using the relation

$$T = T_o - \frac{\Delta VC}{1000} .$$

In 1923, D. A. MacInnes and his co-workers began a very extensive study of the moving boundary method. A summary of this work may be found in the review article by D. A. MacInnes and L. G. Longsworth (66). Many improvements in technique and equipment are discussed in the paper.

One of the greatest contributions to resolving the differences between the moving boundary and the Hittorf transference numbers, after the discovery of the volume correction, was the employment by Longsworth (67, 68, 69) of the solvent correction. Since impurities in the solvent carry current which is essentially in parallel with the current causing the boundary to move, a correction should be made to include this effect. The equation that gives this correction is

$$T = T_o \left[1 + \frac{L_{solvent}}{L_{solution}} \right] .$$

The correction becomes more important at low concentrations because the conductivity of the solution is much lower while the solvent conductivity remains constant.

In recent years little work has been done on the moving boundary method. D. J. Leroy and his co-workers (70, 71, 72, 73, 74) modified the apparatus slightly and used a new electronic current controller. D. A. MacInnes (75) used a novel method to get transference numbers. The method depends on the effects of gradients of centrifugal force on the e.m.f. of simple galvanic cells. The cell is placed in a centrifuge and the e.m.f. is measured while it is whirling at a measured velocity.

The most recent work on transference numbers has been done at Iowa State College by F. H. Spedding, J. Wright and P. Porter (76) and F. H. Spedding and I. S. Yaffe (2). These investigators made very precise measurements of the transference numbers of the rare earth chlorides and the rare earth bromides. Since in general polyvalent ions have a marked tendency to hydrolyze, there had been little work done with them until the study of the rare earths was begun. The present thesis is an extension of that investigation. Any comparisons between the two will be evaluated in the section on the discussion of results.

III. PREPARATION OF MATERIALS AND SOLUTIONS

The rare earth elements used in this work were obtained from the following sources. The lanthanum oxide was purchased from the Lindsay Light and Chemical Corporation. The cerium oxide was derived from cerium ammonium nitrate which was bought from the G. Frederick Smith Chemical Company. All the remaining rare earth oxides were separated from the ore by Dr. F. H. Spedding's Rare Earth Group at The Iowa State College Institute for Atomic Research. These elements were purified by ion-exchange techniques (3, 4, 5, 6, 7, 8) and Marsh's sodium amalgam method (77) for the extraction of samarium and ytterbium from neighboring elements.

Table 1 represents the degree of purity of the rare earth oxides as determined by Dr. V. Fassel's spectrographic group at the Ames Laboratory. The limit of detection of the rare earth elements by emission spectroscopy was about 0.02 to 0.03 per cent. That for the common elements was about 0.01 per cent.

The rare earth oxides were dissolved in the pure acid, corresponding to the salt to be prepared, and reprecipitated

Table 1

Purity of Rare Earth Oxides

Element	Analysis
La	No other rare earths.
Ce	No other rare earths, thorium or common elements.
Pr	No other rare earths or thorium.
Nd	No other rare earths or thorium.
Sm	0.02 ±0.002 per cent of Eu_2O_3 detected.
Gd	Less than 0.1 per cent Sm_2O_3, 0.02 ±0.005 per cent Tb_4O_7 by a new fluorescimetric technique.
Ho	Less than 0.01 Y_2O_3, 0.02 per cent Er_2O_3, less than 0.01 Tm_2O_3, about 0.3 per cent Dy_2O_3.
Er	0.05 per cent Yb_2O_3, Tm_2O_3 and Ho_2O_3. About 0.2 per cent Y_2O_3 but no Dy_2O_3.
Yb	No other rare earths or common elements.
Y	About 0.2 per cent Dy_2O_3 and 0.02 per cent Tb_4O_7 detected.

twice with recrystallized Baker's Analyzed oxalic acid. The oxalates were ignited at about 900°C in platinum dishes. Only sintered glass filters were used so as to avoid contamination from filter paper ash. The above procedure was necessary in order to insure the removal of any traces of iron, calcium, magnesium, etc.

The rare earth sulfates were prepared by dissolving the pure rare earth oxides in a very slight excess of chemically pure sulfuric acid followed by a filtration through a fine sintered glass filter to remove any insoluble matter. The clear solution was then added slowly to a beaker of pure absolute ethanol. The rare earth sulfates are very insoluble in the ethanol in about a fifty per cent solution, while the excess sulfuric acid is quite soluble. This effects a very clean separation of the excess acid. Next, the filtered salt was dried at about 120°C and finally ignited at around 500°C. This temperature was chosen since it is high enough to ignite all the excess alcohol and low enough to prevent the formation of rare earth oxides and rare earth oxysulfates. A slightly higher temperature is permissible with lanthanum sulfate and a slightly lower temperature is necessary with ytterbium sulfate. Further recrystallization from pure conductivity water did not change the pH of the resulting solutions and indicated that essentially all of the excess acid was removed.

The rare earth perchlorates were prepared by dissolving the rare earth oxides in less than an equivalent amount of doubly vacuum distilled perchloric acid. The excess oxides were filtered off leaving solutions that had pH values that were slightly too high. These high pH values were attributed to the hydrolysis equilibrium

$$RE^{+++} + H_2O \rightleftharpoons (REOH)^{++} + H^{+} \quad ,$$

since more rare earth oxide will be dissolved by the excess hydrogen ions present from the hydrolysis.

To overcome this difficulty, an aliquot of each rare earth perchlorate solution was titrated with approximately 0.1 N perchloric acid. A Beckman Model G pH meter was used to follow the titration. A normal strong acid, strong base titration curve was obtained, and evaluation of the equivalence point was made by plotting the differential curve, Δml./ΔpH, versus the average number of milliliters of perchloric acid. Then the stock solution was titrated to this equivalence point with the 0.1 N perchloric acid solution.

It was evident that the above procedure was necessary when diluted solutions of rare earth perchlorates not so treated were observed to precipitate rare earth hydrous oxide or rare earth oxy-perchlorate upon standing. However, solutions that had been titrated to the equivalence point remained clear for months and exhibited very little Tyndall cone upon exposure to a narrow beam of light in a dark room. The hydrolysis did not affect the measured properties beyond the experimental error.

The rare earth nitrates were prepared in a similar manner to the preparation of the perchlorates. Chemically pure nitric acid was used to dissolve the rare earth oxides and the solutions were titrated with 0.1 N nitric acid as outlined above.

In all this work conductivity water with a specific conductance of about 1×10^{-6} mhos per centimeter was used. This water was obtained by distilling ordinary distilled water over potassium permanganate and sodium hydroxide in a block tin Barnsted conductivity still.

Standard solutions were made at 25°C by diluting the stock solutions by volume. Calibrated pipets and volumetric flasks were used throughout. Convenient dilutions of the stock solutions were analyzed for the rare earths by precipitation of the rare earth oxalates with oxalic acid. The rare earth oxalates were then ignited at about 900°C for at least twelve hours and cooled and weighed as rare earth oxides. This method proved to be reproducible to well within the 0.1 per cent precision sought. The heavier rare earth oxalates are slightly soluble in excess oxalic acid, due to the formation of soluble oxalate complexes. Therefore, careful regulation of the oxalate concentration and a long, seventy hour, waiting period was necessary to insure equilibrium and a minimum of solubility. When these precautions were observed, reproducible results were obtained.

As a further check on the sulfate concentrations in the rare earth sulfate solutions, precipitation with barium chloride and weighing as barium sulfate was attempted. However, the method was not accurate enough to be of use. Therefore, aliquots of the rare earth sulfates were evaporated to dryness and ignited at about 500°C. The rare earth sulfate weights gave excellent checks with the rare earth oxide weights for most of the rare earths. However, erbium sulfate and ytterbium sulfate appear to pick up moisture from the air at such a rate that weighing outside a dry box is not practical.

No attempt was made to analyze the perchlorate or nitrate solutions for the anions. However, it is felt that the titration curves exhibited adequate evidence that equivalent solutions had been prepared.

The lithium chloride solutions were prepared by dissolving Baker's Analyzed lithium carbonate in less than an equivalent amount of redistilled hydrochloric acid. The excess lithium carbonate was filtered off and the solutions were boiled while a stream of nitrogen bubbled through them to remove carbon dioxide. This was done until the pH reached about 6.6. The solution was analyzed by evaporating aliquots to dryness with a slight excess of sulfuric acid. The salt was ignited at 900°C and weighed as lithium sulfate.

IV. SOLUBILITIES OF SOME RARE EARTH SULFATES IN WATER AT 25°C

The rare earth sulfates were prepared as described in the previous section. Each salt was dissolved in water until a definite excess was present. Then, since the rare earth sulfates have a negative temperature coefficient, the solution was cooled to at least 20°C. The solution was kept in a cooling bath for at least twelve hours while it was stirred by a magnetic stirrer and a glass covered stirring bar. When complete solution was obtained, the excess rare earth sulfate was filtered off and the clear solution was placed in a thermostat at 25° ±0.05°C.

When the solution warmed up to 25°C the excess rare earth sulfate was seen to crystallize out of solution until equilibrium was reached. After at least forty-eight hours the solution was filtered again. The clear saturated filtrate was then analyzed by diluting a convenient aliquot and precipitating the rare earth as rare earth oxalate. The oxalate was ignited at 900°C for twelve hours and the resulting salt weighed as rare earth oxide. At least two such analyses were carried out for each determination.

Table 2

Solubilities of Some Rare Earth Sulfates in Water at 25°C

Salt	Solubility in grams per 100 grams of water
$La_2(SO_4)_3$	2.1416
$Ce_2(SO_4)_3$	5.0625
$Pr_2(SO_4)_3$	10.88
$Nd_2(SO_4)_3$	5.5906
$Sm_2(SO_4)_3$	1.4876
$Gd_2(SO_4)_3$	3.299
$Ho_2(SO_4)_3$	6.705
$Er_2(SO_4)_3$	15.19
$Yb_2(SO_4)_3$	36.014
$Y_2(SO_4)_3$	9.6731

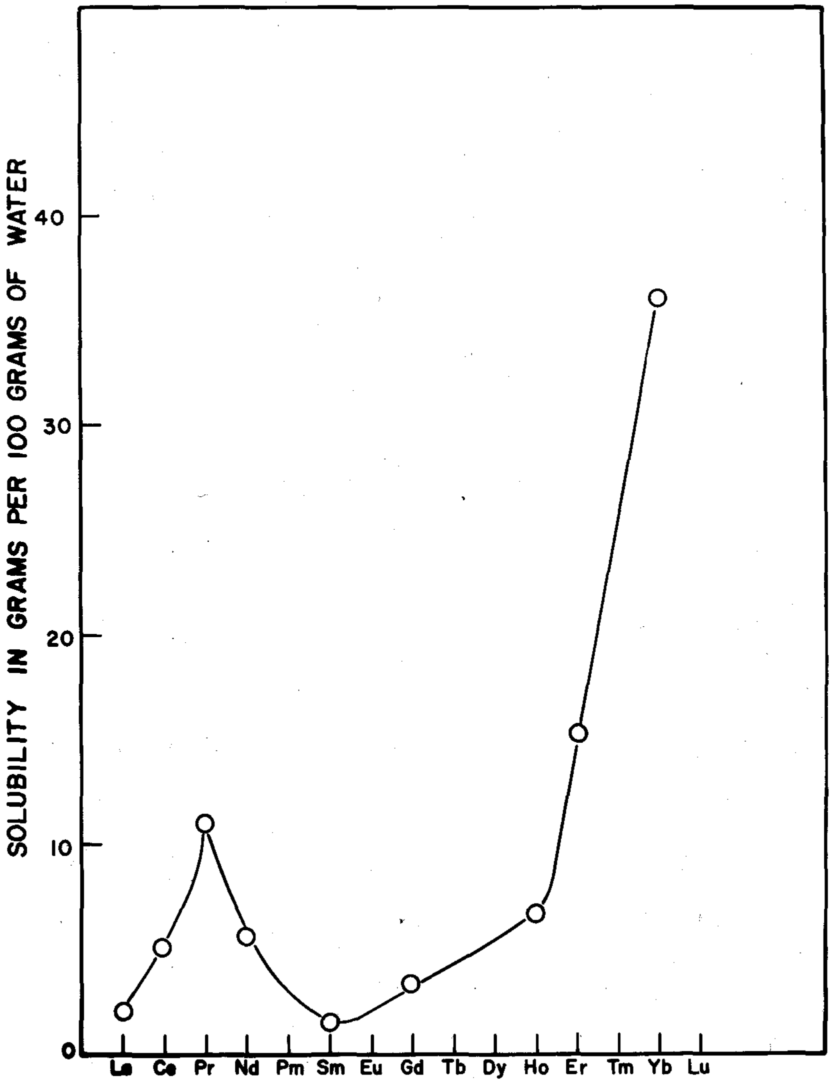


Figure 5. Solubility of Some Rare Earth Sulfates.

In addition, the density of the clear solution was measured with a fifty milliliter pycnometer. From the normality given by the oxide weight and the density of the solution, the solubility of the rare earth sulfate in grams of solute per 100 grams of water was calculated.

These data are tabulated in Table 2. The results seem to indicate that the solubility starts at a low value for lanthanum sulfate, rises to a maximum at praseodymium, reaches a minimum probably at europium and continues to increase for the heavier rare earth sulfates. Figure 5 is a plot of the solubility of the rare earth sulfates in grams per 100 grams of water as a function of atomic number.

V. CONDUCTANCES

A. Apparatus

The resistances were measured using alternating current on a Jones Conductivity Bridge which is completely described by P. H. Dike (78) [Leeds and Northrup catalog number 4666]. The accessories for the bridge included an audio frequency oscillator [Leeds and Northrup catalog number 9842] which could be tuned to give oscillations at 500, 1000, and 2000 cycles per second, and a tuned audio frequency amplifier [Leeds and Northrup catalog number 9847]. The vacuum tube amplifier is designed to be tuned to 500, 1000, and 2000 cycles per second to coincide with the audio frequency oscillator and give the maximum sensitivity possible at the frequency that it is used.

A cathode-ray oscillograph, purchased from the Allen B. Dumont Laboratories Incorporated, was used as a null indicator. This was found to be much more convenient and sensitive than the conventional telephone earpieces used for this purpose. The null point was indicated by a minimum in the sine wave projected on the oscillograph screen.

The constant temperature bath, purchased from the Arthur H. Thomas Company [catalog number 9926-D] was able to maintain a constant temperature to within 0.02°C at 25°C. The temperature was determined by a thermometer calibrated in 0.01°C divisions and was certified by the National Bureau of Standards. The bath liquid consisted of pure mineral oil to reduce capacitance effects.

Three conductivity cells [Leeds and Northrup catalog numbers 4911, 4914 and 4915] were used. In order to reduce polarization effects, the electrodes were platinized by a procedure outlined by Jones and Bollinger (79). To test whether polarization was still effective after platinizing the electrodes, the resistances of standard potassium chloride solutions were measured at three different frequencies. Application of the relation due to Jones and Bollinger proved that polarization effects were negligible. The relation is

$$R_s = R_t + \frac{k}{w}$$

in which R_s is the apparent resistance, R_t is the true resistance and w is the frequency. k is the slope of the curve derived by plotting R_s as a function of $\frac{1}{w}$. If polarization effects are small, the resistance will not vary with frequency.

The cell constants were determined by measuring the resistances of standard potassium chloride solutions at concentrations recommended by Shedlovsky (80). The specific conductances of the potassium chloride solutions are accurately known so that the cell constant is readily obtained from the relation

$$k = LR \ .$$

The cell constants were measured at several concentrations of potassium chloride in order to account for the Parker effect, which is the change in cell constant with resistance and is due to the capacitances between leads of the conductance cells.

B. Procedure

The conductivity cells were soaked in conductivity water for at least two hours and then rinsed three times with the rare earth solution to be measured. They were finally filled completely with solution and the ground glass stoppers were placed in the cells. The cells were placed in the oil thermostat and allowed to reach temperature equilibrium. This usually took about one half hour.

The platinum leads from the bridge were then placed in the mercury filled side arms of the cells. By successive adjustment of resistance and capacitance values on the bridge, a minimum in the sine wave on the oscillograph was obtained. The bridge was adjusted to ground potential and a new null obtained. This represented the final resistance value which was used to calculate the specific conductances and the equivalent conductances.

In order to avoid errors due to soaking out salt absorbed at the electrodes, the lowest concentrations were measured first followed by measurement of solutions of increasing concentrations.

In each case the specific conductance of the conductivity water was known and was subtracted from the total calculated specific conductance so that the resulting value was that of the solute alone.

C. Results

The values of resistance obtained from the Jones bridge were in ohms so that the conductances were calculated directly from the relations

$$L = \frac{k}{R} - L_{H_2O}$$

and

$$\Lambda = \frac{1000\ L}{C} .$$

These equations are described earlier in the thesis.

The data for the rare earth sulfates are listed in Tables 3 through 12 and are plotted in Figures 6 and 7.

The data for the rare earth perchlorates may be found in Tables 13 through 20 and are plotted in Figures 8 and 9.

The rare earth nitrate data are tabulated in Tables 21 through 23 and are plotted in Figure 10.

The equivalent conductances at infinite dilution were obtained in the following manner. The Onsager equation for the equivalent conductance was rearranged in the form

$$\Lambda_0' = \Lambda + [A\Lambda_0' + B]C^{1/2} .$$

Λ_0' is the equivalent conductance at infinite dilution calculated by successive approximations from the Onsager equation using the measured equivalent conductance and the experimental concentrations. A and B are evaluated from the constants described in the theoretical section on conductance.

When Λ_0' is plotted against $C^{1/2}$, as the Onsager equation becomes valid the slope of the curve approaches zero and extrapolation to infinite dilution gives the true Λ_0.

For the rare earth sulfates the Onsager equation takes the form

$$\Lambda_0' = [18.1604y\Lambda_0' + 582.79]\left(\frac{C}{6}\right)^{1/2} + \Lambda$$

Table 3

Equivalent Conductances of Lanthanum Sulfate at 25°C

Normality	(Normality)$^{1/2}$	Specific conductance	Equivalent conductance	Calculated Λ_0'
0.1021	0.3195	0.002572	25.20	
0.08164	0.2857	0.004856	26.77	
0.06123	0.2474	0.001770	28.91	
0.04082	0.2020	0.001315	32.21	
0.02041	0.1429	0.0007891	38.66	
0.01021	0.1010	0.0004720	46.25	122.3
0.005103	0.07143	0.0002831	55.49	95.10
0.002551	0.05051	0.0001694	66.38	91.43
0.0005103	0.02259	0.00005082	99.60	110.7
0.0002551	0.01597	0.00002901	113.7	121.9
0.0000			149.5	

Table 4

Equivalent Conductances of Cerous Sulfate at 25°C

Normality	(Normality)$^{1/2}$	Specific conductance	Equivalent conductance	Calculated Λ_o'
0.5302	0.7281	0.008571	16.17	
0.2121	0.4605	0.004349	20.51	
0.1060	0.3256	0.002607	24.59	
0.07953	0.2820	0.002119	26.65	
0.05302	0.2303	0.001571	29.63	
0.02651	0.1628	0.0009517	35.90	
0.01060	0.1030	0.0004860	45.84	
0.007953	0.08918	0.0003914	49.21	
0.005302	0.07281	0.0002895	54.60	95.42
0.002651	0.05149	0.0001741	65.67	91.32
0.001060	0.03256	0.00009065	85.49	101.4
0.0007953	0.02820	0.00007082	89.05	102.8
0.0005302	0.02303	0.00005306	100.1	111.6
0.0002651	0.01628	0.00003026	114.1	122.5
0.0001060	0.01030	0.00001342	126.6	132.0
0.0000			149.5	

Table 5

Equivalent Conductances of Praseodymium Sulfate at 25°C

Normality	$(\text{Normality})^{1/2}$	Specific conductance	Equivalent conductance	Calculated Λ_0'
1.1477	1.0713	0.1470	12.81	
0.5739	0.7575	0.09089	15.84	
0.1148	0.3388	0.002775	24.18	
0.08608	0.2934	0.002243	26.05	
0.05739	0.2396	0.001671	29.12	
0.02869	0.1694	0.001006	35.05	
0.01148	0.1071	0.0005107	44.50	
0.008608	0.09278	0.0004121	47.87	
0.005739	0.07575	0.0003055	53.24	96.65
0.002869	0.05357	0.0001844	64.27	91.13
0.001148	0.03388	0.00009311	81.13	97.39
0.0008608	0.02934	0.00007461	86.67	100.8
0.0005739	0.02396	0.00005460	95.14	106.8
0.0002869	0.01694	0.00003177	110.7	119.3
0.0000			149.5	

Table 6

Equivalent Conductances of Neodymium Sulfate at 25°C

Normality	(Normality)$^{1/2}$	Specific conductance	Equivalent conductance	Calculated Λ_0'
0.4807	0.6933	0.008098	16.85	
0.3845	0.6201	0.006832	17.77	
0.2884	0.5333	0.005525	19.16	
0.1923	0.4385	0.004094	21.29	
0.09613	0.3101	0.002452	25.50	
0.07210	0.2685	0.001985	27.53	
0.04807	0.2192	0.001474	30.66	
0.03605	0.1899	0.001193	33.08	
0.02403	0.1550	0.0008848	36.82	
0.01202	0.1096	0.0005296	44.07	
0.007210	0.08491	0.0003616	50.16	103.3
0.004807	0.06933	0.0002686	55.87	93.76
0.002403	0.04903	0.0001614	67.14	91.29
0.001202	0.03466	0.00009605	79.94	96.66
0.0007210	0.02685	0.00006500	90.16	103.1
0.0004807	0.02192	0.00004764	99.12	109.9
0.0000			149.5	

Table 7

Equivalent Conductances of Samaric Sulfate at 25°C

Normality	$(\text{Normality})^{1/2}$	Specific conductance	Equivalent conductance	Calculated Λ_0'
0.2575	0.5074	0.004992	19.39	
0.1288	0.3588	0.002989	23.22	
0.07725	0.2779	0.002049	26.52	
0.05150	0.2269	0.001524	29.59	
0.03863	0.1965	0.001232	31.91	
0.02575	0.1605	0.0009134	35.47	
0.01288	0.1135	0.0005462	42.42	
0.006438	0.08023	0.0003272	50.83	98.60
0.003863	0.06215	0.0002243	58.08	91.18
0.002575	0.05075	0.0001661	64.79	79.19
0.001288	0.03588	0.00009980	77.52	87.39
0.0006438	0.02537	0.00005916	91.89	98.95
0.0003219	0.01794	0.00003418	106.2	111.3
0.0000			148.5	

Table 8

Equivalent Conductances of Gadolinium Sulfate at 25°C

Normality	$(\text{Normality})^{1/2}$	Specific conductance	Equivalent conductance	Calculated Λ'_0
0.3272	0.5721	0.006064	18.53	
0.1636	0.4045	0.003631	22.19	
0.09817	0.3133	0.002486	25.32	
0.06545	0.2559	0.001849	28.24	
0.03272	0.1809	0.001102	33.68	
0.01636	0.1279	0.0006605	40.37	
0.009817	0.09908	0.0004508	45.92	
0.006545	0.08090	0.0003341	51.05	
0.003272	0.05721	0.0002000	61.13	90.02
0.001636	0.04045	0.0001198	73.21	92.68
0.0009817	0.03133	0.00008149	83.01	97.95
0.0006545	0.02559	0.00005966	91.15	103.4
0.0003272	0.01809	0.00003462	105.8	114.8
0.0001636	0.01279	0.00001979	121.0	127.8
0.0000			147.4	

Table 9

Equivalent Conductances of Holmium Sulfate at 25°C

Normality	(Normality)$^{1/2}$	Specific conductance	Equivalent conductance	Calculated Λ_0'
0.6509	0.8068	0.01012	15.54	
0.1953	0.4419	0.004407	22.57	
0.09769	0.3126	0.002624	26.86	
0.05858	0.2420	0.001797	30.68	
0.02931	0.1712	0.001070	36.51	
0.009769	0.09884	0.0004710	48.22	
0.005858	0.07655	0.0003222	55.00	99.90
0.002931	0.05414	0.0001923	65.63	92.85
0.0009769	0.03126	0.00008421	86.21	101.4
0.0005858	0.02420	0.00005664	96.68	108.6
0.0002931	0.01712	0.00003216	109.7	118.3
0.00009769	0.009884	0.00001256	128.5	133.8
0.0000			146.3	

Table 10

Equivalent Conductances of Erbium Sulfate at 25°C

Normality	$(\text{Normality})^{1/2}$	Specific conductance	Equivalent conductance	Calculated Λ_o'
1.4536	1.206	0.01985	13.66	
0.2907	0.5392	0.006094	20.96	
0.1644	0.4054	0.003949	24.02	
0.08721	0.2953	0.002457	28.17	
0.05814	0.2411	0.001812	31.16	
0.02907	0.1705	0.001081	37.18	
0.01454	0.1206	0.0006435	44.27	
0.008721	0.09339	0.0004397	50.42	
0.005814	0.07625	0.0003250	55.90	100.8
0.002907	0.05392	0.0001925	66.20	93.71
0.001454	0.03813	0.0001157	79.60	98.30
0.0008721	0.02953	0.00007851	90.01	104.5
0.0005814	0.02411	0.00005696	97.96	109.9
0.0002907	0.01705	0.00003205	110.3	118.8
0.0000			145.9	

Table 11

Equivalent Conductances of Ytterbic Sulfate at 25°C

Normality	(Normality)$^{1/2}$	Specific conductance	Equivalent conductance	Calculated Λ_0'
3.3345	1.826	0.03296	9.884	
0.3335	0.5775	0.007171	21.51	
0.1000	0.3169	0.002841	28.40	
0.06669	0.2582	0.002091	31.35	
0.05002	0.2236	0.001681	33.62	
0.03335	0.1826	0.001243	37.27	
0.01000	0.1000	0.0005055	50.53	
0.006669	0.08166	0.0003702	55.50	
0.005002	0.07072	0.0003003	60.05	100.5
0.003335	0.05775	0.0002222	66.63	97.47
0.001000	0.03169	0.00008971	89.67	105.4
0.0006252	0.02582	0.00006177	98.79	111.29
0.0003335	0.01826	0.00003664	109.9	119.2
0.0001000	0.01000	0.00001319	131.9	137.2
0.0000			145.2	

Table 12

Equivalent Conductances of Yttrium Sulfate at 25°C

Normality	(Normality)$^{1/2}$	Specific conductance	Equivalent conductance	Calculated Λ_0'
1.2357	1.1116	0.01851	14.98	
0.2471	0.4971	0.005456	22.08	
0.1606	0.4008	0.003933	24.49	
0.09885	0.3144	0.002736	27.68	
0.04943	0.2223	0.001628	32.94	
0.02471	0.1572	0.0009676	39.16	
0.01606	0.1267	0.0007001	43.58	
0.009885	0.09942	0.0004866	49.23	
0.004943	0.07030	0.0002896	58.59	
0.002471	0.04971	0.0001730	69.99	93.09
0.001606	0.04008	0.0001251	77.86	97.59
0.0009885	0.03144	0.00008615	87.15	102.5
0.0004943	0.02223	0.00004985	100.9	111.9
0.0002471	0.01572	0.00002843	115.0	123.1
0.0001606	0.01267	0.00001954	121.6	128.4
0.0000			144.7	

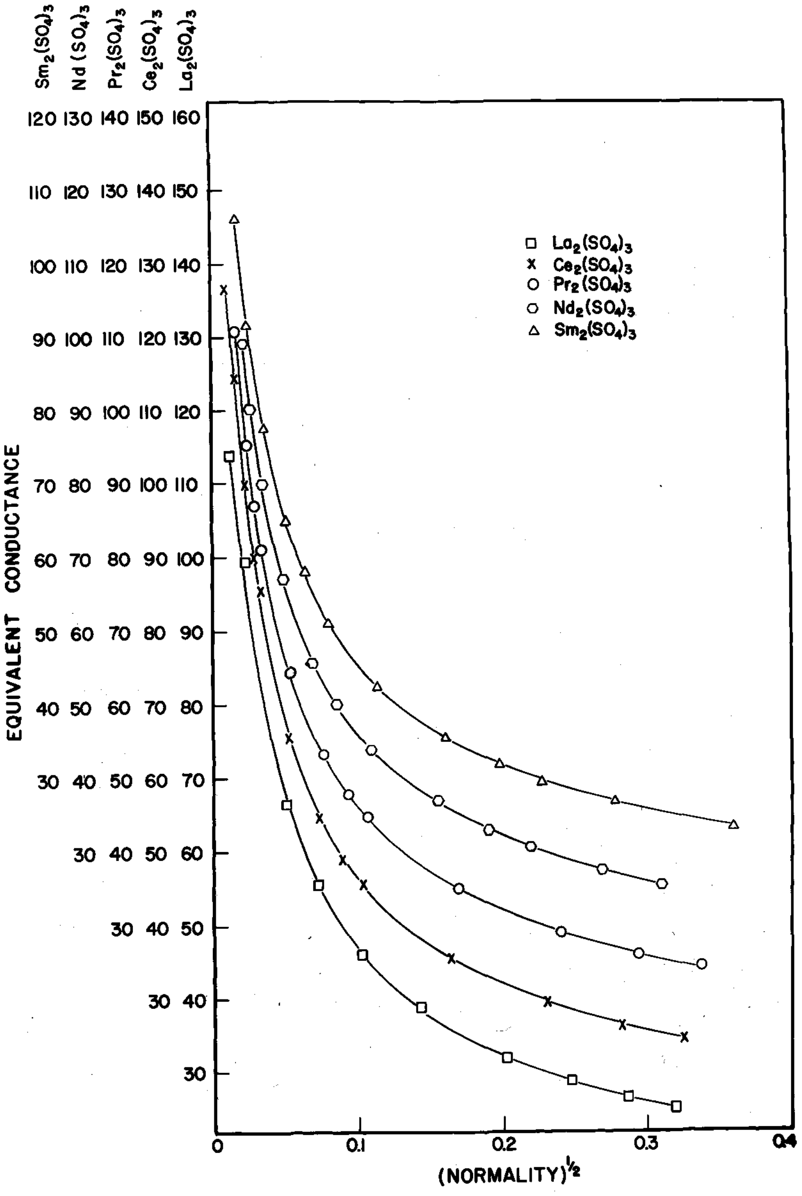


Figure 6. Equivalent Conductances of Lanthanum, Cerium, Praseodymium, Neodymium, and Samarium Sulfates at 25°C.

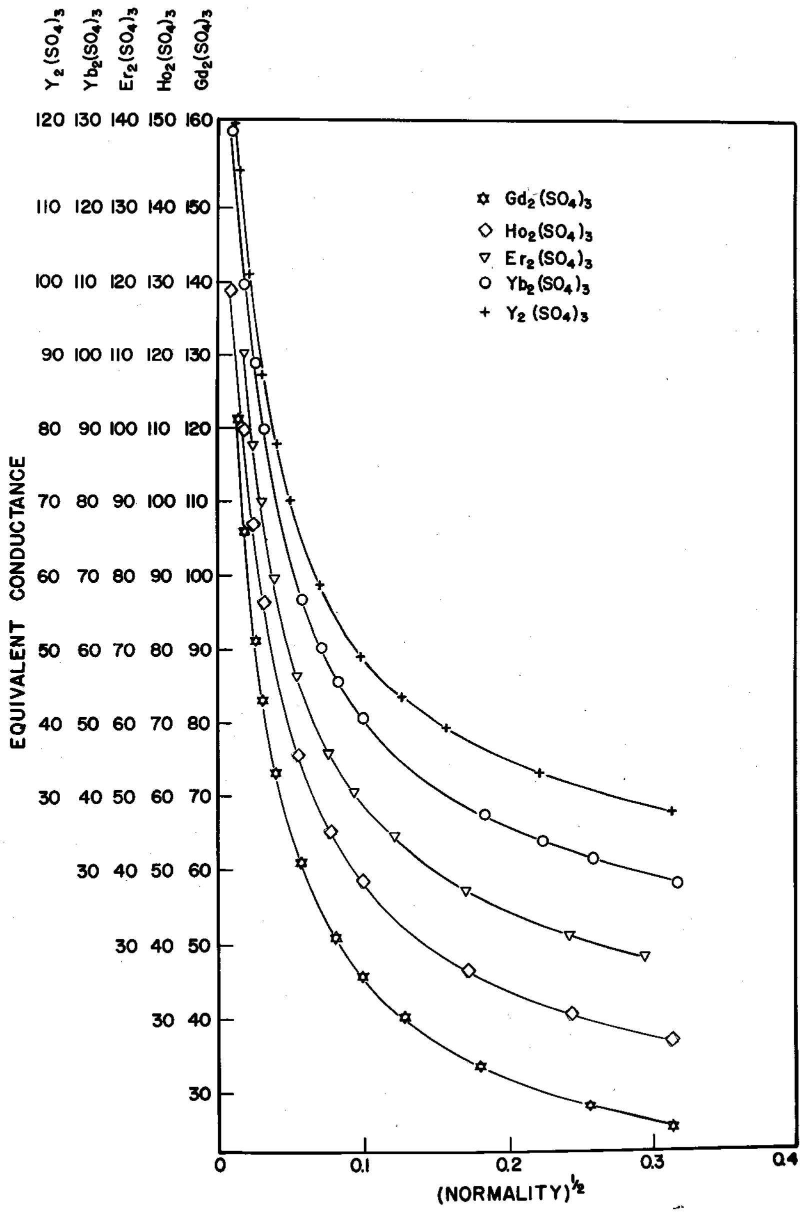


Figure 7. Equivalent Conductances of Gadolinium, Holmium, Erbium, Ytterbium, and Yttrium Sulfates at 25°C.

Table 13

Equivalent Conductances of Lanthanum Perchlorate at 25°C

Normality	(Normality)$^{1/2}$	Specific conductance	Equivalent conductance	Calculated Λ_0'
0.1091	0.3303	0.01048	96.04	
0.07273	0.2697	0.007231	99.43	
0.03636	0.1907	0.003824	105.2	
0.01818	0.1348	0.002019	111.0	
0.01091	0.1044	0.001255	115.1	144.5
0.007273	0.08528	0.0008592	118.2	142.0
0.003636	0.06032	0.0004464	122.8	139.7
0.001818	0.04264	0.0002305	126.8	138.6
0.001091	0.03303	0.0001406	128.9	138.1
0.0007273	0.02697	0.00009478	130.3	137.8
0.0003636	0.01907	0.00004808	132.2	137.5
0.0000			137.0	

Table 14

Equivalent Conductances of Praseodymium Perchlorate at 25°C

Normality	(Normality)$^{1/2}$	Specific conductance	Equivalent conductance	Calculated Λ_0'
0.1058	0.3252	0.01019	96.36	
0.07050	0.2655	0.007018	99.54	
0.05288	0.2300	0.005400	102.1	
0.03525	0.1878	0.003715	105.4	
0.01763	0.1328	0.001962	111.3	
0.01058	0.1028	0.001220	115.3	
0.007050	0.08397	0.0008333	118.2	141.8
0.005288	0.07272	0.0006363	120.3	140.6
0.003525	0.05937	0.0004332	122.9	139.5
0.001763	0.04391	0.0002229	126.4	138.6
0.001058	0.03252	0.0001361	128.7	137.7
0.0007050	0.02655	0.00009168	130.0	137.4
0.0005288	0.02300	0.00006925	131.0	137.3
0.0003525	0.01878	0.00004648	131.9	137.0
0.0001763	0.01328	0.00002348	133.2	136.9
0.0000			136.8	

Table 15

Equivalent Conductances of Neodymium Perchlorate at 25°C

Normality	(Normality)$^{1/2}$	Specific conductance	Equivalent conductance	Calculated Λ_0'
0.09641	0.3106	0.009333	96.80	
0.0427	0.2535	0.006433	100.1	
0.04820	0.2196	0.004948	102.5	
0.03214	0.1793	0.003407	106.0	
0.009641	0.09819	0.001116	115.7	143.4
0.006427	0.08017	0.0007614	118.5	140.9
0.004820	0.06943	0.0005801	120.4	139.7
0.003214	0.05669	0.0003950	122.9	138.7
0.0009641	0.03105	0.0001243	128.9	137.6
0.0006427	0.02535	0.00008366	130.2	137.2
0.0004820	0.02196	0.00006325	131.2	137.3
0.0003214	0.01793	0.00004251	132.3	137.2
0.0000			137.2	

Table 16

Equivalent Conductances of Samaric Perchlorate at 25°C

Normality	$(\text{Normality})^{1/2}$	Specific conductance	Equivalent conductance	Calculated Λ_0'
0.1086	0.3295	0.01035	95.32	
0.06204	0.2491	0.006193	99.83	
0.04653	0.2157	0.004759	102.3	
0.03102	0.1761	0.003276	105.6	
0.01551	0.1246	0.001725	111.2	
0.01086	0.1042	0.001237	113.9	
0.006204	0.07876	0.0007323	118.1	140.1
0.004653	0.06821	0.0005590	120.1	139.2
0.003102	0.05569	0.0003803	122.6	138.1
0.001551	0.03938	0.0001955	126.0	136.9
0.001086	0.03295	0.0001381	127.3	136.3
0.0006204	0.02491	0.00008021	129.3	136.2
0.0004653	0.02157	0.00006054	130.1	136.1
0.0003102	0.01761	0.00004061	130.9	135.8
0.0000			135.8	

Table 17

Equivalent Conductances of Gadolinium Perchlorate at 25°C

Normality	(Normality)$^{1/2}$	Specific conductance	Equivalent conductance	Calculated Λ_0'
0.09692	0.3113	0.009223	95.16	
0.06461	0.2542	0.006357	98.39	
0.04846	0.2201	0.004881	100.7	
0.03231	0.1797	0.003364	104.1	
0.01615	0.1271	0.001773	109.8	
0.009692	0.09845	0.001102	113.7	141.2
0.006461	0.08038	0.0007520	116.4	138.7
0.004846	0.06961	0.0005727	118.2	137.4
0.003231	0.05684	0.0003903	120.8	136.4
0.001615	0.04019	0.0002008	124.3	135.3
0.0009692	0.03113	0.0001222	126.1	134.6
0.0006461	0.02542	0.00008235	127.5	134.4
0.0004846	0.02201	0.00006226	128.5	134.5
0.0003231	0.01797	0.00004187	129.6	134.5
0.0000			134.5	

Table 18

Equivalent Conductances of Holmium Perchlorate at 25°C

Normality	$(\text{Normality})^{1/2}$	Specific conductance	Equivalent conductance	Calculated Λ_0'
0.1073	0.3276	0.01005	93.69	
0.08584	0.2930	0.008197	95.49	
0.06438	0.2537	0.006303	97.90	
0.04292	0.2072	0.004345	101.2	
0.02146	0.1465	0.002293	106.8	
0.01073	0.1036	0.001207	112.5	
0.006438	0.08024	0.0007472	116.1	138.3
0.004292	0.06551	0.0005087	118.5	136.6
0.002146	0.04632	0.0002623	122.2	134.9
0.001073	0.03276	0.0001345	125.3	134.3
0.0006438	0.02537	0.00008172	126.9	133.9
0.0004292	0.02072	0.00005505	128.3	133.9
0.0002146	0.01465	0.00002786	129.8	133.8
0.0000			133.8	

Table 19

Equivalent Conductances of Erbium Perchlorate at 25°C

Normality	(Normality)$^{\frac{1}{2}}$	Specific conductance	Equivalent conductance	Calculated Λ_o'
0.1250	0.3535	0.01154	92.32	
0.09371	0.3061	0.008880	94.76	
0.06248	0.2500	0.006124	98.03	
0.03124	0.1767	0.003241	103.7	
0.01250	0.1118	0.001387	111.0	
0.009371	0.09624	0.001061	113.3	140.2
0.006248	0.07904	0.0007257	116.2	138.0
0.003124	0.05589	0.0003762	120.4	135.8
0.001250	0.03535	0.0001558	124.7	134.3
0.0009371	0.03061	0.0001181	126.0	134.4
0.0006248	0.02500	0.00007944	127.2	134.1
0.0004686	0.02165	0.00006004	128.1	134.0
0.0003124	0.01767	0.00004029	129.0	133.8
0.0000			133.5	

Table 20

Equivalent Conductances of Ytterbic Perchlorate at 25°C

Normality	(Normality)$^{1/2}$	Specific conductance	Equivalent conductance	Calculated Λ_0'
0.1076	0.3279	0.01008	93.68	
0.08604	0.2933	0.008216	95.49	
0.06453	0.2540	0.006311	97.80	
0.04302	0.2074	0.004350	101.1	
0.02151	0.1467	0.002298	106.8	
0.008604	0.09276	0.0009799	113.9	139.7
0.006453	0.08033	0.0007489	116.1	138.3
0.004302	0.06559	0.0005093	118.4	136.5
0.002151	0.04638	0.0002638	122.6	135.2
0.0008604	0.02933	0.0001086	126.2	134.1
0.0000			133.4	

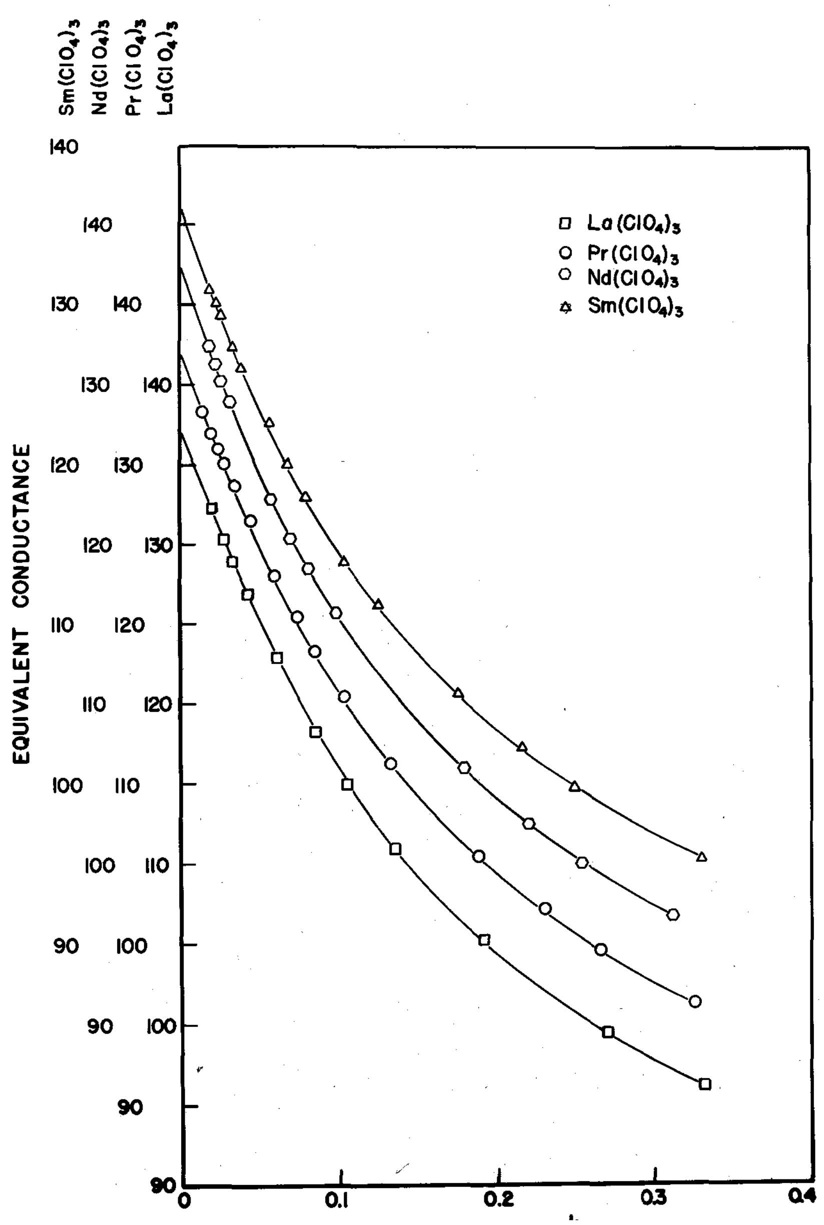


Figure 8. Equivalent Conductances of Lanthanum, Praseodymium, Neodymium, and Samarium Perchlorates at 25°C.

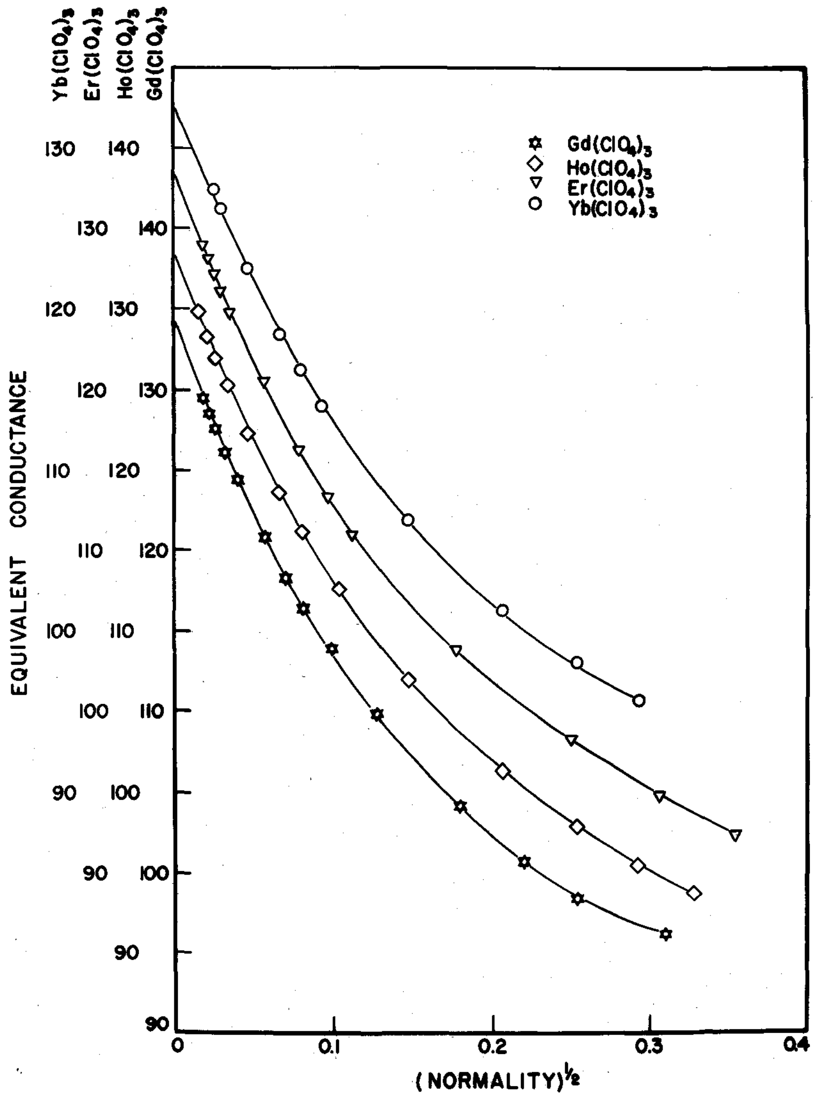


Figure 9. Equivalent Conductances of Gadolinium, Holmium, Erbium, and Ytterbium Perchlorates at 25°C.

Table 21

Equivalent Conductances of Lanthanum Nitrate at 25°C

Normality	$(\text{Normality})^{1/2}$	Specific conductance	Equivalent conductance	Calculated Λ_0'
0.1132	0.3365	0.01024	90.49	
0.07547	0.2747	0.007178	95.11	
0.05660	0.2379	0.005565	98.32	
0.03774	0.1943	0.003890	102.8	
0.01887	0.1374	0.002079	110.2	
0.01132	0.1064	0.001303	115.1	
0.007547	0.08687	0.0008963	118.8	143.0
0.005660	0.07524	0.0006869	121.4	142.3
0.003774	0.06143	0.0004693	124.4	141.5
0.001887	0.04344	0.0002428	128.7	140.8
0.001132	0.03365	0.0001485	131.1	140.5
0.0007547	0.02747	0.0001002	132.8	140.4
0.0005660	0.02379	0.00007581	133.9	140.6
0.0003774	0.01943	0.00005100	135.2	140.6
0.0000			140.6	

Table 22

Equivalent Conductances of Neodymium Nitrate at 25°C

Normality	$(\text{Normality})^{1/2}$	Specific conductance	Equivalent conductance	Calculated Λ_0'
0.1008	0.3175	0.009052	89.82	
0.07559	0.2749	0.007052	93.29	
0.05039	0.2245	0.004943	98.09	
0.02520	0.1587	0.002672	106.1	
0.01008	0.1004	0.001168	115.9	143.9
0.007559	0.08694	0.0008993	119.0	143.2
0.005039	0.07099	0.0006163	122.3	142.1
0.002520	0.05020	0.0003210	127.4	141.4
0.001008	0.03175	0.0001335	132.5	141.3
0.0007559	0.02749	0.0001010	133.6	141.3
0.0005039	0.02245	0.00006804	135.0	141.3
0.0002520	0.01587	0.00003449	136.9	141.3
0.0000			141.3	

Table 23

Equivalent Conductances of Gadolinium Nitrate at 25°C

Normality	(Normality)$^{1/2}$	Specific conductance	Equivalent conductance	Calculated $\Lambda_{\circ}'$
0.1185	0.3442	0.01036	87.42	
0.08886	0.2981	0.008067	90.78	
0.05924	0.2434	0.005652	95.41	
0.02962	0.1721	0.003057	103.2	
0.01481	0.1217	0.001639	110.7	
0.01185	0.1088	0.001334	112.6	
0.008886	0.09426	0.0001027	115.6	141.8
0.005924	0.07697	0.0007057	119.1	140.5
0.002962	0.05442	0.0003684	124.4	139.5
0.001481	0.03848	0.0001901	128.4	139.1
0.001185	0.03442	0.0001531	129.2	138.8
0.0008886	0.02981	0.0001158	130.3	138.6
0.0005924	0.02434	0.00007814	131.9	138.7
0.0000			138.7	

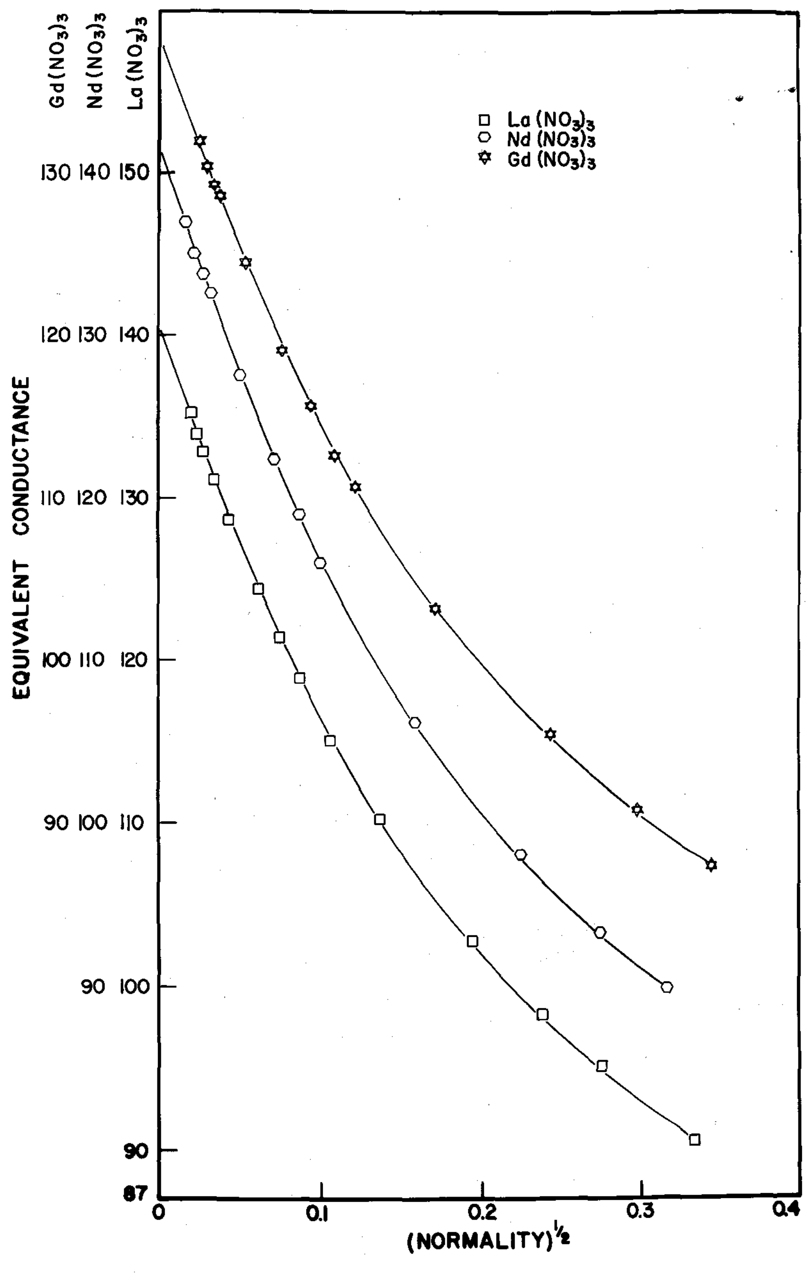


Figure 10. Equivalent Conductances of Lanthanum, Neodymium, and Gadolinium Nitrates at 25°C.

in which

$$y = \frac{\dfrac{1.2\Lambda_0'}{2\Lambda_0' + \lambda_0^-}}{1 + \left(\dfrac{1.2\Lambda_0'}{2\Lambda_0' + \lambda_0^-}\right)^{1/2}} .$$

λ_0^- was taken to be 80 after the value found by D. A. MacInnes (81) and Hartley and Donaldson (82).

The Onsager equation takes the form

$$\Lambda_0' = [3.3158y\Lambda_0' + 170.25]C^{1/2} + \Lambda$$

for both the rare earth perchlorates and the rare earth nitrates. For the rare earth perchlorates

$$y = \frac{\dfrac{0.75\Lambda_0'}{\Lambda_0' + 2\lambda_0^-}}{1 + \left(\dfrac{0.75\Lambda_0'}{\Lambda_0' + 2\lambda_0^-}\right)^{1/2}}$$

and λ_0^- has the value 67.32 as determined by Jones (83). For the rare earth nitrates y is the same as above and λ_0^- was taken to be 71.44 from work by MacInnes, Shedlovsky and Longsworth (84).

Curves representing the extrapolations described above may be seen in Figures 11 through 14. However, the extrapolation of the Onsager values for the rare earth sulfates were very unsatisfactory. The calculated Λ_0' exhibited a

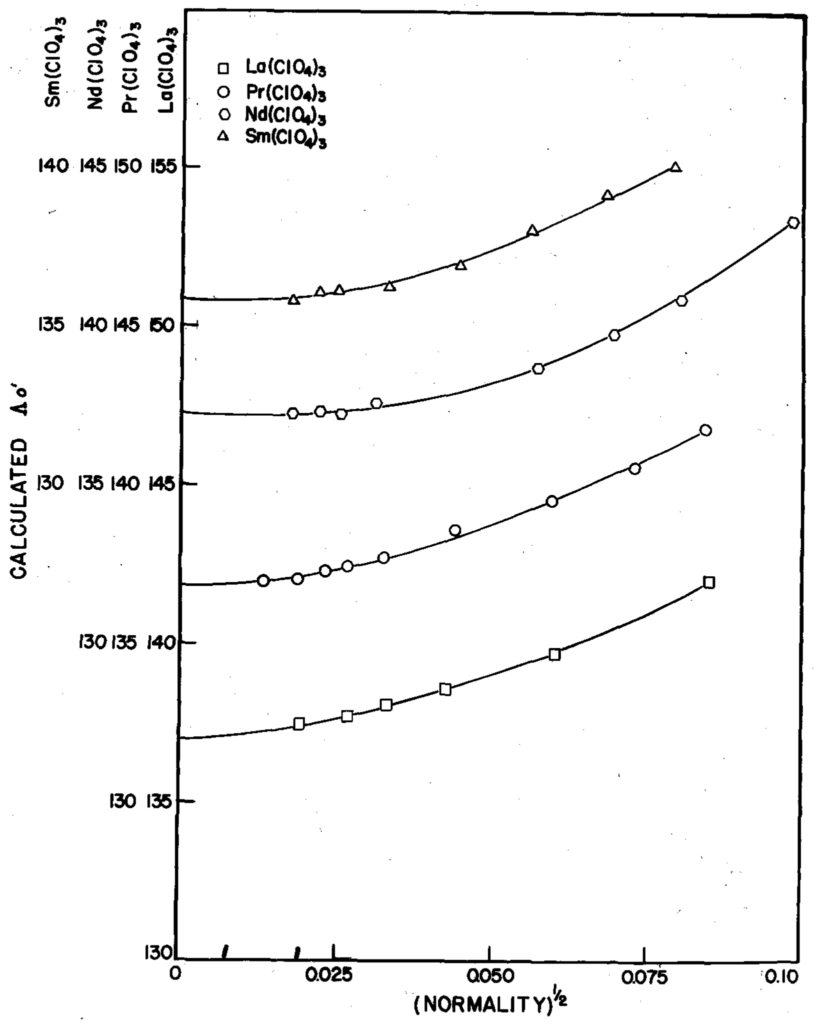


Figure 11. Extrapolation of Equivalent Conductances for Lanthanum, Praseodymium, Neodymium and Samarium Perchlorates.

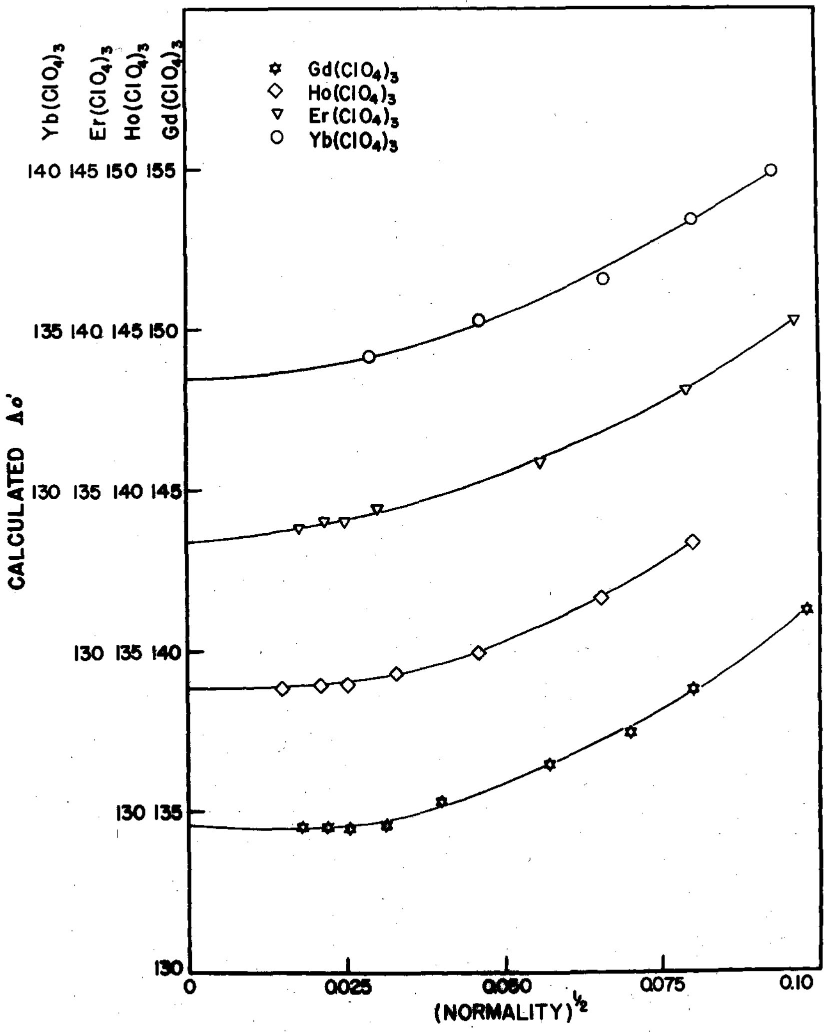


Figure 12. Extrapolation of Equivalent Conductances for Gadolinium, Holmium, Erbium and Ytterbium Perchlorates.

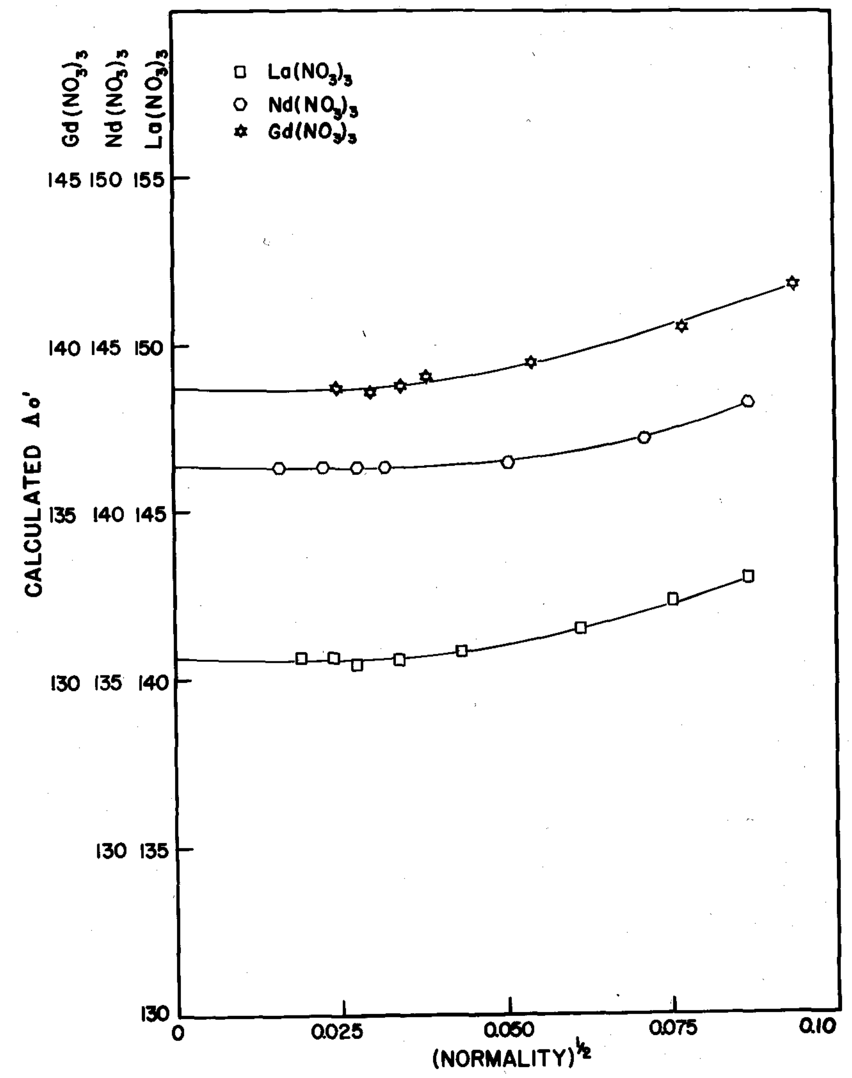


Figure 13. Extrapolation of Equivalent Conductances for Lanthanum, Neodymium and Gadolinium Nitrates.

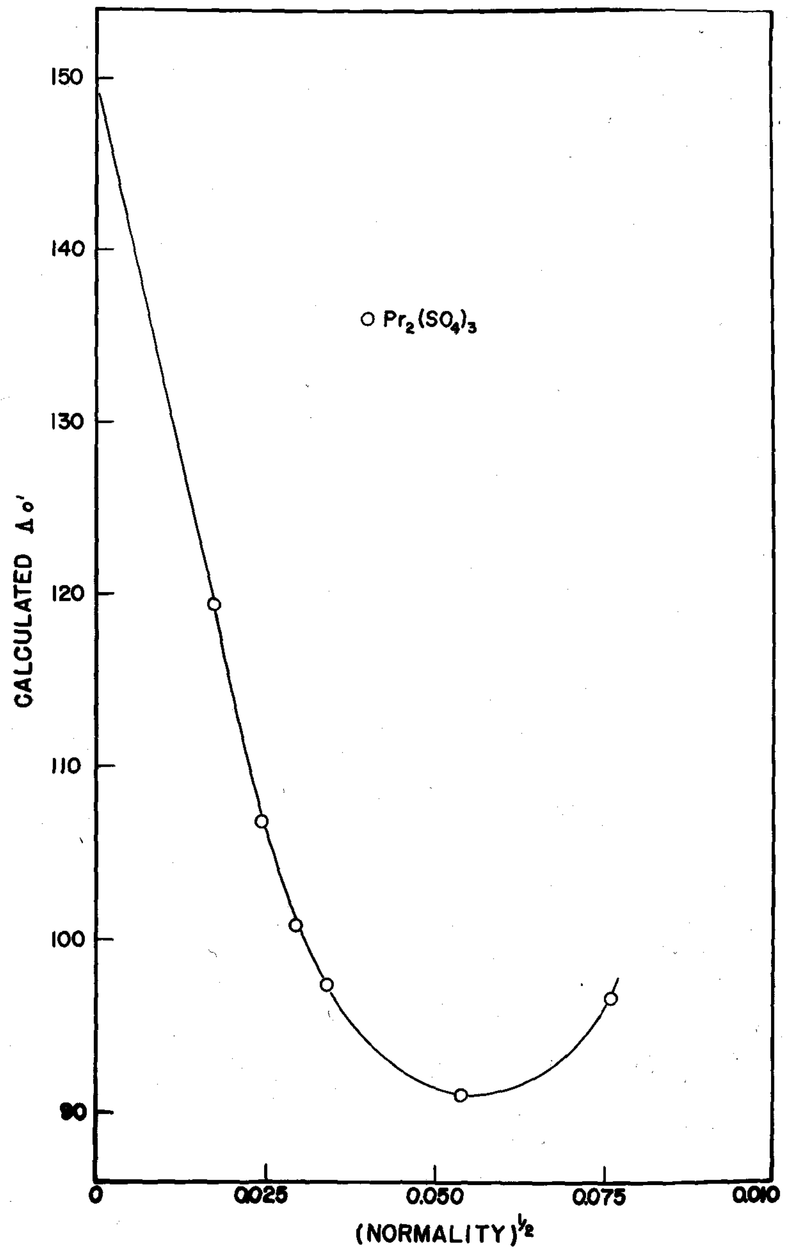


Figure 14. Extrapolation of Equivalent Conductances for Praseodymium Sulfate.

marked minimum around 0.0025 N for most of the sulfates and then the curve rose steeply approaching the proper value of Λ_o. Since the intercepts are not very accurate, only a representative curve is included here. Figure 14 is a plot of the Onsager equation extrapolation for praseodymium sulfate. A proposed explanation of this behavior will be included in the discussion of results.

The Kohlrausch law of the independent mobilities of ions may be expressed for a binary electrolyte at infinite dilution by the relation

$$\Lambda_o = \lambda_o^+ + \lambda_o^- .$$

From a knowledge of the equivalent conductance at infinite dilution of the total solute and the equivalent conductance at infinite dilution of one of the ions, that of the other may be calculated. The values of λ_o^- that are listed above were used for this purpose along with the extrapolated Λ_o values obtained in this work. The results are shown in Table 24.

Table 24

Rare Earth Ionic Equivalent Conductances at Infinite Dilution

Element	λ_o^+ from sulfates[a]	λ_o^+ from perchlorates	λ_o^+ from nitrates
La	69.8	69.7	69.2
Ce	69.9		
Pr	69.7	69.5	
Nd	70.3	69.9	69.9
Sm	68.6	68.5	
Gd	67.4	67.2	67.3
Ho	66.5	66.5	
Er	66.0	66.2	
Yb	65.5	66.1	
Y	64.7		

[a] The sulfate values are probably uncertain to the extent of ±0.5 conductance units because of the unsatisfactory extrapolation of Λ_o'.

D. Discussion

The equivalent conductances of the rare earth perchlorates were found to decrease slightly with an increase in atomic number. The first three elements, lanthanum, praseodymium and neodymium, have very similar conductances; whereas the values for samarium and gadolinium decrease in order. The last three elements, holmium, erbium and ytterbium, are also relatively close to each other and somewhat below the lighter rare earths. This order is about the same as that found for the rare earth chlorides (85) and the rare earth bromides (2).

Although the ionic radii of the rare earths are decreasing with increasing atomic number, their equivalent conductances are decreasing. This seems to indicate that the effective sizes of the ions in solution are increasing rather than decreasing with atomic number since a smaller ion with a given charge would be expected to result in a higher conductance. An increase in hydration of the ions with the series could account for this anomaly since hydration plays a very important part in determining the limiting mobilities of ions. A similar behavior has been observed for the conductance of lithium ions. Although lithium is a much smaller ion than the rest of the alkali elements, it has a much lower mobility which is apparently due to hydration.

The extrapolation of the Λ_o' values as a function of the square root of the normality may be used as an indication of the applicability of the Onsager limiting law for equivalent conductances. The rare earth perchlorates are apparently beginning to obey the simple limiting law only at around 0.0003 N as evidenced by the curves in Figures 11 and 12. Agreement with the theory is reached when the slope of the curve is zero and the extrapolation to infinite dilution gives the true Λ_o value.

Use of the extended Onsager equation has been shown to give much better agreement with experimental results for the rare earth chlorides. The theory is obeyed up to about 0.008 N (86). The extended equation includes the use of the distance of closest approach, a_1, and a graphical integration of the expression for the electrophoretic effect.

The fact that the correction, due to the insertion of a_1 and the use of the extended equation, would have to be larger for the perchlorates than for the chlorides indicates that the distance of closest approach plays an important part in making conductance data agree with theory. This suggests that the value of a_1 may be obtained from the extended theory and the experimental data. A method for making this evaluation is discussed later in the thesis in the section on the calculation of activity coefficients from conductances.

Only three rare earth nitrates were measured so that no general conclusions about the entire series of the rare earth nitrates can be made. However, the data indicate that the expected conductances will be similar in trend with those of the perchlorates. The extrapolations of the Onsager equations in Figure 13 show that the limiting law holds remarkably well for the nitrates out to about 0.001 N. This indicates that the use of a_1 for the rare earth nitrates would lead to a much smaller correction on the conductances.

The equivalent conductances of the rare earth sulfates are very much lower than would be expected for strong electrolytes. This leads to the conclusion that the rare earth sulfates are complexed or form ion pairs in aqueous solution. If a complex of the form $(RESO_4)^+$ is the major one in dilute solutions, two effects would explain the marked decrease in the conductance. The larger effect would be the lowering of the charge on the rare earth ions from three to one. The other effect is the removal of sulfate ions from solution further decreasing the conductance of the solution.

The data reported here were calculated on the basis of the completely dissociated salt. Since it is evident that there must be some association in solution to account for the extensive lowering of the conductance, the concept of equivalent conductance for the salt $RE_2(SO_4)_3$ does not have much significance. Figure 14 shows that the Onsager limiting equation does not apply except at infinite dilution for the rare earth sulfates. The large minimum in the curve is apparently a result of inserting the incorrect charge types and the incorrect concentrations in the Onsager equation.

However, in order to use the correct concentrations and valences of the proposed complexes, their instability constants must be known. In addition, the Onsager equation for the case of more than two kinds of ions in solution has not been explicitly solved. Jenkins and Monk (87) and Davies (88) attempted to calculate instability constants for the $LaSO_4^+$ complex. However, their method was to estimate the limiting mobility of the complex and use this value to calculate the concentrations of the various species and hence the equilibrium constant. Davies estimated that the limiting mobility of the $LaSO_4^+$ ion is about 40. From this he calculated the equilibrium constant to be 2.8×10^{-4} for the dissociation of the complex. Since this constant is a result of a number of assumptions and has not been verified, it will not be used in interpreting the sulfate data.

The order of the equivalent conductances of the rare earth sulfates with an increase in atomic number is quite different from that of the perchlorates, nitrates and halides except at infinite dilution. The equivalent conductances of about 0.1 N solutions change in the following manner. There is a slight decrease in the conductance of cerous sulfate over that of lanthanum and then a rise to a maximum at neodymium. This is followed by a minimum again at samarium and then an increasing conductance from samarium to ytterbium. This order may be explained by the relative stabilities of the rare earth sulfate complexes as the atomic number increases. The more stable the complex, the lower the expected conductance and the lower the equilibrium constant for the dissociation of the complex. Therefore, the dissociation constants would be expected to follow the order that the conductances now exhibit.

At infinite dilution the ions are far enough apart to be virtually uncomplexed. Therefore, the conductances of the solutions approach those of the completely dissociated salt. Figure 15 compares the equivalent conductances of the rare earth sulfates, nitrates and perchlorates at infinite dilution as a function of the atomic number of the rare earth elements. The curves have relatively the same shapes and differ only by the values of the respective anionic conductances.

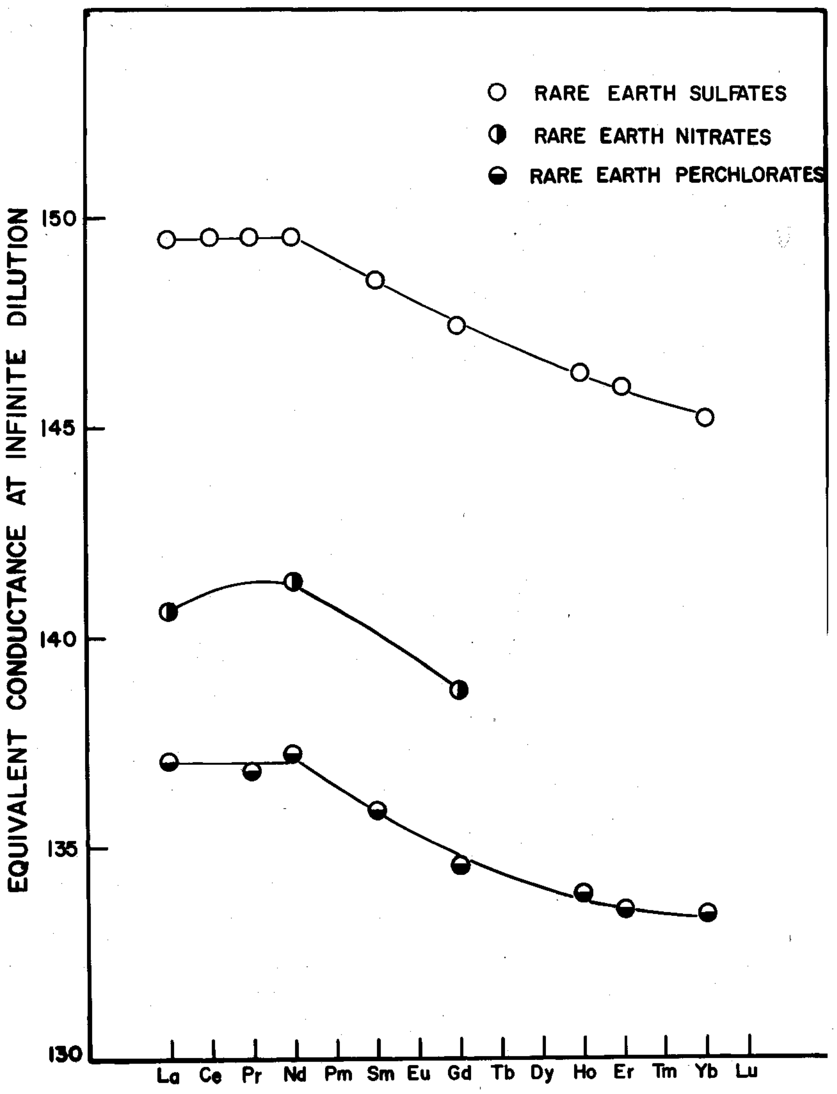


Figure 15. Equivalent Conductances at Infinite Dilution of Some Rare Earth Sulfates, Perchlorates and Nitrates.

The ionic equivalent conductances listed in Table 24 are in relatively good agreement with those of Spedding, Porter and Wright (89) and Spedding and Yaffe (2) which were obtained from the measurement of rare earth halides.

The error in the measurement of the resistances is estimated by the Leeds and Northrup Company to be less than 0.05 per cent. However, the error in analyzing the solutions is about 0.1 per cent and is therefore the error in the measurements reported here.

VI. TRANSFERENCE NUMBERS

A. Apparatus

The apparatus for measuring transference numbers consisted of an electrolytic cell, two stop-watches, an arrangement for viewing the boundary, a constant current controller, a voltage measuring circuit and a constant temperature bath.

The transference number cell was patterned after that employed by MacInnes and Longsworth (66) except that the boundary was sheared by a hollow bore stop-cock instead of the two disc method.

The cathode compartment contained a 29/42 standard taper ground glass joint into which the silver-silver chloride electrode was fitted. This electrode was purchased from the Klett Manufacturing Company and consisted of a silver tube threaded into a silver cylinder coated with silver chloride. The cylinder was made up of alternate layers of flat and corrugated plates of silver. The silver chloride layer was coated on the silver by electrolysis in a 1 N hydrochloric acid solution. The cathode compartment also contained a small bore overflow tube fitted with a stop-cock.

The calibrated measuring tube was sealed to the cathode compartment by means of a large bore U tube. The measuring tube consisted of a two milliliter graduated pipet. The volumes between graduations were calibrated by weighing the mercury displaced between the marks on the tube by the method recommended by Longsworth (68). This was done by sealing a small stop-cock on the bottom of the tube before the cell was assembled. The mercury was allowed to run into a small weighing bottle and the level was observed by means of a telescope cathetometer.

Above the measuring tube was sealed the large hollow bore stop-cock and above this was the anode compartment which was the same as the cathode compartment. The anode consisted of a cadmium metal plug. C.P. cadmium was melted in a test tube under a stream of argon, and, while the metal was still molten, a heavy copper wire was inserted into it and held in position until the cadmium solidified. This electrode was sealed in the male ground glass joint by means of sealing wax.

Two glass electrode cups were used to contain the electrolysis products and prevent mixing of these products with the body of the solutions.

The electrolytic cell is pictured assembled in Figure 16 and in its component parts in Figure 17.

Figure 16. Assembled Transference Number Cell.

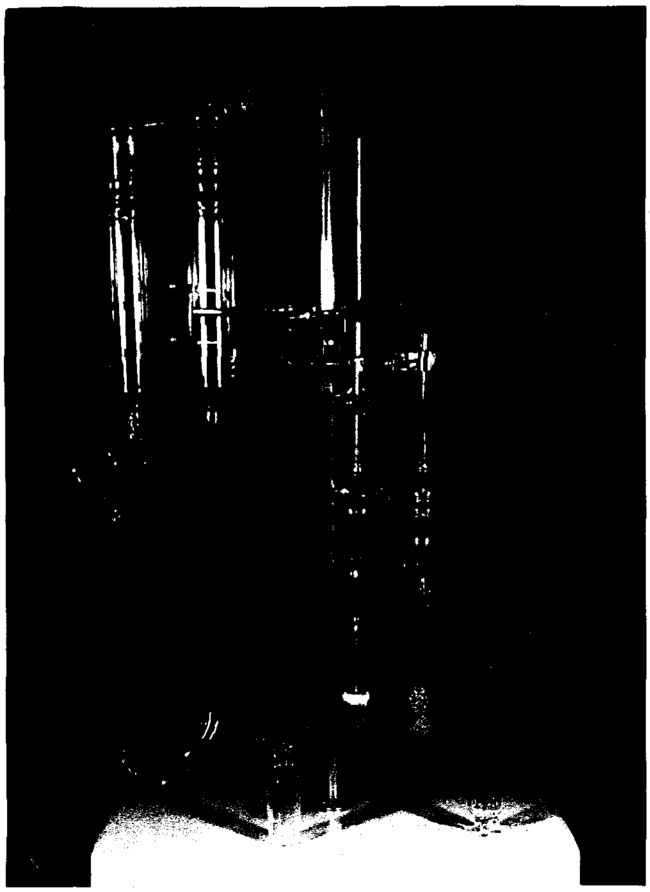


Figure 17. Component Parts of Transference Number Cell.

The time of descent of the boundary between graduated marks was measured by means of two stop-watches, which were checked on a Western Electric Time Rate Recorder. They were shown to be accurate to within four to five seconds for a twenty-four hour period. The watches were mounted side by side in a wooden box which had its front face open. The lid of the box was hinged at the back and rested on the crowns of the watches. Thus, when the lid was pressed down one of the watches was started and the other was stopped at the same time. This afforded a method for taking continuous individual time readings of the boundary's progress between marks.

The boundary was observed by virtue of differences in the refractive indices of the indicator and leading solutions (58, 59). A light was mounted in a metal box placed behind the glass walled water bath. This box had a narrow slit on its front face which was covered with frosted glass. The box was mounted on an elevator shaft and attached by means of a wire to the pulley of a two r.p.m. reversible motor. When the light passed through the tube at a critical angle for total reflection, the boundary appeared as a sharp black line. This was viewed by means of a telescope cathetometer.

The constant current controller was designed and constructed by A. A. Read and D. W. Hilker of the Electronic Shop of the Ames Laboratory. The unit consists of a high voltage rectifier and filter section which is adjustable to provide up to 4000 volts output at ten milliamperes, a regulated 400 volt power supply which provides power for the current regulator amplifier, and a series type current regulator.

The cell is placed in series with an electronic rheostat the resistance of which is controlled by feedback. The feedback is controlled in such a manner as to tend to keep the current constant. The electronic rheostat is essentially a modification of a conventional voltage regulator. Because of the extremes of cell voltage demanded, it was necessary to design the equipment with the load in the plate circuit of the rheostat tube instead of the cathode circuit as is the usual case.

A schematic drawing of the current controller is pictured in Figure 18.

The voltage drop across a 100 ohm standard resistor in series with the electrolytic cell was measured by means of a Rubicon Type B High Precision Potentiometer. The standard resistor was calibrated by the National Bureau of Standards. From the voltage drop and the resistance value, the current through the cell was calculated.

The constant temperature bath was of the large aquarium type with glass sides so that objects are clearly visible through it when it is filled with distilled water. The

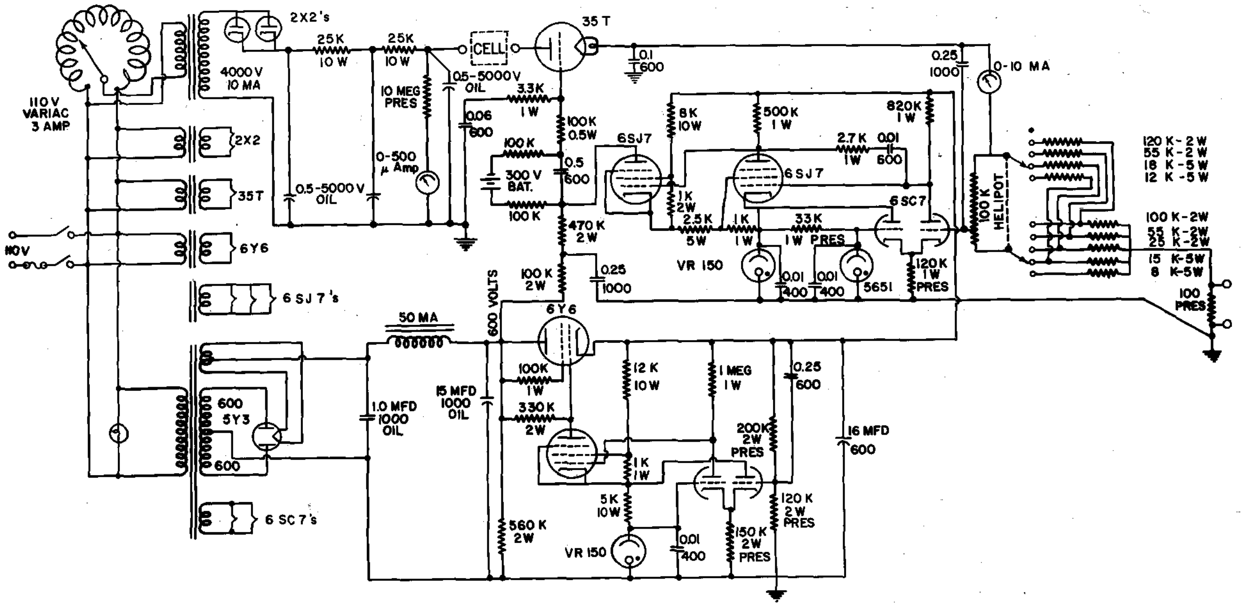


Figure 18. Constant Current Controller.

temperature was controlled at 25 ±0.05°C and was read on a thermometer graduated in 0.01°C divisions. The thermometer was calibrated by the National Bureau of Standards.

The completely assembled apparatus is pictured in Figure 19.

B. Procedure

The transference number cell described in the previous section was cleaned before use by soaking it in hot sulfuric acid and potassium dichromate cleaning solution. It was then rinsed with distilled water and finally soaked in distilled water for several hours.

The hollow bore stop-cock was gently heated and a thin coat of silicone stop-cock grease was spread evenly over the surface. The barrel of the stop-cock was also warmed to insure even coating of the grease and an electrically tight seal.

The cathode compartment along with the measuring tube were rinsed at least three times with the solution to be measured and finally filled to the stop-cock level. After all air bubbles had evolved, the stop-cock was closed and the cathode compartment was filled with rare earth solution.

Following this, the silver-silver chloride electrode and the electrode cup were rinsed with rare earth solution

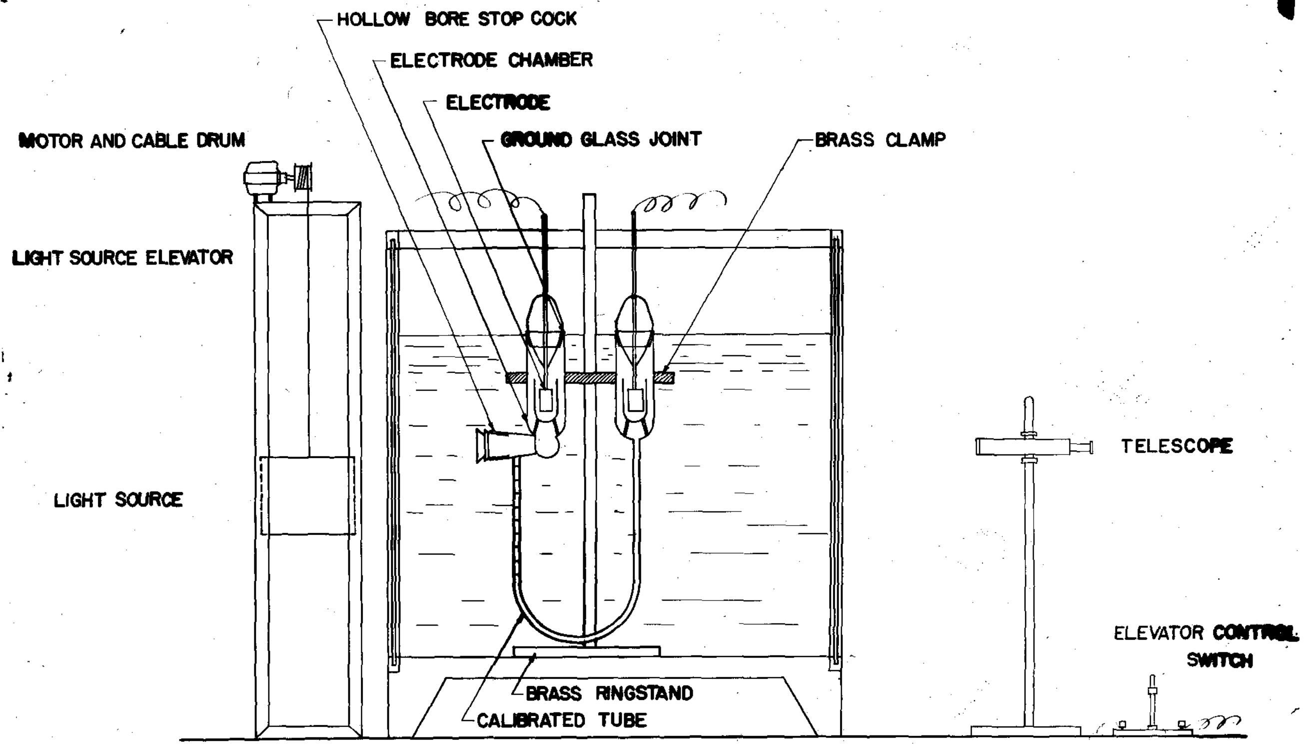


Figure 19. Apparatus Assembly for Determining Transference Numbers.

and inserted into position allowing a little liquid to overflow through the overflow tube. The overflow stop-cock was then closed.

The anode compartment was then rinsed several times with distilled water and at least three times with the lithium chloride indicator solution. The anode compartment was filled carefully to avoid trapping any air bubbles that might affect the volume change. The cadmium electrode together with its cup were rinsed with the indicator solution and inserted into the anode chamber. The anode compartment overflow tube was left open to allow additional overflow of the solution as it warmed up in the thermostat, but the stop-cock was closed before the experiment was begun.

The cell was placed in the water bath so that it was lined up with the light and the marks could be clearly seen with the telescope. A vacuum tube test meter was used to insure that no electrical leaks to ground were present. The experiment was not performed unless infinite resistance to ground was obtained for every possible leak site on the cell. Thermal equilibrium was assumed to have been reached between the time the experiment was started and the time the boundary reached the first calibrated mark. This was usually about one half an hour.

The positive lead from the current controller was clipped to the cadmium electrode and the negative lead was clipped on the silver-silver chloride electrode. The stop-cock on the cell was then opened and the line voltage was turned on. This started the electrolysis and a boundary became visible in a few minutes. The voltage was then increased by adjusting the current controller powerstat until the ammeter indicated that the current was steady and being controlled. The voltage was then increased about twenty-five per cent to account for the expected resistance increase in the measuring tube.

The progress of the boundary was observed by following it down the tube with the light source and the telescope. The hair line of the telescope was placed so that it appeared to be on the calibrated mark and the stop-watch was started just as the boundary merged with the mark and the hair line.

Readings were taken of the voltage and the time whenever the boundary merged with a mark.

C. Results

The average current was computed from the series of voltage readings, and the total time in seconds that it took the boundary to pass a given set of calibrated volumes was recorded. These data were then used to calculate the uncorrected transference numbers using the relation

$$T_{+} = \frac{VCF}{1000It} .$$

The solvent correction was applied using the equation

$$T_{+} = T_{+o}\left(1 + \frac{L_{solvent}}{L_{solution}}\right) ,$$

and the volume correction was calculated from the formula

$$T_{+} = T_{+o} - \frac{\Delta VC}{1000} .$$

All of the above relations have been discussed in previous sections of the thesis. However, the volume correction had to be modified to include the volume change due to the use of lithium chloride as an indicator solution for perchlorate and nitrate systems.

By an argument similar to that outlined in section II C, the volume change in the transference number experiment for perchlorates is

$$\Delta V = \frac{-\overline{V}_{Cd}}{2} + \frac{\overline{V}_{CdCl_2}}{2} + \overline{V}_{ClO_4^-} - \overline{V}_{Cl^-} -$$

$$\frac{T_{+}}{3} \overline{V}_{RE(ClO_4)_3}$$

in which the partial molal volumes are:

$$\overline{V}_{CdCl_2} = 23.24 + 8.82\sqrt{(\text{molality})}, \quad \text{and}$$

$$\overline{V}_{Cd} = 13.0 \quad (90).$$

The partial molal volumes of the rare earth salts were calculated from the expression

$$\overline{V}_{REX_3} = \frac{M_2 - 1000\frac{d\rho}{dm}}{\rho - m\frac{d\rho}{dm}} .$$

The density data and the partial molal volumes are tabulated in Table 25 for the rare earth perchlorates and in Table 26 for the rare earth nitrates. Although the densities of the rare earth sulfates were not used for transference number calculations, the values are listed in Table 27. These densities were measured with a fifty milliliter pycnometer at 25°C. The molar concentration was substituted for the molal concentration without changing the correction.

It is not possible to calculate individual ionic partial molal volumes; however, as a first approximation

$$\overline{V}_{ClO_4^-} - \overline{V}_{Cl^-} \approx \overline{V}_{LiClO_4} - \overline{V}_{LiCl} = 26.48 .$$

This assumes that the major contribution to the volume change is that due to the change in the anion atmosphere around a given cation.

Table 25

Density Equations for $RE(ClO_4)_3$

Salt	Equation	Partial molal volume
$La(ClO_4)_3$	$\rho = .9970 + .334C_m$	$\bar{V} = 104$
$Pr(ClO_4)_3$	$\rho = .9969 + .358C_m$	$\bar{V} = 81.6$
$Nd(ClO_4)_3$	$\rho = .9971 + .347C_m$	$\bar{V} = 99.2$
$Sm(ClO_4)_3$	$\rho = .9968 + .364C_m$	$\bar{V} = 84.8$
$Gd(ClO_4)_3$	$\rho = .9970 + .372C_m$	$\bar{V} = 83.6$
$Ho(ClO_4)_3$	$\rho = .9970 + .369C_m$	$\bar{V} = 94.4$
$Er(ClO_4)_3$	$\rho = .9970 + .382C_m$	$\bar{V} = 84.2$
$Yb(ClO_4)_3$	$\rho = .9970 + .383C_m$	$\bar{V} = 88.5$

Table 26

Density Equations for RE(NO$_3$)$_3$

Salt	Equation	Partial molal volume
La(NO$_3$)$_3$	$\rho = .99695 + .274C_m$	$\bar{V} = 51.1$
Nd(NO$_3$)$_3$	$\rho = .9971 + .279C_m$	$\bar{V} = 51.8$
Gd(NO$_3$)$_3$	$\rho = .9970 + .289C_m$	$\bar{V} = 53.9$

Table 27

Density Equations for $RE_2(SO_4)_3$

Salt	Equation
$La_2(SO_4)_3$	$\rho = .9971 + .565C_m$
$Ce_2(SO_4)_3$	$\rho = .9970 + .553C_m$
$Pr_2(SO_4)_3$	$\rho = .9970 + .554C_m$
$Nd_2(SO_4)_3$	$\rho = .9971 + .568C_m$
$Sm_2(SO_4)_3$	$\rho = .9965 + .667C_m$
$Gd_2(SO_4)_3$	$\rho = .9965 + .5768C_m$
$Ho_2(SO_4)_3$	$\rho = .9969 + .614C_m$
$Er_2(SO_4)_3$	$\rho = .9969 + .617C_m$
$Y_2(SO_4)_3$	$\rho = .9970 + .454C_m$

The partial molal volume was calculated for lithium chloride from the densities obtained from the relation

$$\frac{C_m}{m} = \rho_o - Am + Bm^2 \quad .$$

For lithium chloride A is 0.0182 and B is zero (91). The lithium perchlorate densities were obtained from the equation determined by Jones (83):

$$\rho = 0.9971 + 0.0623m \quad .$$

A similar treatment was used to obtain the volume correction for the rare earth nitrate transference numbers. In this case

$$\Delta V = \frac{-\overline{V}_{Cd}}{2} + \frac{\overline{V}_{CdCl_2}}{2} + \overline{V}_{NO_3^-} - \overline{V}_{Cl^-} - \frac{T^+}{3}\overline{V}_{RE(NO_3)_3}$$

and

$$\overline{V}_{NO_3^-} - \overline{V}_{Cl^-} \approx \overline{V}_{LiNO_3} - \overline{V}_{LiCl} = 10.86 \quad .$$

These values were also calculated from the data in Harned and Owen's text (91).

The correct concentration for the indicator solutions could not be calculated from the Kohlrausch ratio because the transference numbers of lithium perchlorate and lithium nitrate are not known. However, it was possible to obtain the approximate concentration by experiment. Several experiments were made with a given concentration of rare earth solution and a varying concentration of indicator solution. These determinations were continued until a definite plateau region was established in the plot of the transference number of the rare earth solution versus the concentration of the indicator solution. The plateau represents the region in which the Kohlrausch ratio is operative. Within a few per cent, the ratio of the leading solution concentration to the following solution concentration is a constant over the range of concentrations of rare earth solutions measured. Therefore, when a given Kohlrausch ratio was established experimentally for a salt at one concentration, the ratio at the other concentrations could be calculated from the relation

$$\frac{C'}{C} = k$$

in which C is the leading solution's concentration, C' is the following solution's concentration and k is a constant.

k was about 0.85 for the rare earth perchlorates and the rare earth nitrates when lithium chloride was used as following solution.

The transference numbers of the rare earth perchlorates are tabulated in Tables 28 through 35 and those of the rare earth nitrates in Tables 36 through 38. These data are represented in Figures 20 and 21. The least squares equations for the above data appear in Table 39.

By using the relation

$$T_+\Lambda = \lambda_+ ,$$

the individual ionic conductances were calculated. The ionic conductances of the rare earth cations associated with the rare earth perchlorate solutions are tabulated in Table 40 and those for the rare earth nitrates in Table 41. These data are represented in Figures 22 and 23. From the relation

$$\Lambda = \lambda_+ + \lambda_-$$

the anion equivalent conductances were also calculated.

Table 28

Cation Transference Numbers for Lanthanum Perchlorate at 25°C

Normality	$(\text{Normality})^{1/2}$	T_+ (uncorrected)	Volume correction	Solvent correction	T_+ (corrected)
0.109089	0.3303	0.4721	-0.0018	0.0001	0.4704
0.0720726	0.2697	0.4777	-0.0011	0.0001	0.4767
0.036363	0.1907	0.4852	-0.0005	0.0002	0.4848
0.0181815	0.1348	0.4907	-0.0003	0.0003	0.4906
0.0109089	0.1044	0.4929	-0.0002	0.0005	0.4930

Table 29

Cation Transference Numbers for Praseodymium Perchlorate at 25°C

Normality	$(\text{Normality})^{1/2}$	T_+ (uncorrected)	Volume correction	Solvent correction	T_+ (corrected)
0.10575	0.3252	0.4754	-0.0020	0.0001	0.4734
0.070502	0.2655	0.4815	-0.0014	0.0002	0.4802
0.052877	0.2299	0.4837	-0.0009	0.0002	0.4829
0.035251	0.1878	0.4881	-0.0007	0.0003	0.4876
0.017626	0.1328	0.4925	-0.0003	0.0005	0.4925
0.010575	0.1028	0.4965	-0.0002	0.0009	0.4967

Table 30

Cation Transference Numbers for Neodymium Perchlorate at 25°C

Normality	$(\text{Normality})^{1/2}$	T_+ (uncorrected)	Volume correction	Solvent correction	T_+ (corrected)
0.096408	0.3105	0.4791	-0.0016	0.0000	0.4775
0.064272	0.2535	0.4842	-0.0010	0.0001	0.4833
0.048204	0.2196	0.4872	-0.0008	0.0001	0.4865
0.032136	0.1793	0.4903	-0.0005	0.0001	0.4899
0.0096408	0.09819	0.4974	-0.0001	0.0003	0.4975

Table 31

Cation Transference Numbers for Samarium Perchlorate at 25°C

Normality	$(\text{Normality})^{1/2}$	T_+ (uncorrected)	Volume correction	Solvent correction	T_+ (corrected)
0.10856	0.3295	0.4755	-0.0021	0.0000	0.4734
0.062036	0.2491	0.4835	-0.0012	0.0001	0.4824
0.046527	0.2157	0.4860	-0.0009	0.0001	0.4852
0.031018	0.1761	0.4893	-0.0006	0.0001	0.4888
0.015509	0.1245	0.4945	-0.0003	0.0003	0.4945

Table 32

Cation Transference Numbers for Gadolinium Perchlorate at 25°C

Normality	$(\text{Normality})^{1/2}$	T_+ (uncorrected)	Volume correction	Solvent correction	T_+ (corrected)
0.096915	0.3113	0.4720	-0.0020	0.0000	0.4700
0.064610	0.2452	0.4773	-0.0012	0.0001	0.4762
0.0484575	0.2201	0.4798	-0.0009	0.0001	0.4790
0.032305	0.1797	0.4840	-0.0006	0.0001	0.4835
0.0161525	0.1271	0.4884	-0.0003	0.0002	0.4883

Table 33

Cation Transference Numbers for Erbium Perchlorate at 25°C

Normality	$(\text{Normality})^{1/2}$	T_+ (uncorrected)	Volume correction	Solvent correction	T_+ (corrected)
0.0937125	0.3061	0.4618	-0.0018	0.0000	0.4600
0.062475	0.24995	0.4684	-0.0012	0.0001	0.4673
0.031238	0.1767	0.4748	-0.0006	0.0001	0.4743
0.0187425	0.1369	0.4800	-0.0004	0.0002	0.4798
0.012495	0.1118	0.4818	-0.0002	0.0003	0.4819

Table 34

Cation Transference Numbers for Holmium Perchlorate at 25°C

Normality	(Normality)$^{1/2}$	T_+ (uncorrected)	Volume correction	Solvent correction	T_+ (corrected)
0.107296	0.3276	0.4630	-0.0019	0.0000	0.4611
0.085837	0.2930	0.4652	-0.0015	0.0000	0.4637
0.064378	0.2537	0.4682	-0.0011	0.0001	0.4672
0.0429185	0.2072	0.4723	-0.0007	0.0001	0.4717
0.021459	0.1465	0.4772	-0.0004	0.0002	0.4770
0.0107296	0.1036	0.4816	-0.0002	0.0003	0.4817

Table 35

Cation Transference Numbers for Ytterbium Perchlorate at 25°C

Normality	(Normality)$^{1/2}$	T_+ (uncorrected)	Volume correction	Solvent correction	T_+ (corrected)
0.107548	0.3279	0.4590	-0.0020	0.0000	0.4570
0.086038	0.2933	0.4617	-0.0016	0.0000	0.4601
0.064529	0.2540	0.4667	-0.0012	0.0001	0.4656
0.043019	0.2074	0.4702	-0.0008	0.0001	0.4695
0.02151	0.1467	0.4772	-0.0004	0.0002	0.4770

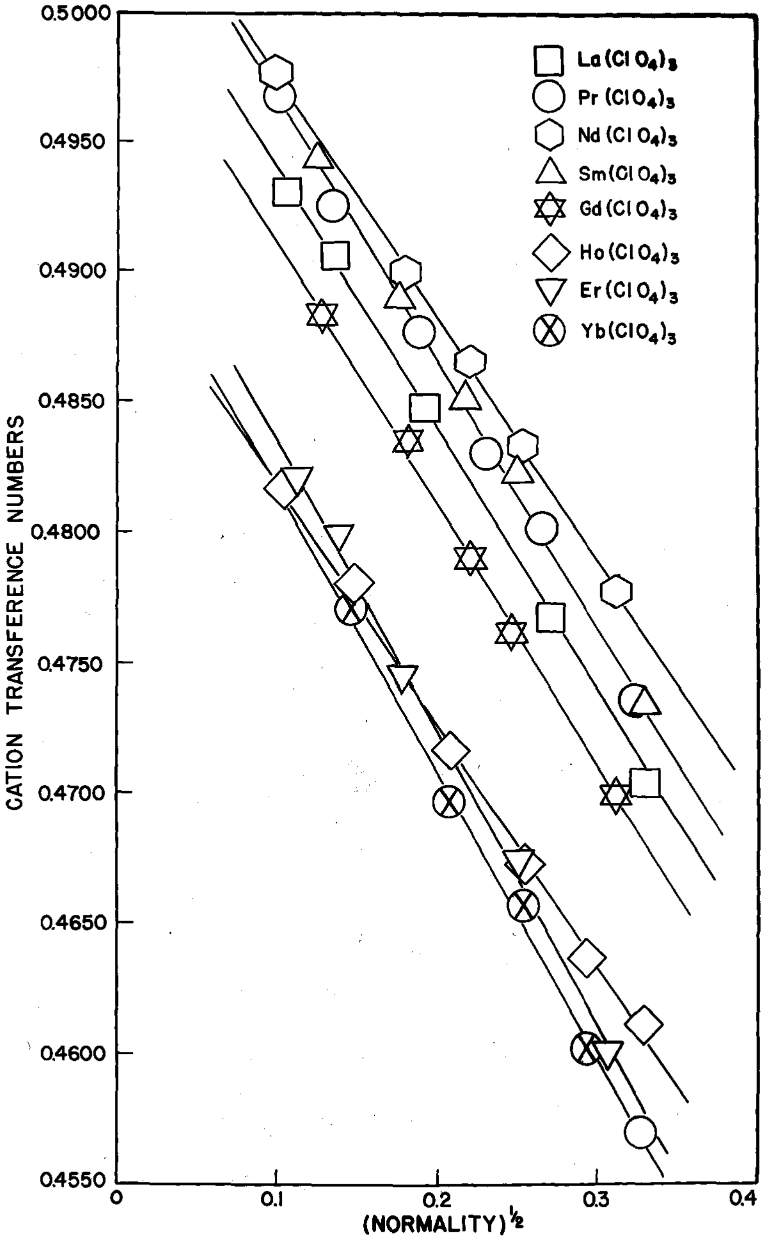


Figure 20. Transference Numbers of Some Rare Earth Perchlorates.

Table 36

Cation Transference Numbers for Lanthanum Nitrate at 25°C

Normality	(Normality)$^{1/2}$	T_+ (uncorrected)	Volume correction	Solvent correction	T_+ (corrected)
0.1132071	0.3365	0.4707	-0.0010	0.0000	0.4697
0.075414	0.2747	0.4731	-0.0007	0.0001	0.4725
0.05660355	0.2379	0.4757	-0.0005	0.0001	0.4753
0.0377357	0.1943	0.4782	-0.0003	0.0001	0.4780
0.0150943	0.1229	0.4823	-0.0001	0.0002	0.4824

Table 37

Cation Transference Numbers for Neodymium Nitrate at 25°C

Normality	$(\text{Normality})^{1/2}$	T_+ (uncorrected)	Volume correction	Solvent correction	T_+ (corrected)
0.10078	0.3175	0.4706	-0.0009	0.0000	0.4695
0.07558	0.2749	0.4744	-0.0007	0.0001	0.4738
0.037794	0.1944	0.4788	-0.0003	0.0001	0.4786
0.025196	0.1587	0.4811	-0.0002	0.0002	0.4811
0.010078	0.1004	0.4847	-0.0001	0.0004	0.4850

Table 38

Cation Transference Numbers for Gadolinium Nitrate at 25°C

Normality	$(\text{Normality})^{1/2}$	T_+ (uncorrected)	Volume correction	Solvent correction	T_+ (corrected)
0.11847	0.3442	0.4601	-0.0010	0.0001	0.4592
0.088856	0.2981	0.4641	-0.0008	0.0001	0.4634
0.059237	0.2434	0.4689	-0.0005	0.0001	0.4685
0.029619	0.1721	0.4726	-0.0002	0.0002	0.4726
0.011847	0.1088	0.4769	-0.0001	0.0003	0.4771
0.044428	0.2108	0.4709	-0.0004	0.0001	0.4706

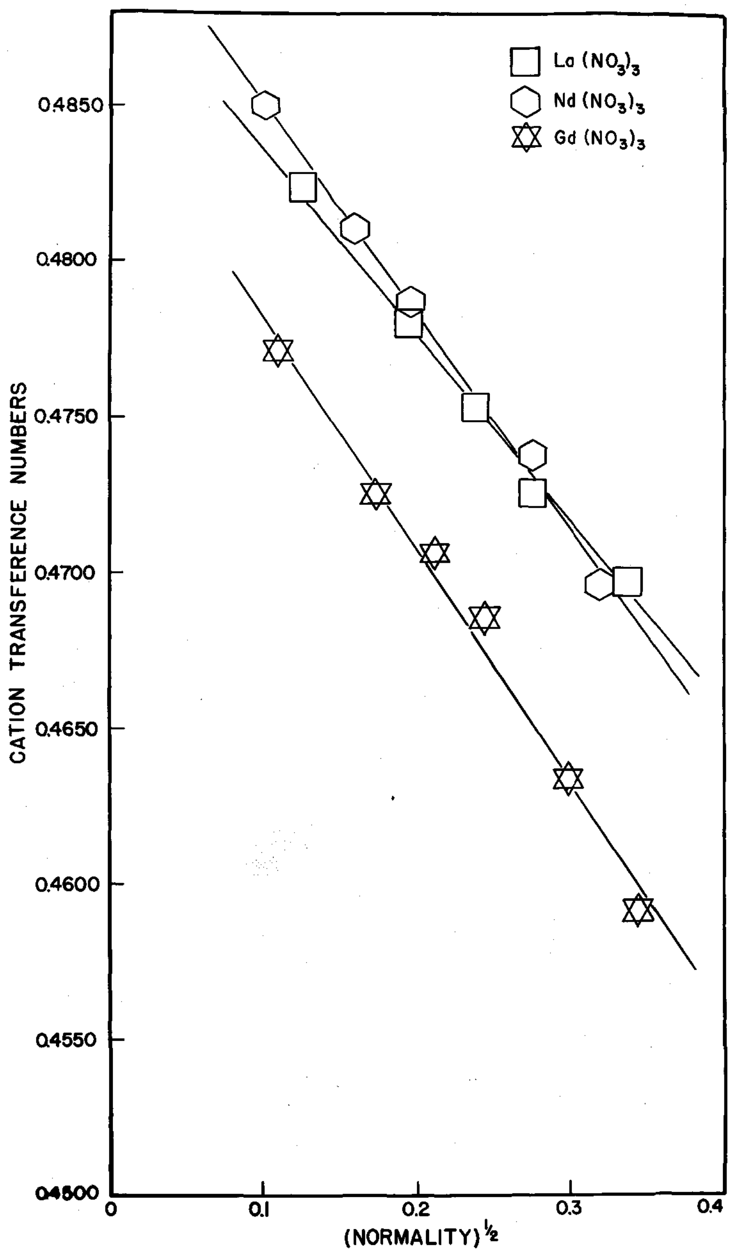


Figure 21. Transference Numbers of Some Rare Earth Nitrates.

Table 39

Equations for the Transference Numbers of Some Rare Earth Salts as a Function of the Square Root of the Normality

Salt	Least-squares equation	T°_+
$La(ClO_4)_3$	$T_+ = .5038 - .1005 \sqrt{N}$	0.5088
$Pr(ClO_4)_3$	$T_+ = .5067 - .1020 \sqrt{N}$	0.5080
$Nd(ClO_4)_3$	$T_+ = .5067 - .09311 \sqrt{N}$	0.5095
$Sm(ClO_4)_3$	$T_+ = .5072 - .1020 \sqrt{N}$	0.5044
$Gd(ClO_4)_3$	$T_+ = .5010 - .09969 \sqrt{N}$	0.4996
$Ho(ClO_4)_3$	$T_+ = .4909 - .09237 \sqrt{N}$	0.4970
$Er(ClO_4)_3$	$T_+ = .4947 - .1123 \sqrt{N}$	0.4959
$Yb(ClO_4)_3$	$T_+ = .4930 - .1105 \sqrt{N}$	0.4955
$La(NO_3)_3$	$T_+ = .4895 - .05968 \sqrt{N}$	0.4922
$Nd(NO_3)_3$	$T_+ = .4922 - .06980 \sqrt{N}$	0.4947
$Gd(NO_3)_3$	$T_+ = .4857 - .07463 \sqrt{N}$	0.4852

Table 40

Ionic Equivalent Conductances of Rare Earth Perchlorates

Salt	Normality		λ_+	λ_-
$La(ClO_4)_3$	0.1091		45.18	50.86
	0.07273		47.40	52.02
	0.03636		51.00	54.20
	0.01818		54.51	56.51
	0.01091		56.72	58.33
$Pr(ClO_4)_3$	0.1058		45.62	50.74
	0.07050		47.80	51.74
	0.05288		49.32	52.81
	0.03525		51.39	54.00
	0.017626		54.83	56.50
	0.010575		57.27	58.03
$Nd(ClO_4)_3$	0.09641		46.22	50.58
	0.06427		48.37	51.71
	0.04820		49.86	52.63
	0.03214		51.93	54.08
	0.009641		57.58	58.15
$Sm(ClO_4)_3$	0.1086	0,3295	45.12	50.20
	0.06204	0,2491	48.16	51.67
	0.04653	0,2157	49.63	52.66
	0.03102	0,1761	51.63	53.99
	0.01551	0,1245	55.00	56.23
$Gd(ClO_4)_3$	0.09692		44.73	50.43
	0.06461		46.85	51.54
	0.04846		48.25	52.48
	0.03231		50.34	53.78
	0.01615		53.61	56.18

Table 40 (continued)

Salt	Normality		λ_+	λ_-
$Ho(ClO_4)_3$	0.1073	0.3276	43.20	50.49
	0.08584	0.2930	44.28	51.21
	0.06438	0.2537	45.74	52.16
	0.04292	0.2072	47.75	53.48
	0.02159	0.1465	50.96	55.87
	0.01073	0.1036	54.20	58.31
$Er(ClO_4)_3$	0.09371		43.59	51.17
	0.06248		45.81	52.22
	0.03124		49.20	54.54
	0.01250		53.48	57.49
$Yb(ClO_4)_3$	0.1076		42.81	50.87
	0.08604		43.93	51.56
	0.06453		45.54	52.26
	0.04302		47.48	53.65
	0.02151		50.95	55.86

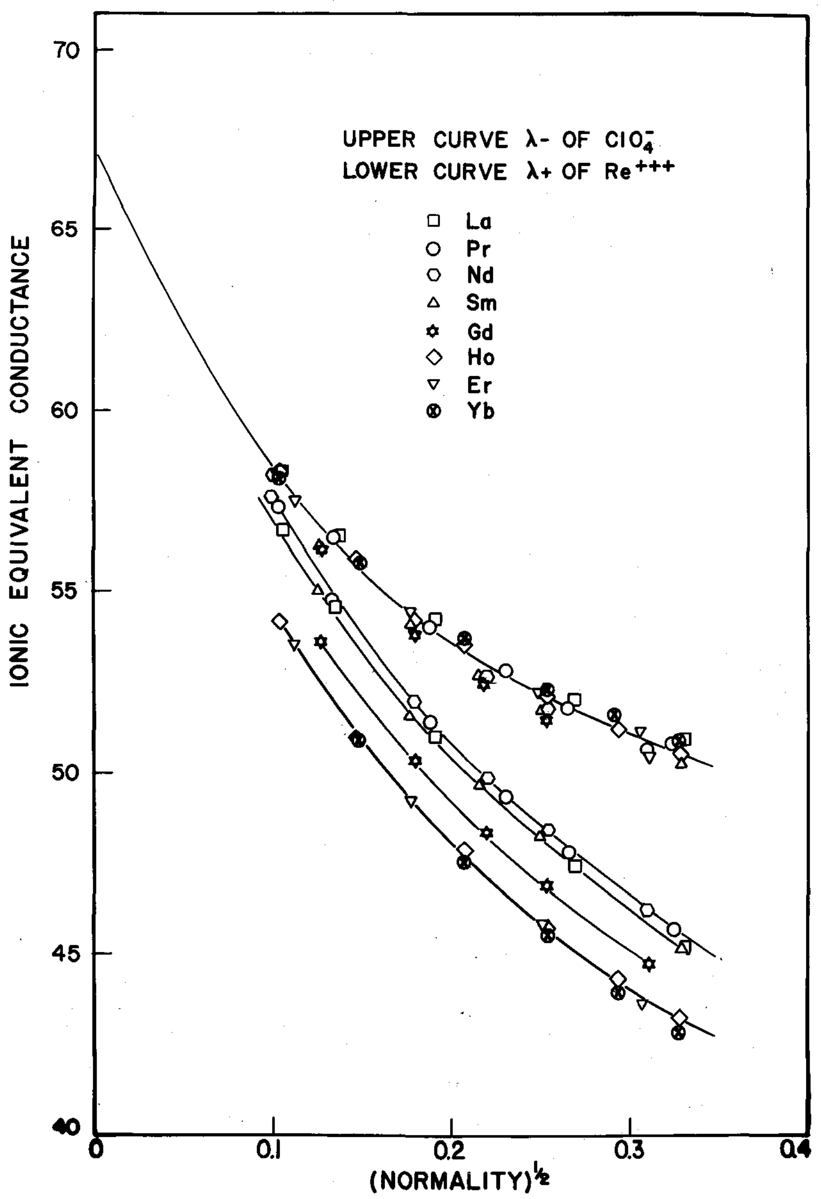


Figure 22. Ionic Equivalent Conductances of Some Rare Earth Perchlorates.

Table 41

Ionic Equivalent Conductances of Rare Earth Nitrates

Salt	Normality		λ_+	λ_-
$La(NO_3)_3$	0.1132	0,3365	42.50	47.99
	0.07541	0.2747	44.94	50.17
	0.05660	0.2379	46.73	51.59
	0.03774	0.1943	49.14	53.66
	0.01509	0.1229	53.14	57.02
$Nd(NO_3)_3$	0.1008	0,3175	42.17	47.65
	0.07559	0.2749	44.20	49.09
	0.03779	0.1944	46.95	51.14
	0.02520	0.1587	51.04	55.06
	0.01008	0.1004	56.21	59.69
$Gd(NO_3)_3$	0.1185		40.14	47.28
	0.08886		42.07	48.71
	0.05924		44.70	50.71
	0.02962		48.77	54.43
	0.01185		52.81	57.89

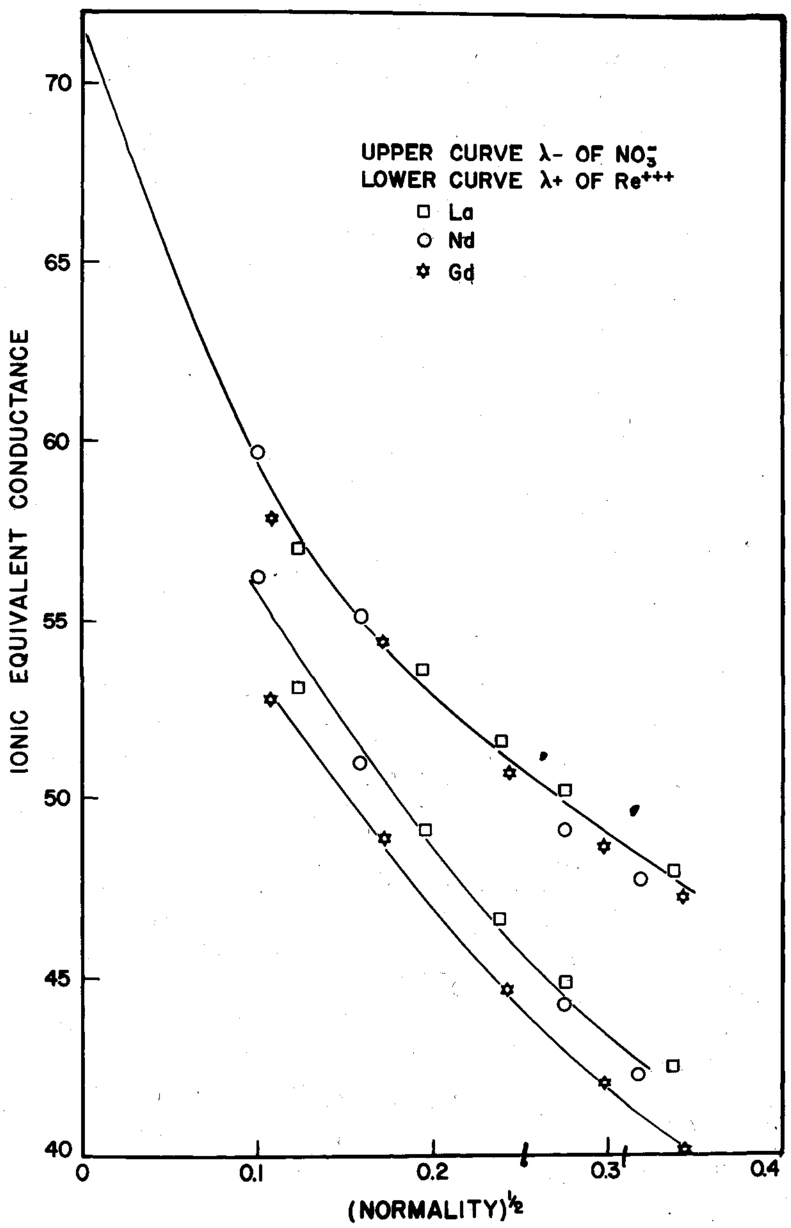


Figure 23. Ionic Equivalent Conductances of Some Rare Earth Nitrates.

D. Discussion

The transference numbers of the rare earth perchlorates behave as anticipated from the conductances of the salts. At a given concentration, the numbers increase slightly from lanthanum to neodymium and then decrease to gadolinium and then they decrease at a slower rate for the group, holmium, erbium and ytterbium. The transference numbers of samarium are anomalously high, since the conductances are lower than those of the first three elements while the transference numbers are almost the same as those of praseodymium. A similar behavior was observed for samaric chloride by Spedding, Porter and Wright (76).

The rare earth nitrate transference numbers are also in the expected order. There is not enough data to predict the behavior of the entire series; however, it is felt that it will be similar to that of the halides and perchlorates.

The least squares equations for the transference numbers indicate that the experimental results deviate markedly from the simple limiting law. The intercepts, however, are in relative agreement with the T_+^0 values in Table 39. The discrepancies in the intercepts may be attributed to the extreme sensitivity of the T_+^0 values to slight changes in the slopes of the curves.

The disagreement between experiment and the simple limiting law may be attributed to the failure of the limiting law to describe the behavior of the ions beyond very dilute solutions. Recently, J. Dye (86) has shown that by a graphical evaluation of the integral in the electrophoretic effect in the Onsager equation, the resulting transference numbers are in much better agreement with experiment. The simple equation had been solved by a series expansion of the exponential and the neglecting of higher terms. Dye's work shows that the series does not converge rapidly and that neglecting higher terms leads to large errors in the calculated transference numbers.

The ionic equivalent conductances of the various rare earths have been calculated from their transference numbers and equivalent conductances. These data help to provide a further check on the correspondence between the conductances and the transference numbers. The values of the anionic conductances in Figure 22 fall relatively on the same curve. This indicates that they are approximately equal for all the rare earth perchlorates. A similar behavior is observed for the nitrates in Figure 23.

The errors in the measurement of the current, the time and the volumes are estimated to be much less than 0.1 per cent. Therefore the inclusive error of the transference number experiments is estimated to be about 0.1 per cent since this is the extent to which the concentrations of the solutions are known.

VII. THE CALCULATION OF ACTIVITY COEFFICIENTS FROM CONDUCTANCES

A. Introduction to the Method

The Debye-Hückel limiting law for activity coefficients may be used to calculate the mean activity coefficients of strong electrolytes in moderately dilute solutions. It has been shown (1, 2) that the activity coefficients of rare earth halides thus calculated agree remarkably well with those obtained experimentally from e.m.f. measurements. Since the rare earth chlorides and bromides obey the theory up to about 0.1 N in aqueous solutions, it may be assumed that the rare earth perchlorates and nitrates also obey the same theory at the same concentrations.

However, in order to evaluate the activity coefficients from the equation

$$\log f^{\pm} = -\frac{z_+ z_- A\,\omega^{1/2}}{1 + Ba_1\omega^{1/2}},$$

the values of the distances of closest approach for the solutes must be known. The distances of closest approach have not been previously evaluated for the rare earth perchlorates and nitrates. Furthermore, since there are no electrodes reversible to the rare earths or the perchlorates and nitrates in water, the experimental determination of activity coefficients for these salts at low concentrations is virtually impossible. The determination of a_1 values from conductance measurements affords a convenient method for calculating activity coefficients from the Debye-Hückel limiting law.

The distance of closest approach may be evaluated from conductance measurements by applying the Onsager equation for the equivalent conductance in a more extended form than that used earlier in the thesis. The electrophoretic effect was evaluated originally by an expansion of the exponential and the neglecting of all terms above the second term. Furthermore, χa_1 was assumed to be small compared to one and was also neglected in the term

$$\frac{1}{1 + \chi a_1} .$$

The result was that the change in the conductance due to the electrophoretic effect had no dependence on a_1.

Instead of expanding the exponential, one may carry through the mathematics and evaluate the resulting integral graphically. James Dye gives a detailed description of this treatment in his thesis (86). The resulting expressions for the change in the equivalent conductances of the positive and negative ions in a 3-1 electrolyte are

$$\Delta\lambda_+ = M \int_{\kappa a_1}^{\infty} \rho \left[e^{-9P\frac{e^{-\rho}}{\rho}} - e^{3P\frac{e^{-\rho}}{\rho}} \right] d\rho$$

and

$$\Delta\lambda_- = M \int_{\kappa a_1}^{\infty} \rho \left[e^{-P\frac{e^{-\rho}}{\rho}} - e^{3P\frac{e^{-\rho}}{\rho}} \right] d\rho$$

in which λ_+ and λ_- are the ionic equivalent conductances of the positive and negative ions respectively, ρ is equal to κr, M is a constant obtained from the various universal constants in the expressions and is equal to 3.209 and

$$P = 7.135 \times 10^{-8} \frac{\kappa e^{\kappa a_1}}{1 + \kappa a_1} .$$

The values of the intergrands may be plotted as functions of κa_1 and the integrals may then be evaluated from the areas under the curves.

The change in the conductance due to the electrophoretic effect is quite sensitive to the a_1 value used since this is the lower limit of the integration and the curve rises rapidly for small values of a_1. The value of P is relatively independent of a_1.

In the section on conductances the method of obtaining the equivalent conductance at infinite dilution by extrapolation of the Onsager equation was discussed. When the slope of the extrapolation curve becomes zero, the Onsager theory is being obeyed. However, when the electrophoretic correction on the conductance is inserted in the Onsager equation, agreement with theory is improved considerably. This was shown to be true for the rare earth chlorides out to about 0.008 N (86).

It may be assumed, therefore, that if a_1 were known for the rare earth perchlorates and nitrates, their conductances would also agree with the extended theory to a greater degree. Thus, a series of a_1 values for the perchlorates and nitrates is assumed and the electrophoretic correction for each a_1 is calculated at various concentrations. These are included in the equation for the equivalent conductance. An extrapolation to infinite dilution of the calculated Λ_0' values as a function of $C^{1/2}$ is made. When the proper a_1 value is used, the curve remains flat from infinite dilution to about 0.004 to 0.008 N. If the a_1 value is too small, the curve rises from the flat portion at very low concentrations, and if the a_1 value is too large, the curve dips below the true Λ_0 value. Figure 24 is an example of the evaluation of

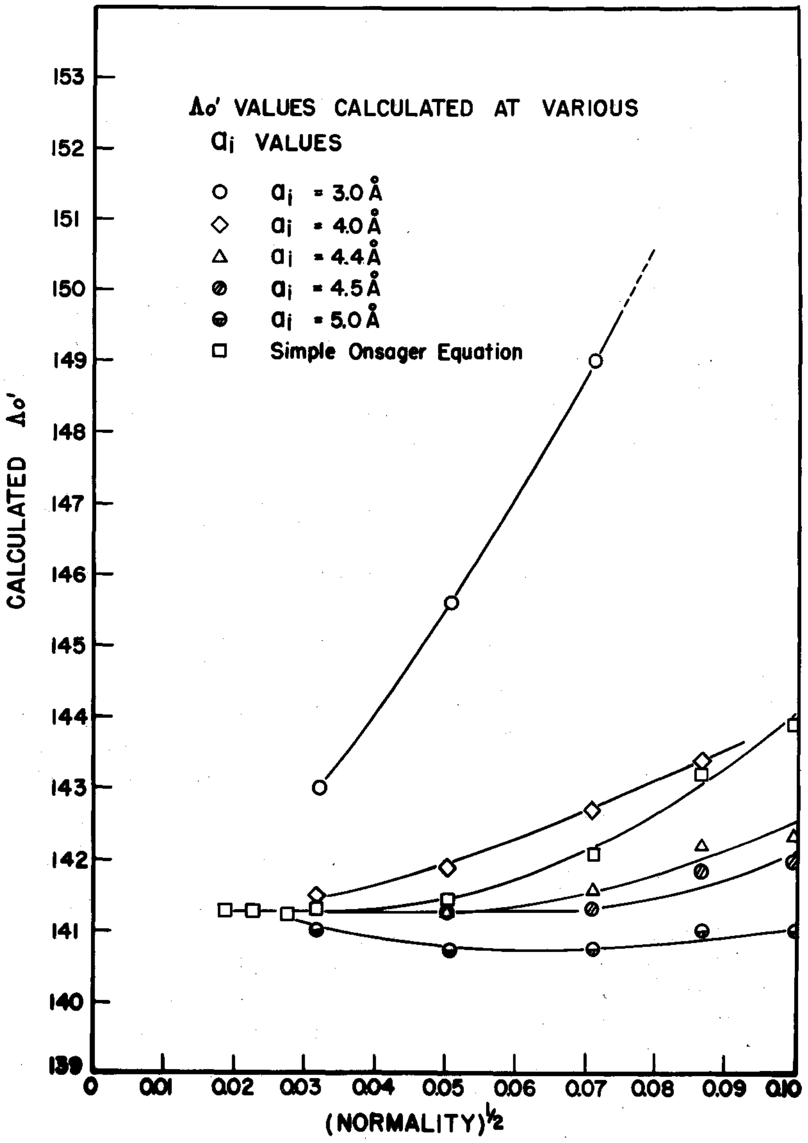


Figure 24. Evaluation of Distance of Closest Approach for Neodymium Nitrate.

a_i for $Nd(NO_3)_3$ by the method described above. It can be seen that a reasonable a_i value can be obtained when the best extrapolation curve is found.

B. Results

The changes in the equivalent conductances due to the electrophoretic effect were calculated for several a_i values at several concentrations by the graphical method described above. Table 42 lists a convenient selection of these values. A series of curves were plotted to obtain interpolated values of the equivalent conductance corrections at intermediate a_i's and concentrations.

The a_i values that were obtained for the rare earth perchlorates and nitrates are listed in Table 43.

The rational activity coefficients are calculated from the relation

$$\log f_{\pm} = -\frac{A\sqrt{C_m}}{1 + Ba_i\sqrt{C_m}} .$$

In this case, A is 3.745 and B is 0.8051. The mean molal activity coefficients may be calculated from the expression

$$\log \gamma_{\pm} = -\frac{A\sqrt{C_m}}{1 + Ba_i\sqrt{C_m}} - \log(1 + 0.001m\nu M_1)$$

Table 42

Electrophoretic Corrections on Conductance at Various a_i Values for 3-1 Electrolytes

a_i in Angstroms	$\Delta\Lambda$ at 0.010 N	$\Delta\Lambda$ at 0.0035 N	$\Delta\Lambda$ at 0.0010 N
3.0	28.34	15.60	7.15
4.0	16.90	10.66	5.57
5.0	14.20	9.04	5.07
5.49	13.62	8.64	4.87
5.92	13.01	8.35	4.77
6.5	12.30	8.00	4.65
7.0	11.95	7.75	4.61
7.5	11.50	7.25	4.50

Table 43

Mean Distance of Closest Approach from Extrapolation of Conductance Data

Salt	a_i in Angstroms
$La(ClO_4)_3$	7.0
$Pr(ClO_4)_3$	7.2
$Nd(ClO_4)_3$	6.0
$Sm(ClO_4)_3$	6.8
$Gd(ClO_4)_3$	6.4
$Ho(ClO_4)_3$	6.3
$Er(ClO_4)_3$	6.8
$Yb(ClO_4)_3$	7.2
$La(NO_3)_3$	4.4
$Nd(NO_3)_3$	4.5
$Gd(NO_3)_3$	4.4

in which the second term on the right relates the rational activity coefficients to the mean molal activity coefficients. m is the molality of the solution obtained from the equation

$$m = \frac{C_m}{\rho - 0.001M_2C_m} ,$$

ν is the number of ions into which the solute dissociates and M_1 is the molecular weight of the solvent while M_2 is that of the solute.

A representative set of mean molal activity coefficients were calculated for praseodymium perchlorate and neodymium nitrate. These values are shown in Table 44.

C. Discussion

The distances of closest approach that were calculated for the perchlorates and nitrates seem to be in reasonable agreement with those found for the rare earth chlorides by the e.m.f. method. In the case of the chlorides, the average a_i is about 5.7 Å. This value supports the physical picture that a monomolecular layer of water surrounds the rare earth cation. If the same picture holds for the perchlorates, the main change in the a_i value would be due to the increase in the radius of the perchlorate ion over that

Table 44

Mean Molal Activity Coefficients

Molality	$\gamma_\pm$ $Pr(ClO_4)_3$	$\gamma_\pm$ $Nd(NO_3)_3$
0.001002	0.7940	0.7831
0.002508	0.7157	0.6939
0.005018	0.6487	0.6152
0.007526	0.6080	0.5663
0.01003	0.5789	0.5306
0.02512	0.4901	0.4061
0.05036	0.4302	0.3432

of the chloride ion. This difference in radius is estimated to be about 1 Å. Therefore, the estimated a_1 for the perchlorates would be about 6.7 Å. This estimate is in remarkable agreement with the values found by the conductance method. The value of a_1 for the nitrates may also be made to agree with the physical picture if one considers that the effective radius of the nitrate ion in this case is about 1 Å. Since the rare earth ion is about 1 Å in radius and the water molecule is about 2.8 Å in diameter, the value of 4.5 Å for the nitrate ion seems reasonable.

The sensitivity of the method for obtaining a_1 values from conductances increases as a_1 becomes smaller. Therefore, the values reported for the nitrates are more precise than those for the perchlorates. It is estimated that the perchlorate values are accurate to about ± 0.2 Å while the nitrate values are known to about ± 0.1 Å.

Although these represent errors of about three per cent in the distance of closest approach, they will not reflect comparable errors in the activity coefficients that are calculated from them.

The mean molal activity coefficients of the rare earth perchlorates and rare earth nitrates calculated from the conductance method are compared with those of the rare earth chlorides as determined by e.m.f. measurements (1). The curves are for praseodymium perchlorate, neodymium nitrate

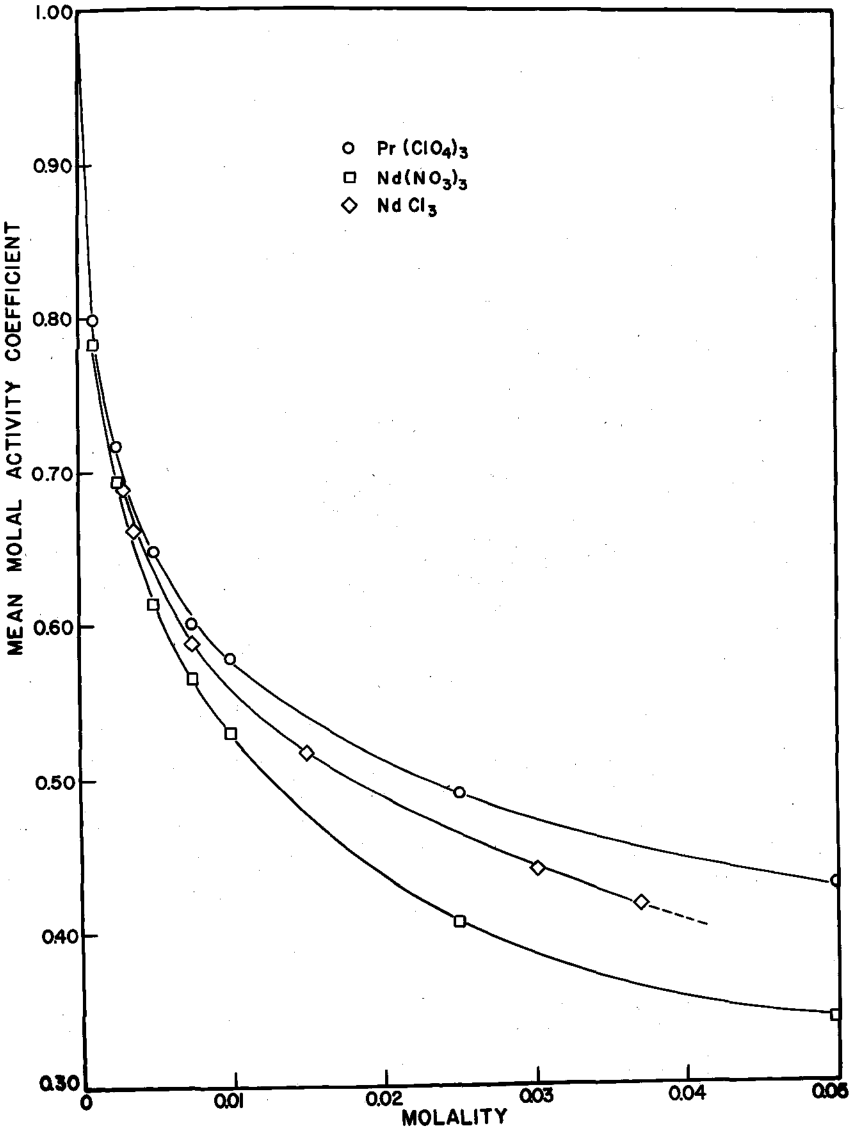


Figure 25. Mean Molal Activity Coefficients of Praseodymium Perchlorate, Neodymium Chloride and Neodymium Nitrate.

and neodymium chloride and are plotted in Figure 25. Since the activity coefficients do not change much with the individual rare earths, these curves are representative of the series for each anion. It can be seen that the activity coefficients reflect the value of a_1. The perchlorates have the largest a_1 and have the highest activity coefficients, the chlorides are a little lower and the nitrates are lowest.

The differences in the distances of closest approach between the various rare earth perchlorates are relatively in agreement with those found for the rare earth halides. However, the differences are not large enough nor are the determinations accurate enough to give this trend any physical significance. All that can be said at this time is that the trend seems to be present but might be merely a reflection of experimental error. The value for neodymium perchlorate seems to be out of order and is probably a result of the adding of errors.

VIII. SUMMARY AND CONCLUSIONS

The conductances and transference numbers of the perchlorate salts of lanthanum, praseodymium, neodymium, samarium, gadolinium, holmium, erbium and ytterbium were measured. The conductances and transference numbers of the nitrate salts of lanthanum, neodymium and gadolinium were also measured. In addition, the conductances of the sulfate salts of lanthanum, cerium, praseodymium, neodymium, samarium, gadolinium, holmium, erbium, ytterbium and yttrium were determined. These were all measured in aqueous solutions at 25°C.

The Jones bridge and its accessories were employed to measure the conductances over a concentration range of about 0.0002 N to 0.1 N. The accuracy of the conductance measurements is estimated to be about 0.1 per cent which is the extent to which the concentrations of the solutions are known.

The perchlorate conductances appear to decrease with increasing atomic number except for lanthanum, praseodymium and neodymium. These three salts have very similar conductances. The behavior of the series is attributed to the effective increase in the size of the ions due to hydration, in spite of the fact that the ionic radii from crystallographic measurements are decreasing with atomic number. The three nitrates measured exhibit similar behavior to that of the perchlorates.

However, the conductances of the perchlorates as a whole are higher than those of the nitrates except at very low concentrations. This seems to indicate that the interaction of the perchlorate ions with the rare earths, at concentrations above about 0.01 N, is less than the corresponding interactions of the nitrates and the halides. This behavior would tend to increase the total conductance of the perchlorates as compared with the nitrates. The conductances of the nitrates and the halides are parallel from infinite dilution to 0.1 N; whereas, the conductances of the perchlorates cross those of the halides and nitrates, and are higher than both of them above 0.1 N.

The conductances of the rare earth sulfates are much lower than expected for completely dissociated strong electrolytes. The low mobilities of the sulfates are attributed to the formation of complexes or ion pairs even in dilute solutions. The most prevalent complex at moderate dilutions is proposed to be MSO_4^+ in which M is the rare earth.

The series of rare earth sulfate conductances exhibit a far different order from that of the other salts measured.

At appreciable concentrations the sulfate conductances decrease slightly from lanthanum to praseodymium and then rise a little at neodymium. They fall again to a minimum at samarium and finally increase steeply from samarium to ytterbium. Yttrium behaves much like the heavy rare earths in its conductance. This order in the sulfate conductances may be attributed to the relative stabilities of the rare earth complexes as the atomic number is increased.

The conductances of the rare earth sulfates are completely different at infinite dilution. They are completely dissociated at infinite dilution and they behave as do the other rare earth salts.

The ionic equivalent conductances at infinite dilution were calculated for these salts and the values are in good agreement with those previously calculated from the rare earth halide data.

The transference numbers of the rare earth perchlorates and nitrates were measured by the moving boundary method. The accuracy of the method is estimated to be about 0.1 per cent. However, it is conceivable that the errors in the measurement of time, volume and current could add up in such a way as to give an overall accuracy of only 0.2 per cent.

The order of the perchlorate transference numbers is in relative agreement with the rare earth halide transference numbers. Lanthanum is a little lower than expected but still quite close to the light rare earths. However, samarium appears to behave contrary to its conductance. The transference number is close to that for praseodymium while its conductance is much lower than that of praseodymium.

The ionic conductances of the rare earth perchlorates and nitrates were calculated from the conductance data and the transference numbers. They provide a cross check with the conductances, since the ionic conductances of the anions fall on relatively the same curves.

The use of the Onsager equation for the extrapolation of the conductances to infinite dilution indicated that a further correction on the conductances would give much better agreement with theory. This agreement was obtained when the extended Onsager equation was used. The extended equation includes a dependence on the mean distance of closest approach in the electrophoretic effect correction. This led to a method for determining the distances of closest approach for the rare earth perchlorates and nitrates from conductance data. The a_1 values determined from the conductance data were quite reasonable and were used to calculate activity coefficients. The activity coefficients appear to be satisfactory and compare favorably with those of the rare earth halides which were determined from e.m.f. measurements. Since the activity coefficients for the rare earth perchlorates and nitrates are not available from experimental measurements, the conductance method affords a convenient and reasonably accurate method of obtaining them.

The data on the transference numbers and conductances presented in this thesis should be of valuable importance in the study of equilibria and kinetics of rare earth salt solutions. It is hoped that these data will help point the way towards extentions in the present theories and provide a better understanding of the physical chemistry of electrolytic solutions.

IX. LITERATURE CITED

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